

FFC-NMR Relaxometric Characterization of Nanosponges for Rationalizing their Adsorption and Release abilities

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INTRODUCTION

Nanosponges (NSs), i.e. hyper-reticulated materials obtained joining supramolecular host units (such as cyclodextrins and calixarenes) by means of suitable linker units, constitute a versatile class of functional materials useful in different application fields, spanning from environment remediation, to supports for catalytic systems and drug delivery. These materials take advantage from their easy synthesis and chemical modification, which allow to design materials with stimuli-sensitive properties. NSs are characterized by a thick network of nanochannels in their highly disordered structure. However, their textural features (mean pore size, specific surface area and specific pore volume) cannot be reliably assessed by means of ordinary adsorption-based techniques such as BET or BJH methods.

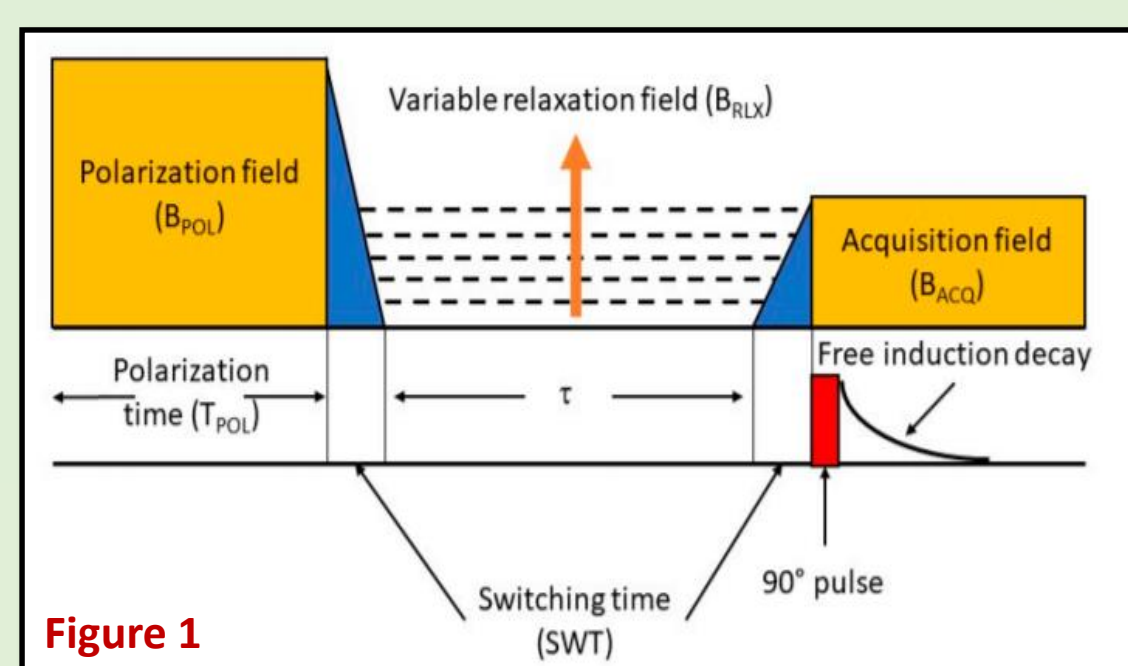
In this study, the results are reported from NMR Fast-Field-Cycling (FFC) relaxometric experiments carried out on a panel of diversely structured cyclodextrin, calixarene and mixed cyclodextrin-calixarene NSs. The study is aimed at obtaining suitable parameters, proposed in recent literature [1], useful for defining the microscopic and the textural properties of the materials, and in particular the functional mobility of aqueous media within the porous structure. The results obtained aided the rationalization of a dataset pertaining to the adsorption and the controlled release kinetics of a model guest molecule such as *p*-nitro-aniline.

FFC-NMR THEORY

The longitudinal relaxation rate (R_1) is strictly bound to molecular motions. In particular, the Bloembergen-Purcell-Pond (BPP) theory provides that in the case of an ideal molecular system subjected to a single motion regime, R_1 depends on the Larmor frequency (ν_L) according to the relationship (the so-called BPP function):

$$\frac{1}{T_1} = \frac{3}{10} \frac{\mu_0^2 \gamma^4}{h^2 \tau_c^6} \left(\frac{\tau_c}{1 + (\nu_L \tau_c)^2} + \frac{4\tau_c}{1 + 4(\nu_L \tau_c)^2} \right)$$

where τ_c is the "correlation time", i.e. the average time taken by the molecule to rotate by one radian or to move a distance as large as its gyration diameter, that quantifies the speed of molecular motions. Hence, τ_c can be evaluated by regression analysis of the NMRD dispersion curve (i.e. the R_1 vs ν_L plot), obtained by measuring R_1 under variable magnetic field. This can be achieved by applying the Fast-Field-Cycling (FFC) technique.


Figure 1

The sample is subjected to quick cyclic variations of the magnetic field (Figure 1). In a first polarization step a magnetization is created; the sample is then allowed to relax at a suitable field for a given time (t_{rel}), finally a FID is acquired to recover the residual magnetization. Relaxation kinetics usually follows a first-order trend, from which R_1 can be obtained by fitting analysis.

In the case of complex systems more complex treatments are needed, based on either a rigorous or a 'model free' approach [2]. We have recently proposed that NMRD dispersion curves for diverse systems can be treated as the sum of three main contributions, i.e.:

$$R_1 = \frac{1}{T_1} = R_0 + R^{HH} + R^{NH}$$

Here R_0 relates to fast motions (HB exchange or short chain conformational rearrangements); R^{NH} accounts for possible N-H quadrupolar interaction; R^{HH} is the contribution from homonuclear H-H relaxation. The latter one can be expressed in an integral form [2,3] as:

$$R^{HH} = \int_0^\infty \left[\frac{\tau_c}{1 + (\nu_L \tau_c)^2} + \frac{4\tau_c}{1 + 4(\nu_L \tau_c)^2} \right] f^*(\tau_c) d\tau_c$$

where the distribution function $f^*(\tau_c)$ defines the overall dynamics of the system. When a NS is saturated with water, the magnetization evolution results from two different first-order contributions, a 'fast' (R_{1f}) and a 'slow' (R_{1s}) one, corresponding respectively to the relaxation of: *i*) the NS scaffold and the water molecules bound to the NS surface (solvation shell), *ii*) the water molecules flowing into the pores. Hence, magnetization evolution can be modelled as a bi-exponential trend and two NMRD curves can be built. According to theory [1], the relaxation rates can be led back to the texture properties of the material by the relationships:

$$\begin{aligned} R_{1s} &= R_w + x_s \cdot (R_{1f} - R_w) & R_1 &= R_w + \lambda \cdot (m/D) \cdot (R_{1s} - R_w) \\ x_s &= \lambda \cdot (S/V) = \lambda \cdot m/D & R_1 &= R_w + \rho \cdot (m/D) \\ & & R_1 &= R_w + \rho \cdot (S/V) \end{aligned}$$

where x_s is the mole fraction of water molecules strictly interacting with the surface, i.e. its solvation shell; R_w is the relaxation rate of bulk water; D , S and V are the average pore diameter, the specific pore surface and the specific pore volume, ρ is the relaxivity of surface water molecules, λ is the thickness of the surface solvation layer and m is a shape coefficient. Hence, one can evaluate the mole fraction of surface water by the relationship:

$$x_s = (R_{1s} - R_w) / (R_1 - R_w)$$

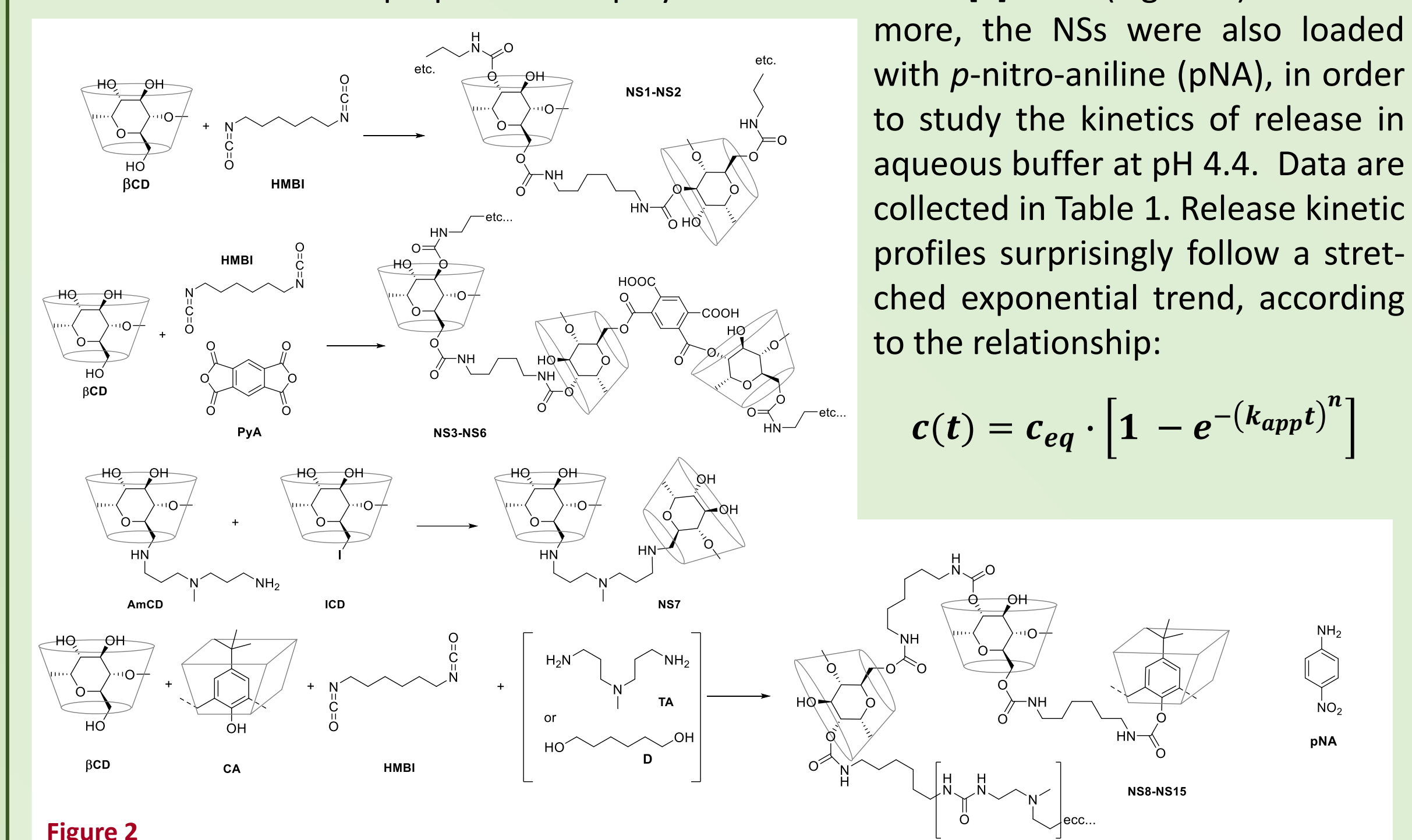
For NSs, however, suitable values for parameters λ and m cannot be properly defined, even because of swelling phenomena. Hence, based on similar studies in soil science [4], we proposed to define a 'Pore Connectivity Index' (PCI) [1] able to describe the functional mobility of an aqueous medium within the porous NS architecture, by the relationship:

$$PCI = \frac{\left(\int_{T_{A,fast}}^{T_{B,fast}} \Phi(T_{fast}) T_{fast} dT_{fast} \right)^{-1} - R_w}{\left(\int_{T_{A,slow}}^{T_{B,slow}} \Phi(T_{slow}) T_{slow} dT_{slow} \right)^{-1} - R_w}$$

where $\Phi(T_{fast})$ and $\Phi(T_{slow})$ are the relaxation time distribution functions for the fast and slow components respectively obtained from the Inverse Laplace transforms of the relaxation kinetics.

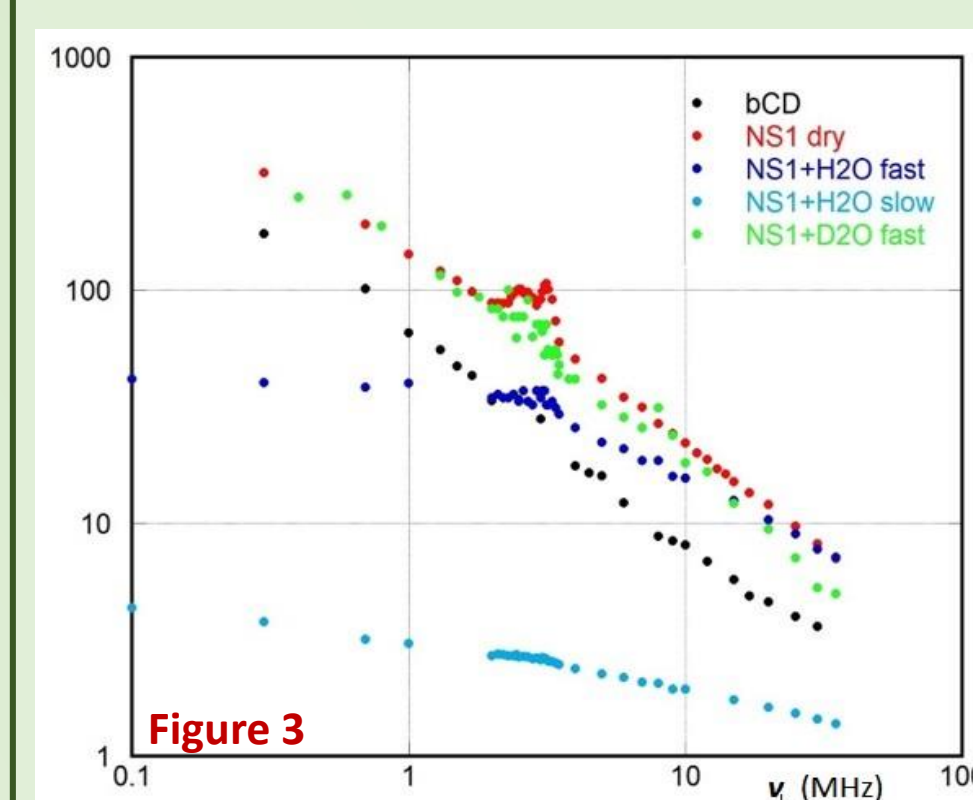
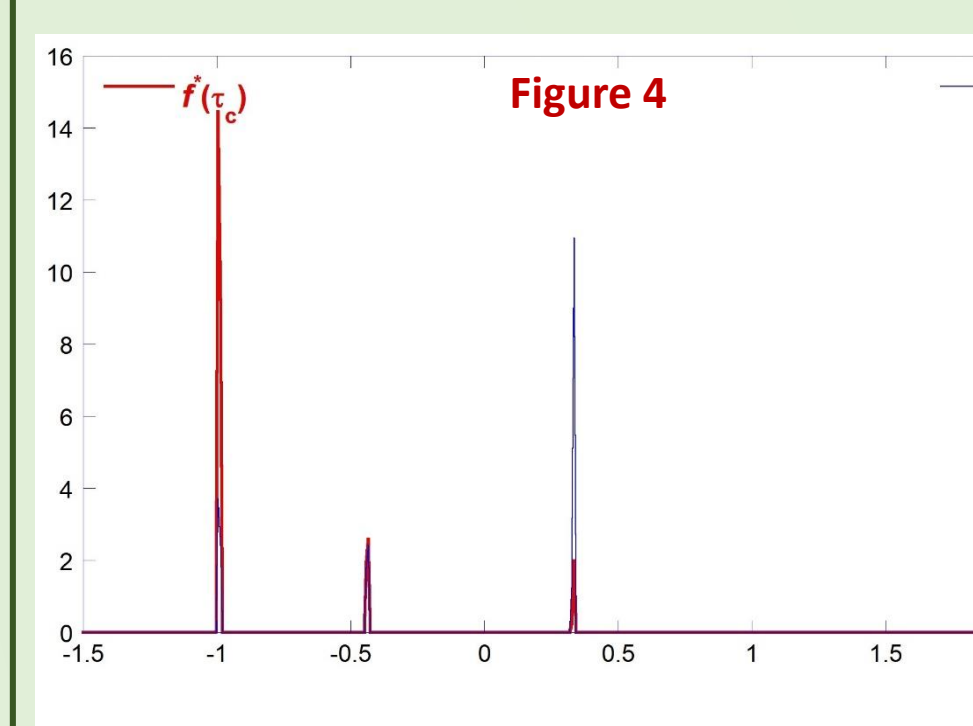
RESULTS and DISCUSSION

The FFC-NMR relaxometric technique was applied to the study of a set of 15 diversely structured NS materials prepared from β -cyclodextrin and calix[4]arene (Figure 2). Further-

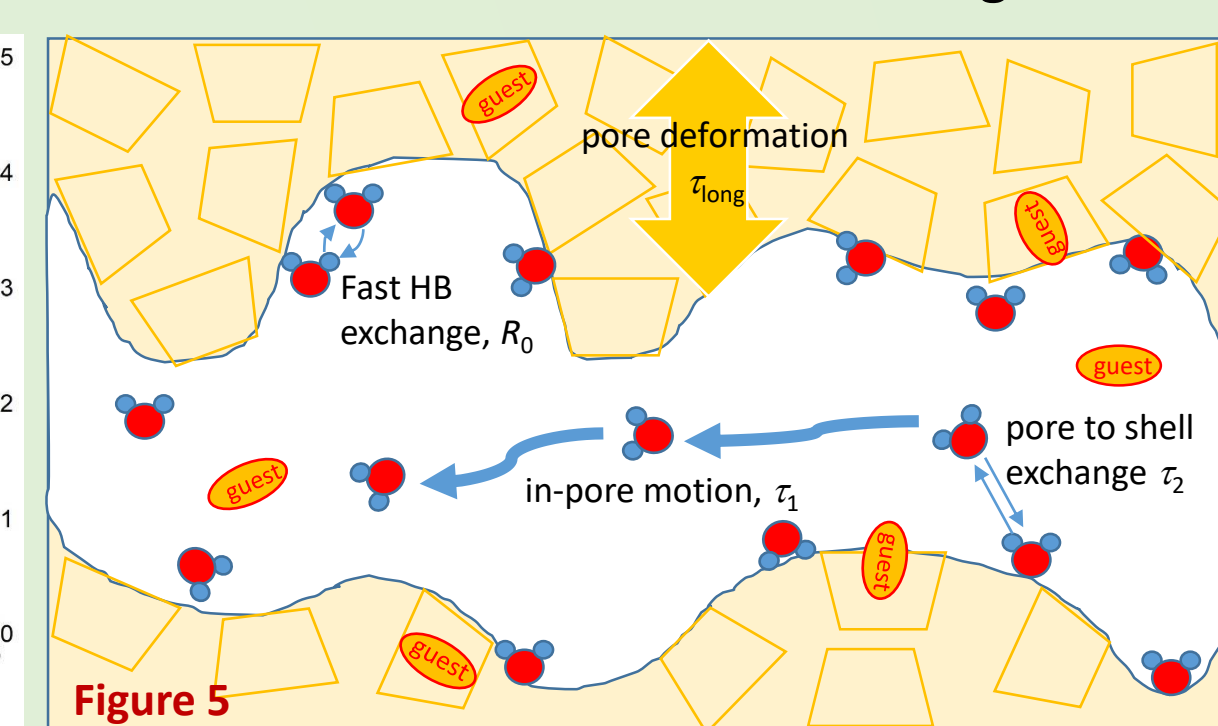

Figure 2
Table 1

material	composition	k_{app} ($s^{-1} \cdot 10^4$)	n	PCI	x_s	R_0 (ms)	τ_1 (ns)	τ_2 (ns)	τ_{long} (μs)
NS1	β CD/HMBI 1:2	4.71	0.745	87.5	0.033	1.08	18.2	135	-
NS2	β CD/HMBI 1:4	4.77	0.759	27.7	0.068	1.66	17.4	190	21.5
NS3	β CD/HMBI/PyA 1:4:4	6.17	0.713	1.5	0.21	1.81	18.2	161	1.4
NS4	β CD/HMBI/PyA 1:8:4	1.67	0.776	22.7	0.065	2.11	16.2	343	13.8
NS5	β CD β CD/HMBI/PyA 1:8:4 +25% w poplar char	18.1	0.623	7.5	0.21	3.31	21.2	391	3.5
NS6	β CD/HMBI/PyA 1:8:4 +25% w baker yeast	14.7	0.665	1.6	0.21	3.02	19.1	351	1.8
NS7	AmCD/CD 1:1	3.13	0.584	19.3	0.145	1.03	17.4	153	1.9
NS8	β CD/HMBI/D 1:6:5	3.83	0.727	18.7	0.151	2.46	18.2	81	2.5
NS9	CA/HMBI 1:2	1.63	0.557	-	-	1.16	20.4	157	0.4, 1.43
NS10	CA/HMBI/TA 1:8:6	4.31	0.678	-	-	0.96	14.2	102	1.0
NS11	CA/HMBI/D 1:6:5	1.15	0.398	-	-	1.09	39.8	891	1.1
NS12	β CD/CA/HMBI 1:1:8	4.26	0.808	31.2	0.029	1.79	29.9	290	1.6
NS13	β CD/CA/HMBI 1:1:4	5.43	0.638	83.2	0.034	0.45	5.8	81	2.1
NS14	β CD/CA/HMBI 1:2:16	5.45	0.783	47.5	0.14	1.15	21.9	290	1.8
NS15	β CD/CA/HMBI/TA 1:2:16:3	10.96	0.944	4.5	0.22	2.07	19.6	163	2.0

The NS materials were equilibrated with water before subjecting them to FFC-NMR relaxometric analysis, to obtain the relevant NMRD curves (Figure 3). Different behaviors were observed depending on the hydrophobic character of the material. In fact, for the most hydrophobic calixarene-based NSs the evolution of the magnetization had to be modelled as a single stretched mono-exponential trend, accounting for a structuration of the solvent shell due to hydrophobic effects. Heuristic analysis of the NMRD curves for the


Figure 3

Figure 4

slow relaxometric component [3] results in a set of delta-like functions (Figure 4, material NS5 as an illustrative example), that identify well-defined dynamic domains each corresponding to a particular motion mode (Figure 5). Analysis of numerical results suggests that the quickest ones may correspond to the translational motions of water molecules within the channel (τ_1) and to the fast exchange between the channel and the pores surface (τ_2). Further slow dynamic domains (τ_{long}) might rather account for slow motions related to swelling.


Figure 5

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