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High Frequency Modulated Gradient Spin Echo Diffusion Measurements with Chemical Shift Resolution

John Georg Seland

Department of Chemistry, University of Bergen, Norway

Corresponding author: John Georg Seland, Dept. of Chemistry, University of Bergen,
NO-5007, Bergen, Norway, E-Mail: John.Seland@kj.uib.no

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Abstract

We present a Modulated Gradient Spin Echo pulse sequence that enables diffusion measurements with chemical shift resolution in the obtained spectra at higher modulation frequencies (1600 Hz) than previously obtained. The modulation is generated using a Carr-Purcell-Meiboom-Gill train of radiofrequency pulses in a constant gradient. To avoid distortions from eddy currents, a longitudinal eddy current delay was added between gradient modulation and spectrum acquisition. To suppress the effects from gradient-slicing and unwanted coherences, while maintaining high chemical shift resolution, short samples (height of 0.5 mm) were prepared in a 5 mm Shigemi™ tube. The pulse sequence was successfully tested on a sample of distilled water and a sample of a water-continuous microemulsion (Winsor's type I).

Keywords

NMR, diffusion, modulated gradients, eddy currents, chemical shift.

1. Introduction

In a wide range of materials liquids are located in confined geometries. Measurements of the time-dependent self-diffusion of liquids using NMR can give valuable information about the confined geometry of the material [1]. NMR self-diffusion measurements are frequently performed using the Pulsed-Gradient-Spin-Echo (PGSE) technique [2], where the average displacement propagator [3] is measured using short gradient pulses. In systems with sub-micrometer confinements the average displacement propagator has to be measured at very short displacements and diffusion times, in order to fulfil the short-gradient-pulse (SGP) approximation [2]. This necessitates strong and short gradient pulses, which are outside the limit of the standard NMR hardware.

The use of the Modulated Gradient Spin Echo (MGSE) technique [4, 5] enables self-diffusion measurements at short displacements in a manner that does not depend on the SGP approximation. The diffusion-dependent signal attenuation can be accumulated over several rapidly oscillating cycles of the modulated gradients, making the measurement sensitive to much shorter time scales than what is achieved in the PGSE experiment. MGSE measurements of restricted diffusion in confined geometries have been successfully performed in porous silica [5], biological tissue [6] and emulsions [7, 8], but with exception of the method presented in ref. [8], chemical shift information was not obtained. Here we present a

MGSE pulse sequence that enables diffusion measurements with chemical shift resolution in the obtained spectra at higher modulation frequencies then previously obtained [8].

2. Methods and Materials

The diffusion measurements were performed using the pulse sequence shown in Fig. 1. When the Gaussian approximation is valid [4], the diffusive attenuation of the echo signal is given by

$$S = S_0 e^{-\beta} \tag{1}$$

The attenuation factor, β is given by [4, 5]

$$\beta(te,\omega_m) = \frac{8\gamma^2 G^2}{\pi^2 \omega_m^{\ 2}} D(\omega_m) te \tag{2}$$

The motion is described in the form of a diffusion spectrum, $D(w_m)$, which is probed by varying the modulation period, T, while keeping the gradient strength, G, and total echo time, te, constant. Varying the number of π-pulses in the Carr-Purcell Meiboom-Gill (CPMG) train results in a varying T. Since the constant gradient is turned off abruptly, strong eddy currents are generated, which distorts the NMR spectrum if it is recorded immediately. To avoid such distortions a longitudinal eddy current delay (LED), with a length Te, was added between the end of the gradient modulation and acquisition of the spectrum, resulting in what we call an MGSE-LED sequence. Due to gradient distortions of the radiofrequency pulse, we also found it necessary to add an additional delay, t1, between the end of the gradient and the first π/2-pulse in the LED.

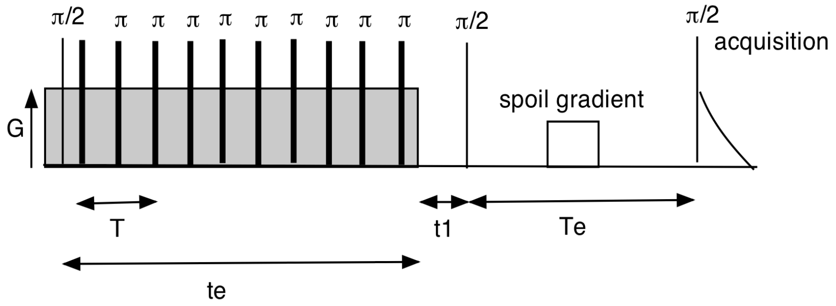

Fig. 1: The MGSE-LED sequence used in our diffusion experiments.

The experiments were performed at 25 °C on a Bruker Avance 500 MHz instrument (Bruker Biospin, Ettlingen, Germany), using a commercial probe (DIFF30). Experiments were performed in a sample of distilled water and a sample of water-continuous microemulsion. (Winsor's type I) [9]. The microemulsion has brine (NaCl/H_2O) as the water phase, heptane as the oil phase, sodium dodecyl benzene sulfonate (SDBS) as surfactant, and 2-butanol as co-surfactant. To avoid effects from gradient-slicing and unwanted coherences, it is necessary to keep the sample short [5]. To maintain high chemical shift resolution using a short sample, we used a 5 mm Shigemi™ tube. This enabled us to operate with a sample height of only 0.5 mm. The parameters used were: te = 80 ms, $t1$ = 5 ms, Te = 500 ms. T was varied between 0.5 and 10 ms in 32 steps. The gradient strength, G, was set to 60 Gauss/cm in all experiments.

3. Results and Discussions

Fig. 2 shows the diffusion spectrum obtained in a sample of distilled water. The measurements are stable up to modulation frequencies of approximately 1600 Hz. The average value of $D(\omega_m)$ obtained in the range 400-1600 Hz is $2.29 \cdot 10^{-9}$ m^2/s, which is in good agreement with the literature value at 25 °C [10].

The obtained NMR spectra presented in Fig. 3 verify that there are no severe phase distortions when using modulation frequencies in the range 600-1600 Hz, compared to what is obtained in a standard one-pulse NMR experiment.

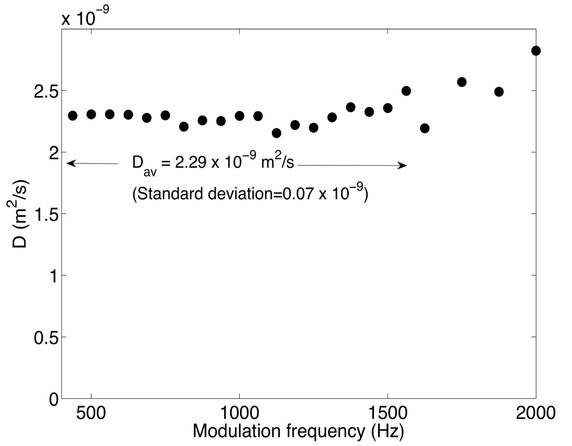

Fig. 2: Diffusion spectrum ($D(\omega_\mathrm{m})$) obtained in a sample of distilled water.

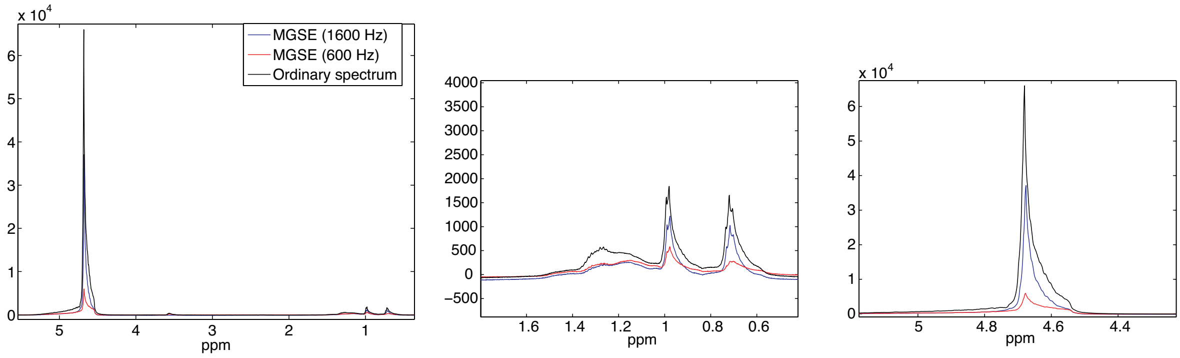

Fig. 3: Obtained NMR spectra in a sample of a Winsor's I type microemulsion. The main figure on the left shows the spectral range covering both the signal from water (4.7 ppm) and heptane (0.6-1.0 ppm). The smaller figures show the magnified heptane peaks (middle figure) and water peak (right figure).

The diffusion spectrum obtained in a sample of a Winsor's I type microemulsion (Fig. 4) is flat for both oil and water. The average value of $D(\omega_m)$ obtained in the range 600-1600 Hz is $1.6 \cdot 10^{-9}$ and $8.0 \cdot 10^{-10}$ m^2/s, respectively for water and oil (heptane). As a comparison, the respective values obtained in a PGSE measurement with a diffusion time of 10 ms were $1.6 \cdot 10^{-9}$ and $5.0 \cdot 10^{-10}$ m^2/s. The water molecules are diffusing in a continuous phase between closely packed and nano-sized oil droplets (size range of 10-100 nm), so already at a 'diffusion time' (T) of 0.6 ms the tortuosity limit is reached. Unlike water, oil molecules are confined inside the small droplets, but also here the long-time diffusion behaviour is reached already for the highest modulation frequencies. Thus, neither for water or oil we were able to observe any short-time diffusion behaviour [1]. The results are as expected in this type of microemulsion, with nano-sized and closely packed droplets [11]. In future applications we will employ the MGSE-LED sequence in samples where the short-time diffusion behaviour is within the range of the method, for instance emulsions, liquid saturated mesoporous materials, and dairy products.

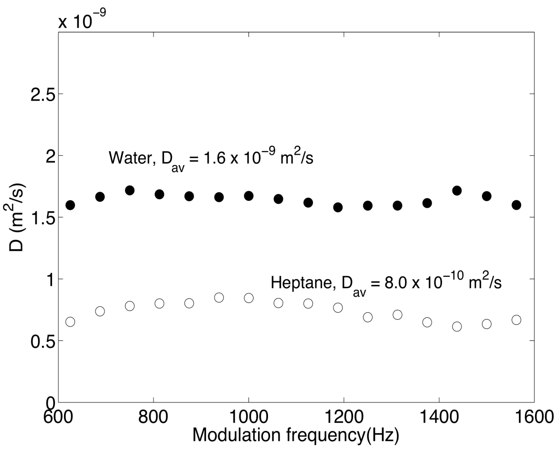

Fig. 4: Diffusion spectrum ($D(\omega_\mathrm{m})$) obtained in a sample of a Winsor's I type microemulsion. The average value of $D(\omega_m)$ obtained for water and oil in the range 600-1600 Hz is indicated.

The instability for modulation frequencies higher than 1600 Hz is due to eddy currents, which are hard to suppress when having sharp edges of the gradient pulse. This may be further improved by using smoother edges of the gradient pulse, or by combining a LED with sine-shaped gradient pulses and CPMG [8]. We will pursue these experimental approaches in the near future.

4. Conclusions

We have presented an MGSE pulse sequence that enables diffusion measurements with chemical shift resolution in the obtained spectra, and with reliable results at modulation frequencies up to 1600 Hz. The gradient modulation is generated using CPMG in a constant gradient, combined with a longitudinal eddy current delay (MGSE-LED). To avoid effects from gradient-slicing and unwanted coherences, while maintaining high chemical shift resolution, a Shigemi™ tube was used. The pulse sequence gave reliable results when applied to a sample of distilled water and a sample of a water-continuous microemulsion.

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