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NMR Diffusive Diffraction Studies of Emulsions

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1. Introduction

Droplet concentration, size, polydispersity, and interfacial properties/interactions are key features which influence emulsion characteristics such as stability, texture and appearance [1]. Several techniques are available for measuring these features [2-6] however nuclear magnetic resonance (NMR) is particularly suited to studying the structure of emulsions because it is non-invasive and it can measure highly concentrated and opaque emulsions. One way in which NMR can be used to study emulsions is by measuring the translational diffusion of molecules confined within the droplets. Under certain experimental conditions, the results of the NMR measurements display coherence features analogous to optical diffraction. These coherence features can be used to determine morphological characteristics of the emulsion. Here we have used NMR diffusive diffraction coherence features to determine structural characteristics of a highly concentrated emulsion and discuss factors which impede accurate quantification.

2. Theory

NMR pulsed gradient spin-echo (PGSE) measurements can measure the translational diffusion of molecules by labelling the phase of spins via magnetic field gradients. When the phase of these spins is recorded at two instants in time, the phase change can then be related to the mean squared displacement (MSD) given by [7, 8]

$$\left\langle \left(\mathbf{r}'-\mathbf{r}\right)^2 \right\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \left(\mathbf{r}'-\mathbf{r}\right)^2 \rho\left(\mathbf{r}\right) P\left(\mathbf{r}\,|\,\mathbf{r}',\Delta\right) d\mathbf{r}d\mathbf{r}' \qquad (1)$$

where $\rho(\mathbf{r})$ is the spin density and $P(\mathbf{r} \mid \mathbf{r}', \Delta)$ is the probability of a molecule moving from $\mathbf{r}$ to $\mathbf{r}'$ during the diffusion time (Δ). Within a confined space (i.e., an emulsion droplet) the maximum distance the molecule can move is limited by the boundaries hence the MSD becomes sensitive to the size and shape of the confining geometry. Analytical solutions to describe this motion quickly become mathematically intractable hence approximation methods are generally used. The two most common approximation methods are the Gaussian phase distribution (GPD) approximation [9] and short gradient pulse (SGP) approximation [10]. In the study of emulsions, the GPD approach has primarily been used because the SGP approximation in theory requires gradient pulses with infinitely fast rise and fall times which place impossible demands on the NMR hardware. However with the increasing availability of NMR spectrometers equipped with greater gradient strength generation capabilities, it is becoming easier to approximate the pre-conditions of the SGP approximation. An advantage of using the SGP approximation to model diffusion in restricted system is that it can describe diffusive diffraction coherence features which the GPD approach cannot.

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3. Results and Discussion

The results of NMR PGSE diffusion experiments on a tetramethylammonium chloride (TMA) emulsion are given in Fig. 1. The two sets of experimental data are from two separate resonances of TMA; one in which the TMA resonance is overlapped with the H_2O resonance. Two models were fitted to the experimental data: one based on the GPD approach (see ref. [11]) and another based on the SGP approximation which included a distribution of characteristic dimensions [12]. Both models assumed a log-normal distribution of droplet radii. Droplet dimensions obtained from the SGP model gave a median radius of 2.7 μm with a variance of 0.2 whilst the GPD model gave a median radius of 1.5 μm with a variance of 0.2. As seen in Fig. 1 the SGP model gave a much better fit compared to the GPD model however some anomalies still exist. These anomalies can be attributed to the size distribution not being perfectly log-normal, possible violations of the SGP condition, or contact between adjacent droplets.

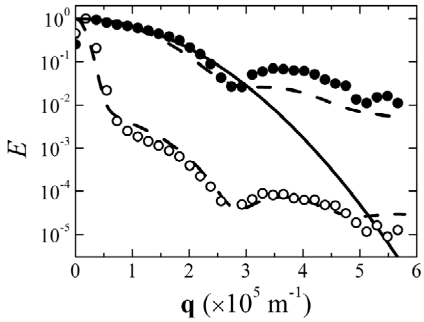

Fig. 1: Spin-echo signal attenuation (E) profiles from ^{1}H NMR diffusion experimental on a concentrated TMA emulsion. The model based on the SGP approximation (dashed line) gave a median droplet radius r = 2.7 μm with a variance of σ = 0.2 when fitted to the data while the GPD model gave r = 1.5 μm with σ = 0.2.

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