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Magnetic Resonance Spectral Characterization of Diffusion with Chemical Shift Resolution

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Abstract

We present a modulated gradient spin-echo method (MGSE), which uses a train of sinusoidally shaped gradient pulses separated by 180-degree RF pulses. The RF pulses efficiently refocus chemical shifts and de-phasing due to susceptibility differences, resulting in undistorted, high-resolution diffusion weighted spectra. This allows for simultaneous spectral characterization of diffusion of several molecular components with different chemical shifts. Feasibility of the technique is demonstrated by following the diffusion of water, oil, and water-soluble salt in a highly concentrated water-in-oil emulsion.

Keywords

MGSE, restricted diffusion, velocity autocorrelation, chemical shift, emulsion

1. Introduction

The modulated gradient spin-echo method (MGSE) [1,2] provides information about molecular diffusion in frequency domain. It generates a periodically oscillating phase factor and results in signal attenuation which is proportional to the spectrum of velocity autocorrelation function. The effect of spin de-phasing, due to diffusion, is accumulated over many gradient modulation cycles, giving rise to adequate diffusive attenuation on a shorter time scale compared to the pulsed field gradient method. Different kinds of MGSE experiments have already been employed to study water diffusion in porous media [3] and emulsions [4] but without chemical shift resolution. Here we present an application of the MGSE method, which produces an apodized cosine effective gradient waveform, similar to the one employed by Parsons et al. in combination with imaging [5].

2. Method

If the relaxation is factored out and there is zero net flow the normalized spin-echo signal is given by the Gaussian approximation of the cumulant expansion [6] as

$$\beta = \frac{1}{\pi}\int_0^\infty |F(\omega)|^2 D(\omega) d\omega\,, \qquad (1)$$

where $F(\omega)$ is the spectrum of the phase factor $F(t) = \gamma\int_0^t G(t')dt'$ and $D(\omega)$ is the spectrum of velocity autocorrelation function or diffusion spectrum [1,2].

Our experiment consists of a CPMG train of RF pulses and interspaced sinusoidally shaped gradient pulses as indicated in Fig. 1. Only the last echo is acquired at a fixed time $t_e = NT_m$, where N is the number of modulation periods T_m. The sequence generates an effective gradient waveform identical to the one described in [5]. The phase factor oscillates around zero with period T_m. Its spectrum has a peak centered on $\omega_m = 2\pi/T_m$ with the width inversely proportional to NT_m. For $N > 3$ the attenuation can be approximated as $\beta_k = bD_k(\omega_m)$, where

$$b = \left(\frac{\gamma G_0}{8\pi}\right)^2 t_e^3 \frac{8N-1}{N^3}\,. \qquad (2)$$

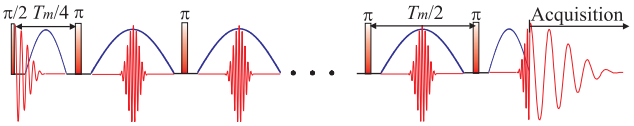

Fig. 1: Schematic timeline of RF pulse sequence with sinusoidal gradient lobes. The refocusing pulses are repeated with the period $T_m/2$. Sketched is also the evolution of magnetization.

The modulation frequency and number of periods are varied in order to sample the diffusion spectrum. The advantage of using spin echoes instead of gradient echoes [5] is the reduction of field inhomogeneity effects. More modulation periods can be used, thus higher sensitivity at short times can be achieved. The smooth gradient modulation results in reduced eddy currents and high resolution spectra (Fig. 2). As the polarity of the gradient pulses is not switched, we avoid the effect of asymmetry of gradient pulses with opposite polarity, which can be significant in case of gradient-echo experiment.

3. Experimental results

We studied a highly concentrated water-in-oil emulsion, which consists of 95 wt% 0.2 M tetramethyl ammonium chloride (TMA-Cl) in Millipore water as aqueous phase, 3.5 wt% heptane as oil phase and 1.5 wt% Brij 92 as surfactant [8]. The experiment was performed at 25°C on Bruker DMX-200 spectrometer. Gradients where generated by a Bruker DIFF-25 probe capable of delivering a maximum gradient strength of 9.6 T/m in z-direction. The experiment was performed with $t_e = 150$ ms and 32 different modulation periods between 2 ms and 30 ms. Gradient amplitude was adjusted so that the same 20 linearly stepped b values were applied at each modulation period. The maximum gradient amplitude used was 2.9 T/m. The standard 8 steps CPMG phase cycling was applied.

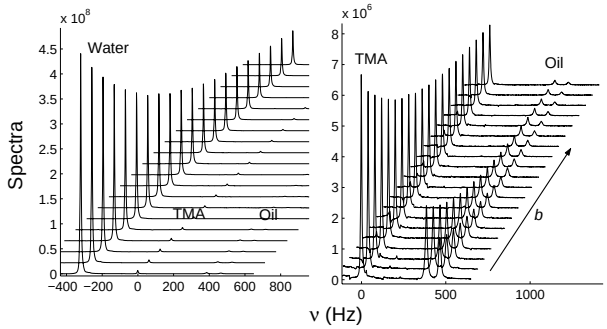

Fig. 2: Diffusive attenuation of emulsion spectrum at $T_m = 2$ ms. The spectrum consists of water, TMA and Oil peaks. On the right side is a close up of TMA and Oil peaks. The arrow indicates linearly increasing b values.

The data was fitted to the restricted diffusion model for spherical geometry provided in [7]. Free diffusion coefficients of TMA and water in solution were measured by the same experiment. The diffusion coefficients are time independent as expected. Within 5 % of accuracy the respective values for TMA and water are 10^{-9} m^2/s and 2.1×10^{-9} m^2/s. These values are used to model the diffusion in the emulsion. The TMA ions are not soluble in oil. Because the emulsion droplets are poly-disperse the TMA decay curves (Fig. 3.a) are multi-exponential. The data fits well to the log-normal size distribution with mean radius 1.5 μm and standard deviation 0.9 μm. Water molecules on the other hand can migrate between droplets, their long range diffusion coefficient obtained by extrapolation to long times is around 10^{-10} m^2/s. Due to migration the diffusion spectrum of water can be assumed to be a superposition of spectra with different restrictions, giving rise to a mono-exponential decay (Fig. 3.b). Data for water fits roughly to the same size distribution as TMA. In the case of oil diffusion, in agreement with the expectation, we see no time dependence of diffusion. Oil diffusion is not restricted but hindered. The measured diffusion coefficient for oil is 0.8×10^{-9} m^2/s. In this case the error of 7 % is higher due to lower signal-to-noise ratio. Further details on data modeling will be presented elsewhere.

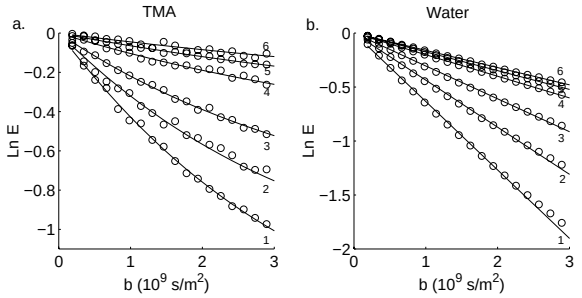

Fig. 3: TMA (a) and water (b) signal attenuation vs. b for selected modulation periods. Marked 1-6 are T_m = 2, 3.3, 5.5, 11.5, 16.7 and 21.4 ms corresponding to N = 7, 9, 13, 27, 45 and 75 modulation periods. Data are obtained by integration of spectral peaks shown in Fig. 2.

4. Conclusions

The MGSE technique which enables spectral characterization of diffusion with chemical shift resolution is introduced. Its potential is demonstrated on the study of highly concentrated water-in-oil emulsion. The results are in good agreement with [8] and contribute to experimental evidence necessary in understanding of emulsion morphology. The method is robust against susceptibility artifacts, field in-homogeneity and imperfections in gradient generating equipment. The technique is particularly suited for in-vitro studies of samples where diffusion of several compounds with different chemical shifts is of interest.

Acknowledgement

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