diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Investigating pore to pore exchange in systems saturated with water and oil

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Abstract

Relaxation Exchange Spectroscopy (REXSY) has not previously been performed on samples containing different liquids. We present a pulse sequence that combines a Pulsed Gradient Spin Echo with REXSY, which we call PGSE-REXSY. Using this pulse sequence it is possible to separate the signals from two liquid components, here oil and water, simultaneously present within a sample due to the difference in diffusion properties. A REXSY analysis can then be performed on the individual liquids. The technique is very relevant to applications in petroleum research, and could potentially be used to determine how the mobility of one liquid is influenced by the presence of the other. We also show that compared to a two-dimensional Inverse Laplace Transform, a discrete multi-exponential component model is more robust when performing a quantitative analysis of REXSY data.

Keywords

NMR, diffusion, transverse relaxation, Relaxation Exchange Spectroscopy

1. Introduction

The Relaxation Exchange Spectroscopy (REXSY)[1] enables measurements of exchange based on migration of molecules between environments having different transverse (T_2) relaxation times. Recently the REXSY technique has been further developed and applied to evaluation of pore to pore exchange in water saturated systems of cement[2, 3] and porous rocks[4, 5]. However, REXSY has previously never been tested on samples containing different liquids, for instance oil and water. An overlap between T_2 values of oil and water in an oil/water-saturated sample is expected, complicating the analysis. However, due to their relatively low diffusivity, oil molecules should not significantly exchange between pores and contribute to cross peaks in the REXSY plots. Furthermore, we present a pulse sequence that combines a Pulsed Gradient Spin Echo (PGSE) with REXSY (PGSE-REXSY) that potentially makes it possible to separate the oil and water signals prior to REXSY analysis. The separation is based on the difference in diffusivity between the liquids[6]. The technique is very relevant to applications in petroleum research, where oil and water are simultaneously present in a porous system (rock material). In this study we have investigated the possibility to perform REXSY and PGSE-REXSY experiments on model systems of porous samples where signals from both water and oil will contribute to the obtained relaxation data. We also present an alternative approach to analyse RESXY data that does not depend on a two-dimensional Inverse Laplace Transform.

2. Methods and Materials

The experiments were performed at 25 °C on a Bruker Avance 500 MHz instrument (Bruker Biospin, Ettlingen, Germany), using a commercial probe (DIFF30). Close packings of sand particles were used as a model system. The sand particles (Baskarp sand) had a diameter in the range 80-300 μm. Samples were prepared by adding sand particles to an NMR tube filled with water, followed by treatment in an ultrasonic bath. Excess water was removed. The sand particles are strongly water-wet, and it is therefore challenging to prepare samples that are saturated with both water and oil. Therefore we chose to prepare samples of particles saturated with water only, and then introduce the signal from oil by adding a layer of oil on top of the particles in some of the samples. The dynamic behaviour of water should therefore be the same in these two samples. This enables us to test the PGSE-REXSY technique on samples where we have full control of the system. In future studies the technique will be applied to real samples saturated with both water and oil.

The PGSE-REXSY pulse sequence is shown in Fig. 1. The PGSE-part contains bipolar pair of gradient that minimizes the influence of internal gradients in the diffusion weighting. We keep the echo time 2τ fixed at 0.2 ms and in the usual manner vary the number of refocusing π-pulses (between 2 and 300) in the first part of the REXSY experiment. We found that this value of τ was sufficient to avoid influences from internal gradients in the T_2-decays. Longer values of τ resulted in unwanted cross-peaks in the REXSY plots[7]. It is also important to keep τ' as short as possible to avoid loss of signals due to dephasing caused by diffusion in internal gradients. The gradient strength, g, was varied (16 steps) between 0.98 and 700 Gauss/cm. The other parameters used were $\tau' = 1.3$ ms, $\delta = 0.8$ ms.

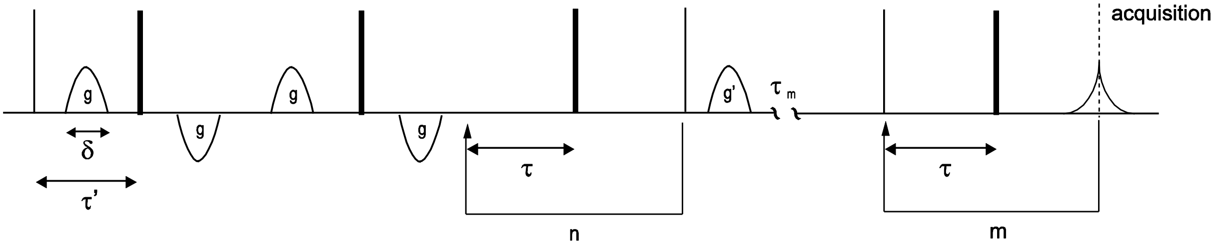

Fig.1: The PGSE-REXSY pulse sequence used to measure diffusion weighted T_2-T_2 exchange correlations.

The data set obtained using PGSE-REXSY contains a set of REXSY decays for each value of the applied gradient, g. At a certain gradient strength g_c the signal from the faster diffusing molecules of water has decayed. For each echo in the REXSY decays obtained at $g > g_c$ a regular diffusion analysis (linear regression) can be performed on the remaining signal from oil, and can then be extrapolated to find REXSY decays for oil at the minimum gradient strength g_m. The REXSY decays for oil can then be subtracted from the original REXSY decays obtained at g_m to obtain REXSY decays for water. We have previously used a similar approach to separate signals from oil and water confined in a porous material, but then in a simple PGSE-CPMG measurement [6].

REXSY data are normally analysed using a two-dimensional Inverse Laplace analysis (2D-ILT). However, it is well known that the ILT analysis (1D and 2D) is very sensitive to noise. When using diffusion weighing to separate REXSY decays from oil and water, noise is introduced[8], which may lead to unreliable results using 2D-ILT. We therefore suggest an alternative data analysis that is based on a discrete multi-exponential component model applied to the REXSY decays. The idea is that a sufficiently high number of π-pulses (n) in the first part of REXSY effectively works as a T_2-filter that suppresses signals from discrete components with shorter T_2-values. However, as the exchange time τ_m increases molecules will migrate between environments with different T_2-values, influencing the magnitude of the discrete components. Others have presented a similar approach[9], but using 1D-ILT to analyse the data. In our REXSY data analysis presented below we have used both 2D-ILT and the discrete multi-exponential component model.

3. Results and Discussion

The 2D-ILT REXSY plot of the sand sample saturated with water was obtained using regular REXSY at τ_m=400 ms (Fig. 2, top, left) shows the well-known cross peak pattern.

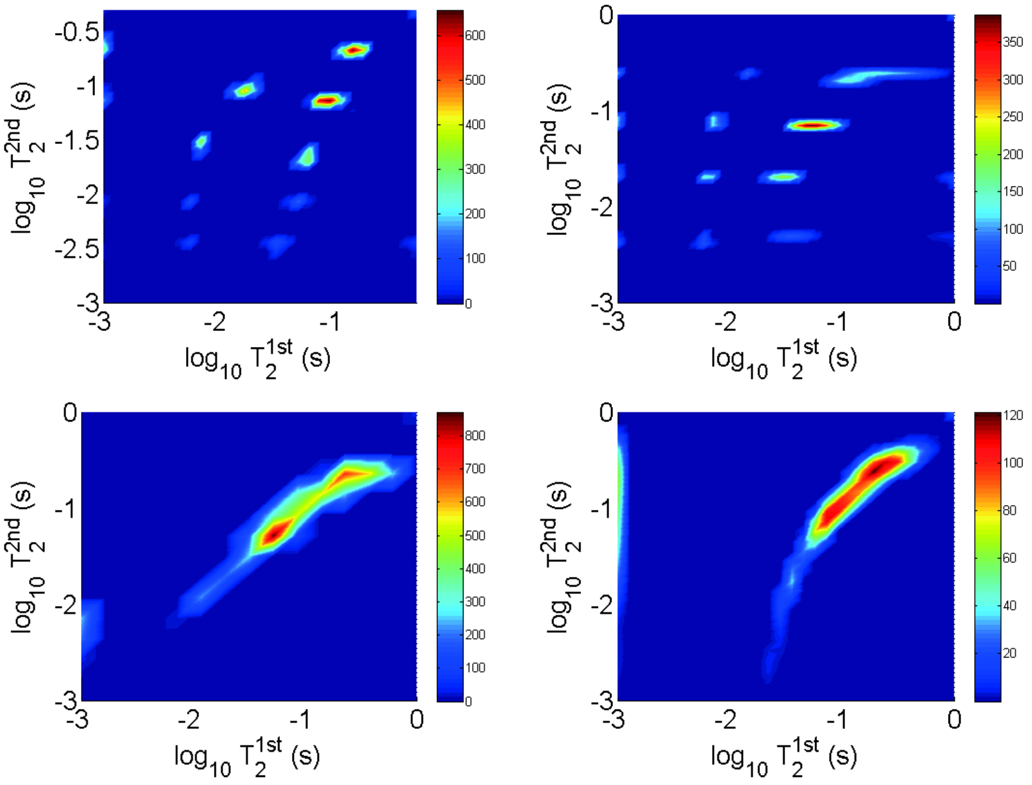

Fig. 2: 2D-ILT REXSY plots of the water saturated sand sample obtained using regular REXSY (top, left), the water saturated sand sample with a top layer of bulk crude oil obtained using regular REXSY (top, right), of bulk crude oil obtained using regular REXSY (lower, left) and of the separated oil signal obtained using PGSE-REXSY on a water saturated sand sample with a top layer of bulk crude oil (lower, right). τ_m=400 ms in all plots.

The REXSY plot of the sample containing water saturated sand particles with a top layer of bulk crude oil obtained using regular REXSY (Fig. 2, top, right), indicate weak exchange peaks, but the expected diagonal signal from oil does not occur. The 2D-ILT REXSY plots of bulk crude oil obtained using regular REXSY (Fig. 2, lower, left) and the separated oil signal from the PGSE-REXSY experiment of a water saturated sand sample with a top layer of bulk crude oil (Fig. 2, lower, right), show similar diagonal peaks, and strongly indicate that the separation of water and oil signal was successful. However, when performing 2D-ILT on the separated water signal, no clear cross peaks were observed. Therefore, to perform any further analysis based on 2D-ILT is not sustainable in samples containing both water and oil, and we choose to use the discrete multi-exponential component model to investigate the behaviour of the separated water signal and compare it to results obtained in the sample with no bulk crude oil present.

Results from the discrete multi-exponential component model are presented in Table 1. When using this model on the data from the water saturated sand sample with τ_m=1 ms and n=2, the best fit was obtained using three T_2 components. When increasing the number of π-pulses to n=300 the data analysis verified that there is an effect from the T_2-filter in the measurements, consequently leading to the suppression of the shortest component (the best fit was obtained using two T_2 components). With n=2 and τ_m=400 ms there is only an effect from T_1, which decreases the intensity of each component to the same degree. This corresponds well with inversion recovery measurements on this sample, which showed a mono-exponential behaviour, with a T_1-value of 1.4 s. However, when increasing the number of τ_m to 400 ms, and with n=300, the shortest component reappears due to molecular migration between environments with different T_2-values influencing the magnitude of the shortest component.

Table 1: Values for T_2 in milliseconds obtained based on the discrete multi-exponential component model. The fraction of each component is given in parenthesis below the T_2 value.

		Sand particles H_2O			**Sand particles H_2O + crude oil**		
τ_m	***n***	**T_2**			**T_2**		
1 ms	**2**	10 (0.24)	61 (0.47)	226 (0.29)	-	65 (0.59)	357 (0.41)
	300	-	77 (0.58)	260 (0.42)	-	94 (0.59)	325 (0.41)
400 ms	**2**	12 (0.23)	70 (0.50)	245 (0.27)	14 (0.22)	86 (0.49)	312 (0.29)
	300	12 (0.17)	75 (0.45)	259 (0.38)	12 (0.17)	81 (0.45)	302 (0.38)

Using the discrete multi-exponential component model on the separated water signal in the sand particles with a top layer of bulk crude oil it is clear that here the shortest T_2 component is suppressed at shortest exchange time even at n=2. This is caused by the presence of internal gradients, which will suppress the shortest T_2-component during the PGSE part of the experiment (τ'=1.3 ms). For T_2 values obtained with τ_m=400 ms, the shortest component has reappeared. This is the situation for both *n*=2 and *n*=300. Therefore, as in the sample with water-saturated sand, the magnitude of the shortest component will increase due to molecular migration. Comparing the results obtained for water-saturated sand with and without the presence of bulk crude oil, the dynamic behaviour of water is the same, which verifies that we are able to separate the signal from water and oil using the PGSE-REXSY technique.

4. Conclusions

We have shown that by using PGSE-REXSY it is possible to separate signals from oil and water simultaneously present within a sample. A REXSY analysis can then be performed on the individual liquids. Furthermore, we have shown that compared to a 2D-ILT analysis, a discrete multi-exponential component model is more robust and reliable when performing a quantitative analysis of REXSY data.

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