Journal of Magnetic Resonance 286 (2018) 82–90

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Probing numerical Laplace inversion methods for two and three-site molecular exchange between interconnected pore structures

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ARTICLE INFO

Article history:
Received 7 September 2017
Revised 14 November 2017
Accepted 26 November 2017

Keywords:
NMR methods
Molecular exchange
Numerical inverse Laplace transform
Pore size distribution
Polymeric porous network

ABSTRACT

Two-dimension (2D) Nuclear Magnetic Resonance relaxometry experiments are a powerful tool extensively used to probe the interaction among different pore structures, mostly in inorganic systems. The analysis of the collected experimental data generally consists of a 2D numerical inversion of time-domain data where T_2-T_2 maps are generated. Through the years, different algorithms for the numerical inversion have been proposed. In this paper, two different algorithms for numerical inversion are tested and compared under different conditions of exchange dynamics; the method based on Butler–Reeds–Dawson (BRD) algorithm and the fast-iterative shrinkage-thresholding algorithm (FISTA) method. By constructing a theoretical model, the algorithms were tested for a two- and three-site porous media, varying the exchange rates parameters, the pore sizes and the signal to noise ratio. In order to test the methods under realistic experimental conditions, a challenging organic system was chosen. The molecular exchange rates of water confined in hierarchical porous polymeric networks were obtained, for a two- and three-site porous media. Data processed with the BRD method was found to be accurate only under certain conditions of the exchange parameters, while data processed with the FISTA method is precise for all the studied parameters, except when SNR conditions are extreme.

1. Introduction

Porous materials are spread in a great variety of systems in nature and complex technological applications. Knowledge of the fluid dynamics of a liquid imbibed in a porous medium is a central issue in most applications, where the pore size, liquid-surface interactions, and pore interconnectivity are among the main parameters that drive the fluid dynamics. Nuclear magnetic resonance (NMR) is considered today an indispensable tool for the study of porous media in many research and industrial areas such as in sedimentary rocks in oil industry [1,2], soil research [3] or cement pastes [4]. For interconnected pores, a central question concerns the migration of molecules from site to site under conditions of detailed balance.

Two-dimensional (2D) relaxation exchange NMR is a tool that is able to map diffusion of a fluid from one pore to another. In particular, T_2-T_2 correlation spectroscopy tracks changes in transverse relaxation time T_2 of molecules that change their environments during the experimental time [4–6]. The experiment consists of two Carr-Purcell-Meiboom-Gill (CPMG) [7,8] sequences encoding T_2, with a variable storage time in between during which molecules are able to exchange sites and to relax with the longitudinal relaxation time, T_1. The resulting 2D matrix contains information on relaxation in both dimensions and can be converted in a T_2-T_2 spectrum by a Numeric Laplace inversion (NLI) of the 2D data. Different approaches for the numeric inversion have been proposed and many of them use the Tikhonov regularization [9–13]. After data inversion, a T_2-T_2 map is generated whose main features are the peaks present in the diagonal which, for short storage times, reflect the number of molecules present in each environment, weighted by longitudinal relaxation. For long storage times, given that effectively an exchange process occurs, off-diagonal peaks appear. From the intensity of these peaks as a function of the storage time, exchange rates can be calculated [6,14].

The numerical inversion approach most widely used up to the moment is the data compression proposed by Venkataramanan et al. [9], using singular value decomposition of the involved kernel matrices, which uses an adaptation of Butler-Reeds-Dawson (BRD) method to solve 2D and 2.5D Fredholm integrals of the first class [15]. The interpretation of the intensity evolution of off-diagonal peaks is not straightforward, especially for systems with more than

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https://doi.org/10.1016/j.jmr.2017.11.016
1090-7807/

two coupled pores. Since exchange is a symmetric process, the T_2-T_2 map should be symmetric in relation to the diagonal for every storage time. However, this is not the case for many of the T_2-T_2 maps reported in the literature [4,6,16,17] and many hypotheses were made in order to explain this phenomenon. Washburn et al. [6] argued that the symmetry of the experiment was broken due to T_1 relaxation during the storage time. In a latter report, Mitchell [4] showed that the observed asymmetry was, in fact, originated during the data inversion algorithm. Additionally, the influence of the signal to noise ratio (SNR) of the experimental data on the NLI was presented by Fleury and Soualem [16], where synthetic 2D time-domain signals were generated for a two-site system. There, displacements of the position of the four peaks obtained after numerical inversion for three different values of SNR were shown. These calculations evidenced that even with a low level of the SNR, small off-diagonal peaks can be detected but their locations differ from the theoretical position while for high SNR (500), the positions are the expected ones. Another effect observed when the experiments are done with a poor SNR is the appearance of spurious peaks. Apparently, the SNR did not affect the symmetric character of the process in the sense that both off-diagonal peaks are of the same amplitude. In the same work, T_2-T_2 relaxation maps for a smectite gel at a clay fraction of 30% as a function of the storage time were presented (see Fig. 9 in Ref. [16]). In those experiments, it is clear that the non-diagonal peaks are not only deviated from the perfect square position as predicted but also their amplitudes are not the same. Recently, Song et al. argued that the typical T_2-T_2 inversion of the signal does not place the diagonal symmetry constraints in the data, and consequently allows for an asymmetrical T_2-T_2 spectrum. They introduced a different approach, showing that by analysing the time-domain 2D data in a two-site system, the exchange may be determined, preventing the presence of asymmetries [18]. The method is qualitative but it has the potential to be improved to quantify exchange and extended to systems larger than two-site. With a different strategy, d'Eurydice et al. have adjusted the experimental procedure in such a way that the exchange among different populations can be quantified without the numerical 2D inversion of the data [19]. They introduced the T_2 filtered T_2-T_2 sequence in which the first CPMG acts as a filter and the exchange rates can be calculated monitoring the 1D T_2 distributions as a function of the storage time.

Recently, Teal and Eccles [10] proposed an algorithm which does not require a matrix factorization. The idea of the algorithm is based on the fast iterative shrinkage-thresholding algorithm (FISTA) [20] but with the NMR convention, which is l_2 regularization. More recently, Zhou et al. used the FISTA algorithm for the inversion of the 2D NMR relaxometry data using l_1 regularization [21].

In the present work, two different approaches for the Numerical Laplace Inversion of the 2D data [9,10] are contrasted for a two- and three-site porous system. From a theoretical point of view, 2D synthetic signals are numerically generated, processed with the studied NLI algorithms and compared with the exact analytical solutions for different sets of parameters of the exchange dynamics. For an experimental perspective, a porous polymeric network which can be prepared with a controlled hierarchy of micro-, meso-, and macro-porous spatial domains [22] was used as a realistic model. The two algorithms were studied under different conditions, limiting values for the exchange parameters at which each of the processing algorithms begins to fail were obtained.

2. Materials and methods

In order to shed some light on the correct interpretation of the T_2-T_2 NMR data, two theoretical methods will be compared: synthetic 2D signals will be generated through numeric calculations, numerically inverted with both studied algorithms, and compared to the analytic solution of the same problem. Both theoretical results will be contrasted with the experimental data for two- and three-site porous media showing exchange among all of the reservoirs involved.

2.1. NMR measurements

The NMR pulse sequence used to acquire the T_2-T_2 signals is shown in Fig. 1. The experiment consists of three blocks; a first period encodes transverse magnetization which evolves under the influence of a CPMG pulse sequence of variable duration τ_1. A subsequent $\pi/2$ rotation stores the magnetization along with the external magnetic field axis, where diffusion takes place together with longitudinal relaxation, T_1, during a variable storage time t_s. Finally, another $\pi/2$ pulse is applied and transverse relaxation is detected by a second CPMG block of fixed duration τ_2. This sequence is repeated using a range of storage times to observe the movement of water between the different pools.

Measurements were carried out at 30 °C using a MagritekKea2 spectrometer operating at 60 MHz for protons and a Varian EM360 permanent magnet. The length of the radiofrequency pulses was set to 16 μs, the echo time t_E = 0.5 ms and 8000 echoes were acquired in the direct dimension while 32 logarithmically spaced points, from 1 to 8000 echoes, were used for the indirect dimension. The storage time was varied from 1 to 350 ms averaging 64 scans.

2.2. Two and three-site porous media: sample preparation

The study was performed using polymer beads with hierarchical pore structure corresponding to copolymers of ethylene glycol dimethacrylate and 2-hydroxyethyl methacrylate [poly(EGDMA-co-HEMA)] synthesized as previously reported [22]. Polymer networks prepared with a cross-linker content of 33 mol% of EGDMA were reported to render a system with hierarchically distributed pore sizes. The system has a porosity of 84% both in the dry state or fully saturated with water. This is an important fact as the system is used fully and partially saturated with water in this study, thus, it can be assured that the pore network is not modified. The void space sizes were previously determined by mercury porosimetry for the dry state [22] and by NMR using the Decay due to Diffusion in the Internal Field (DDIF) sequence [23] for the swollen state. Assuming a distribution of spherical pores three mean sizes were reported. The relevant parameters are listed in Table 1 [24].

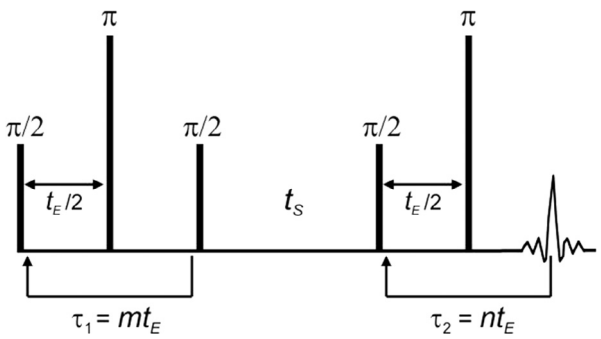

Fig. 1. Two-dimensional pulse sequence T_2-T_2 for the measurement of transverse relaxation exchange. The first CPMG encodes T_2, followed by a storage period t_s in which the magnetization is along with the z-axis and relaxes due to T_1. When finalized that period, the magnetization is turned to the plane and a second CPMG acquires the data. The 2D sequence is repeated for different storage times t_s.