

● *Short Communication***DIFFRACTION-LIKE EFFECTS IN A HIGHLY CONCENTRATED W/O EMULSION: A PFG NMR STUDY**

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Diffraction-like effects have been observed by applying pulsed field gradient (PFG) nuclear magnetic resonance (NMR) to a highly concentrated water-in-oil (W/O) emulsion, made up of the nonionic surfactant $C_{12}E_4$ [$CH_3(CH_2)_{11}(OCH_2CH_2)_4OH$], *n*-decane, and brine [1 wt% NaCl(aq) solution]. The pulsed field gradient NMR data show one pronounced maximum and the shoulder of a second maximum in the attenuation curve of the NMR signal from water, the so-called Bragg interference peaks. From the diffraction-like peaks, the average distance (center to center) between the emulsion droplets can be obtained, in this case related to the average size of an emulsion droplet. Furthermore, we note that the long-term stability of the emulsion can be followed by pulsed field gradient NMR. © 1998 Elsevier Science Inc.

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INTRODUCTION

During the last 10 years the interest in studying non-Gaussian diffusion by means of pulsed field gradient (PFG) nuclear magnetic resonance (NMR) methods has increased considerably. The main reason for this state of affairs is that these experiments do not only give the transport behaviors of the constituents of the system, but they also convey structural information about the systems under study. This was first experimentally shown by Callaghan et al.,¹ using randomly packed polystyrene spheres, measuring the solvent diffusion (in this case water). Another reason for the increased interest in PFG NMR is due to the instrumental developments and improvements that have taken place, as these kind of experiments require good sensitivity and accurate and large magnetic field gradients.

An interesting class of systems that has been the object of many recent studies (see Ref. 2) is the highly concentrated emulsions that are of great importance in a number of technical applications. Examples can be found in pharmaceutical, cosmetic, and food technologies.^{3–5} They are also used in the field of emulsion explosives.⁶

Furthermore, they are used as precursors for polymeric materials.² As a consequence it is important to understand the basic properties of such systems, and here the non-invasive PFG NMR technique can provide a valuable tool to obtain information, such as structural and dynamic properties of the systems.

The diffraction ideas were first introduced to NMR by Mansfield and Grannell.⁷ Two different diffraction concepts in NMR can be identified. The Mansfield (*k*-space) diffraction and the Callaghan (*q*-space) diffraction. The difference and similarities are thoroughly discussed by Callaghan in Ref. 8. In this work we will be concerned with the latter, i.e., the diffusive (*q*-space) diffraction. Diffraction-like effects in highly concentrated emulsions have to date only been reported once to our knowledge. This was in a report by Balinov et al.,⁹ dealing with a highly concentrated water-in-oil (W/O) emulsion, consisting of a fluorinated nonionic surfactant ($C_nF_{2n+1}CH_2E_2$, where *n* is 6, 8, or 10), perfluorodecalin, and water. In this work we apply the technique to a different emulsion to show that the effect is quite general.

One feature of this work is that we have taken special care to design an emulsion system that is easy to prepare

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and yields emulsions with reasonably reproducible properties. Furthermore, we note that the technique can be used to investigate the long term stability of the emulsion.

MATERIALS AND METHODS

Materials

The tetraethylene glycol dodecyl ether, $C_{12}E_4$, was obtained from Nikko Chemicals Co., Japan, and *n*-decane was of analytical grade. Both chemicals were used without further purification. The water used was Millipore-Q treated (Millipore Corp., Bedford, MA, USA).

Sample Preparation

The sample preparation was carried out by a method recently suggested by Pons et al.¹⁰

NMR Self-Diffusion Measurements

The self-diffusion of the water in the emulsion was measured with the Fourier transform-PFG technique, monitoring the ^1H NMR spectra and following procedures as suggested previously.^{11,12} The measurements were performed in 5-mm NMR tubes on a Bruker DMX 200 spectrometer equipped with a wide bore magnet. The gradient probe used is a Bruker probe and has a gradient strength of approximately $0.22 \text{ T m}^{-1} \text{ A}^{-1}$. The temperature was $30 \pm 0.1^\circ\text{C}$ in all measurements. The pulse sequence, $90^\circ - \tau - 180^\circ - \tau - \text{echo}$, with two pulsed magnetic field gradients of amplitude g and duration δ sandwiched around the 180° radiofrequency pulse with a time separation of Δ (where Δ is kept equal to τ) was used throughout.

RESULTS AND DISCUSSION

The aim of this presentation is not to give a detailed description of the theory behind the observed effects. Detailed accounts can be found elsewhere.^{1,13,14} Instead, we want to show how the PFG NMR method can be used to study highly concentrated emulsions.

PFG NMR Results

We now turn to the obtained results of the PFG NMR measurements. In Fig. 1 the normalized attenuation of the water NMR signal is shown for one diffusion time ($\Delta = 70 \text{ ms}$). The attenuation curve shows one pronounced maximum and the shoulder of a second maximum. The origin of the maxima can be understood in the following way. These systems consist of densely packed water droplets separated by a thin oil film (on the order of $100 \text{ \AA}$). As a consequence, the water molecules are able to permeate the film. The mechanism by which the water molecules cross the film is not of importance in the present application and will not be considered here.

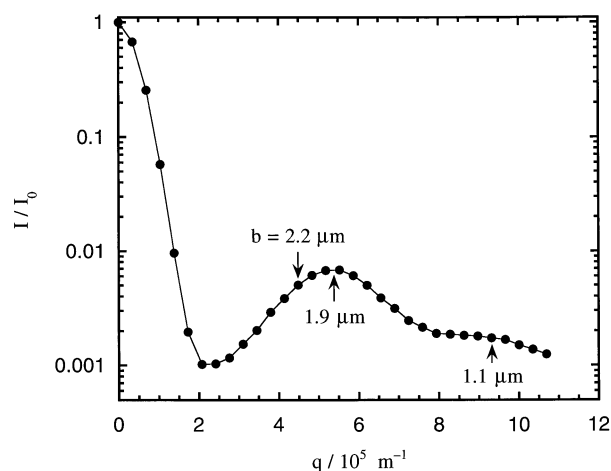


Fig. 1. Normalized intensities vs. $q [q \equiv \gamma g \delta / (2\pi)]$ for one diffusion time ($\Delta = 70 \text{ ms}$). The emulsion contains 90 wt% brine. The arrows in the figure indicate the first and the second maximum. The solid line is a guide for the eye.

Assume now that we measure on a time scale where some of the water molecules visit two or more droplets during the experimental time. In cases where the systems show a well defined structure, only certain distances will be preferred, and some more than others. This implies that the fraction of water molecules that visits two or more droplets will only move certain distances, the values of which will be given by the structure of the system in question. For the most preferred distances, diffraction-like peaks will be obtained at q -values equal to the inverse of the distances (see Fig. 1).

As shown in Fig. 1 the diffraction-like peaks occur at q -values of 5.3×10^5 and $9.3 \times 10^5 \text{ m}^{-1}$, respectively. These correspond in real space to 1.9 and $1.1 \mu\text{m}$, respectively. The ratio of these two numbers can be

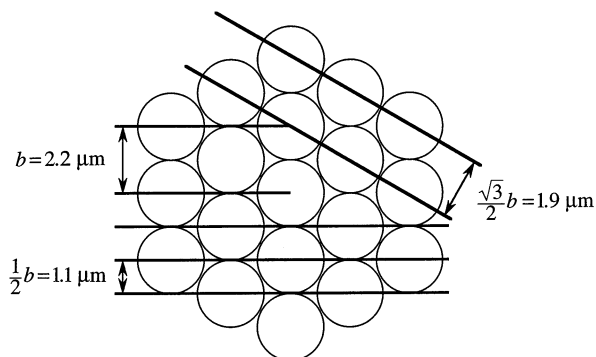


Fig. 2. Schematic picture of the droplet distribution in an emulsion. The distances indicated in the figure correspond to the peaks in Fig. 1.

understood from Fig. 2, where an ensemble of spheres has been packed in a hexagonal pattern (Fig. 2 shows only a slice of the ensemble, cut in the middle of the spheres). This is certainly not a realistic picture of a highly concentrated emulsion, but nevertheless it illustrates the relationship among the characteristic distances in the system.

Using concepts from scattering theory for hexagonal symmetry, the q -values at the maxima should be proportional to $(1 \div \sqrt{3} \div 2 \div \sqrt{7} \div 3 \div \dots)$. If we divide the second q -value by the first ($5.3 \times 10^5 \text{ m}^{-1}$) we obtain a value of 1.75, which is close to $\sqrt{3} \approx 1.73$. The agreement is surprisingly good, and one might argue that the position of the second peak is somewhat inexact (as we do not have any pronounced maximum). Nevertheless, the effect of shifting the position one point to the left or to the right is marginal (1.7 and 1.8, respectively).

Furthermore, we note one interesting feature in Fig. 2 by examining the characteristic distances and comparing them with the obtained values for the diffraction-like peaks. The first peak will not be described by the average distance, b (center to center), of two neighboring droplets. Instead, the first peak will correspond to the distance $b\sqrt{3}/2$, and the second peak to the distance $b/2$, which gives a value of $b = 2.2 \text{ }\mu\text{m}$.

Figure 1 and the positions of the peaks indicate that the droplets are fairly monodisperse in size and that the packing is close to hexagonal. Furthermore, the widths of the peaks are an indication of the spread in droplet size (or actually the spread in the distances between the droplets, which in this case is related to the spread in droplet size).

To obtain a more detailed picture of the system, one has to use some theoretical model that describe the attenuation curve in detail. The pore-hopping formalism, developed by Callaghan and co-workers,^{1,13,14} has successfully been used to describe the diffusion of water between randomly packed polystyrene spheres.¹ In this case we have been less successful at using the pore-hopping formalism to describe the attenuation curve in Fig. 1. There may be several reasons for this, but one could be that the emulsion system is not very stable with time. This can be seen in Fig. 3, where the signal attenuation for the water signal is shown for two different times after the preparation of the emulsion, using the same diffusion time in both cases ($\Delta = 50 \text{ ms}$). From Fig. 3 we clearly see how the maximum moves toward lower q -values (i.e., larger distances). The emulsion is breaking down. Another reason may be that the structure factor cannot be described as a pore glass. A more detailed account of this work will be presented (B. Håkansson, R. Pons, and O. Söderman, manuscript in preparation).

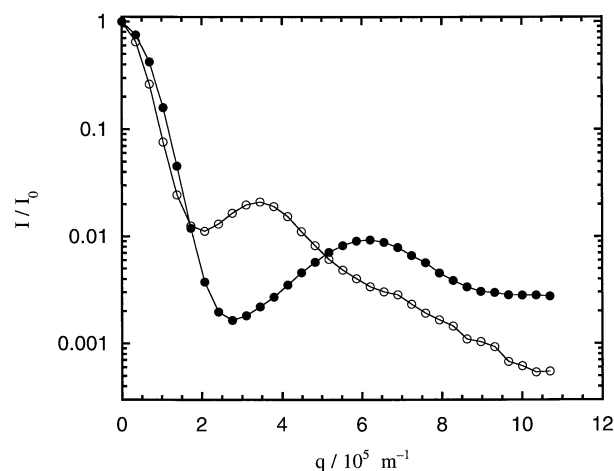


Fig. 3. Normalized intensities vs. $q[q \equiv \gamma g \delta / (2\pi)]$ for one diffusion time ($\Delta = 50 \text{ ms}$) at 2 (●) and 8.5 (○) h after preparation, respectively. The emulsion contains 90 wt% brine. The solid lines are a guide for the eye.

CONCLUSION

In conclusion, we have shown the appearance of diffraction-like peaks in a highly concentrated W/O emulsion, using PFG NMR. Furthermore, we have obtained a second peak that can be directly correlated to the symmetry of the packing of the droplets. Finally, we note that the obtained mean droplet diameter seems reasonable compared to the results of previous studies.¹⁰

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