OPTIMISED DROPLET SIZING OF WATER-IN-CRUDE OIL EMULSIONS USING NMR

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ABSTRACT

Water-in-crude oil emulsions are an increasing problem during production. Essential to any emulsion breaking method is an ability to accurately measure droplet size distributions; this is rendered extremely difficult given that the samples are both concentrated and opaque. Here we systematically consider the use of a standard, low-field bench-top NMR apparatus to accurately measure the droplet size distributions. Such measurements are challenging because the NMR signal from the oil phase erroneously contributes to the measured water droplet size distribution. Conventionally the oil phase signal is nulled-out based on differences in the NMR T_1 relaxation parameter between water and oil. However in the case of crude oil, the oil presents a broad T_1 distribution rendering this approach infeasible. Based on this oil T_1 distribution, we present an optimisation routine that adjusts various NMR measurement timing parameters (observation time (Δ) and inversion time (T_{inv}) to effectively eliminate this erroneous crude oil contribution. An implementation of this optimisation routine was validated against measurements performed using unambiguous chemical shift selection of the water (droplet) signal, as would conventionally be provided by high field super-conducting NMR spectrometers. We finally demonstrate successful droplet sizing of a range of water-in-crude oil emulsions.

Keywords: NMR, crude oil emulsions, droplet sizing

INTRODUCTION

Water-in-crude oil emulsions are prevalent in the global petroleum industry and can form during crude oil production as fluids are transported through various high shear regions (*e.g.* valves, chokes and pumps). They are stabilized by natural surfactants¹ (*e.g.* asphaltenes and resins) and solids² (*e.g.* clays, sands) present in the crude oil. These emulsions generally have higher viscosities and are more voluminous than their constituent fluids²⁻³, they can transport corrosive material (*e.g.* salts dissolved in the water phase) to downstream processing equipment, cause environmental concern due to chemical de-emulsifier usage and can also cause difficulties in meeting crude oil specifications. These factors make crude oil emulsions a significant economic problem, which will only become more pronounced as oil fields age and more deep water fields are produced⁴. A variety of methods are used to break crude oil emulsions including the use of de-emulsifiers, electrostatics, heat treatment and gravity (*e.g.* centrifugation)⁵. To effectively implement these methods, knowledge is required of microstructural changes occurring in the emulsion, with temporal changes in droplet size distribution (*DSD*) being particularly important. For example, obtaining the correct *DSD* is paramount when using viscosity correlations as the friction between droplets is related to the interfacial area,⁶ and the degree of emulsion drop size poly-dispersity can have a significant effect on both emulsion stability⁷⁻⁸ and rheological behaviour⁹⁻¹¹.

Methods used to determine droplet size distributions generally rely on image acquisition and analysis (*e.g.* optical microscopy, confocal microscopy, electron microscopy), electromagnetic radiation scattering (*e.g.* laser scattering) or ultrasonics; these have been reviewed extensively^{12,13}. These methods are, however, limited by the opaqueness of crude oil,

high concentration of water, variability in the physicochemical properties of crude oil and the presence of gas bubbles and suspended solids. For nuclear magnetic resonance (NMR) none of these factors are a significant problem, in fact a high concentration of water droplets is beneficial as it increases the available signal to noise ratio (SNR). NMR also benefits from requiring no sample preparation or treatment, and it is completely non-destructive, hence allowing multiple re-runs of the same sample. The use of NMR for studying emulsions has been reviewed by Johns^{14,15}, while extensive work using NMR to study water-in-crude oil emulsions has been conducted by various researchers¹⁶⁻²².

In this work we present a systematic procedure to allow for droplet sizing of water-in-crude oil emulsions using bench-top NMR apparatus featuring permanent magnets. Such apparatus are cheaper and hence more readily available compared to conventional high field NMR spectrometers featuring super-conducting magnets. They are widely employed for measuring the droplet size distribution (*DSD*) of food emulsions²³⁻²⁴, both for oil in water and water in oil emulsion food products. Essential to these *DSD* measurements is selective signal detection from the droplet phase (*i.e.* water or oil). In the case of water in oil emulsions, selective water signal detection is realised by what is known as $T_{1,\text{nulling}}$, which essentially eliminates the oil phase's NMR signal. This approach works by effectively inverting the oil NMR and allowing it to evolve to a null point, under T_1 relaxation, where it provides no NMR signal before initiating the acquisition sequence. This approach relies on there being a significant difference in T_1 between the oil and water phase, and on there being a well-defined value of T_1 for the oil phase. The case of crude oil is, however, complicated by the broad multi-modal T_1 distribution for the oil signal, which reflects its multi-component composition. While T_2 relaxation can also

be used as a primary contrast mechanism to distinguish water and oil NMR signals it is affected by internal magnetic field gradients making it a less reliable method for complex emulsion systems, additionally the nulling of the oil NMR signal presented in this work is unique to T_1 relaxation allowing a more robust approach than simply relying on NMR signal decay. In the current work, we detail a procedure to allow for optimum T_1 suppression of the signal from this crude oil, based on both inversion nulling and conventional T_1 relaxation weighting. This more robust approach is demonstrated using a commercially available bench-top NMR spectrometer on two West Australian crude oils that readily form water-in-oil emulsions upon agitation. The results obtained are compared with those from a novel bench-top NMR spectrometer featuring a sufficiently homogeneous magnetic field such that chemical shift resolution allows for unambiguous detection of the water (droplet) signal only. We conclude with a consideration of the future potential of this alternative technology for robust, routine oilfield emulsion characterisation.

EXPERIMENTAL METHODS

BACKGROUND THEORY

An excellent range of textbooks²⁵ are available which explain the relevant fundamentals of NMR. For the sake of brevity only the pertinent details relevant to the experiments in this paper are presented. NMR involves exciting nuclear spins located in a magnetic field ($\mathbf{B}_0$) from thermal equilibrium by applying an oscillating magnetic field ($\mathbf{B}_1$), ^1H nuclei are exclusively considered in the work presented here. The frequency of oscillation is known as the Larmor frequency (ω_0) and is related to the static field (B_0) through $\omega_0 = \gamma B_0$, where γ is the gyromagnetic ratio of the nuclei. The NMR signal decays via two mechanisms: spin-spin (T_2)

relaxation is the loss of magnetic phase coherence due to nuclear spins exchanging energy with each other, which causes no net loss of energy to the surroundings, while the energy loss to the surroundings is quantified by the spin-lattice (T_1) relaxation.

To measure the T_1 relaxation time an inversion recovery pulse sequence (figure 1a) is used in which a 180° radiofrequency (RF) pulse is applied to invert the net magnetization. This magnetization will relax to thermal equilibrium given sufficient time. To probe this relaxation process a 90° RF pulse at variable inversion time (T_{inv}) is applied and the resulting NMR signal is then acquired. The evolution of the acquired NMR signal $S(t)$ during this relaxation process can be expressed as,

$$S(t) = S(0) \int f(T_1) (1 - 2e^{-t/T_1}) dT_1, \quad (1)$$

where $S(0)$ is the NMR signal at time $t = 0$, T_1 is the spin-lattice relaxation time and $f(T_1)$ is the distribution of T_1 . This distribution is obtained in practice by inverting $S(t)$ using mathematical regularisation²⁶. Note that when $t = \ln(2) \cdot T_1$ there is no signal ($S(t) = 0$) from the material featuring this value of T_1 , this is known as the null point (t_{null}). The rest of the T_1 distribution will however still provide NMR signal. By an appropriate choice of T_{inv} (*i.e.* $T_{inv} = t_{null}$) it is possible to selectively suppress the NMR signal from material featuring the specific T_1 .

To measure the emulsion droplet size distribution using conventional benchtop NMR hardware we use an inversion recovery weighted pulsed field gradient stimulated echo (PFG-STE) pulse sequence (figure 1b). This sequence uses two pulsed magnetic field gradients (PFG) on either side of the 90° - 90° RF pulse pair of a stimulated echo (STE) pulse sequence. These gradients add phase (ϕ_1 and ϕ_2) to the ^1H in opposite sense such that if no displacement occurs in

the gradient direction during the observation time (Δ) the phase modulations cancel and the NMR signal is refocussed (*i.e.* $\varphi_{\text{net}} = \varphi_1 - \varphi_2 = 0$); while any displacement during the observation time (Δ) causes a net phase ($\varphi_{\text{net}} = \varphi_1 - \varphi_2$) which is proportional to the molecular displacement. This net phase can be expressed for a linear magnetic field gradient in an arbitrary direction as:

$$\varphi_{\text{net}} = \gamma g \delta x, \quad (2)$$

where g and δ are respectively the amplitude and duration of the pulsed linear magnetic field gradient (as presented in figure 1b) and x is the molecular displacement. The motivation for using a stimulated echo (STE) sequence is to take advantage of systems where $T_1 > T_2$, as only T_1 relaxation affects relevant signal-bearing molecules during t_{delay} allowing longer experimental diffusion observation times (Δ) than would otherwise be possible due to T_2 spin relaxation. It is also well established²⁷ theoretically and experimentally that for a homogeneous spherical body (*e.g.* emulsion droplet) within a uniform imposed magnetic field, that the field within the body is uniform independent of magnetic susceptibility differences between the droplet and suspending fluid.

When diffusing molecules experience restriction due to the constraints of being within a spherical cavity (*i.e.* emulsion droplets) the NMR signal attenuation (*i.e.* $E = S(t)/S(0)$) deviates from that observed due to free-diffusion (*i.e.* $E = \exp(-D(\gamma g \delta)^2(\Delta - \delta/3))$, where γ is the gyro-magnetic ratio of ^1H). To solve the problem of determining $S(t)$ for diffusion inside a sphere with radius a it has been common to make assumptions about how the diffusion affects the signal's phase during the application of magnetic field gradients. Two common approaches to this problem are (i) the short gradient pulse (sgp) method²⁸, where no displacement and therefore no phase spread is assumed during gradient application and (ii) the Gaussian phase distribution

(gpd) method²⁹, where a Gaussian phase spread due to diffusion is assumed. Both assumptions have drawbacks³⁰⁻³² which motivated the development and adaptation of the block gradient pulse (bgp) method for emulsion droplet sizing, where the restricted diffusion within a spherical geometry is approached using the general technique of quantifying signal attenuation due to an arbitrary magnetic field based on the general gradient waveform set of methods³³⁻³⁵. This allows a more general approach where the phase spread due to diffusion, and gradient de-phasing, can be quantified more accurately with surface relaxation effects easily added into the mathematical framework if necessary. In this approach the macroscopic attenuation within a spherical boundary is obtained by solving the Bloch-Torrey equation³⁶ re-posed in a matrix (Laplace operator eigenbasis) form^{32,37-38}

$$S(\tilde{t}) = \mathbf{v}^\dagger \left(\prod_{k=1}^{N_e} e^{[(-\mathbf{\Lambda} + i(\tilde{\gamma}_k \cdot \hat{\mathbf{z}})\mathbf{Z})\tilde{t}_k]} \right) \mathbf{v}, \quad (3)$$

for a reflective boundary with no surface relaxation, where $\mathbf{v}_j = \delta_{j1}$, $\tilde{t} = Dt/a^2$, $\tilde{\gamma} = -c\gamma ga^3$, $\Lambda_{jk} = \alpha_{nm}^2 \delta_{jk}$, while $\mathbf{Z}$ for a sphere is given analytically by Grebenkov³⁷. Here δ is the Kronecker delta, a is the radius of the droplet causing restricted molecular diffusion and α_{nm} are the roots of a Bessel function, as detailed in Lingwood *et al.*³⁹. Note that $\mathbf{\Lambda}$ and $\mathbf{Z}$ respectively represent the evolution of magnetization due to diffusion and gradient de-phasing, and an additional term representing different surface relaxivity can also easily be introduced³⁷.

Expansion of Eqn. (3) for the stimulated echo PFG pulse sequence used in the current work (figure 1 (b)) allows the signal attenuation ($E = S/S_0$) to be expressed as,

$$E = \frac{\mathbf{v}^\dagger e^{(-\mathbf{\Lambda} + i(\tilde{\gamma} \cdot \hat{\mathbf{z}})\mathbf{Z})\delta} e^{-\mathbf{\Lambda}(\Delta - \delta)} e^{(-\mathbf{\Lambda} + i(\tilde{\gamma} \cdot \hat{\mathbf{z}})\mathbf{Z})\delta} \mathbf{v}}{\mathbf{v}^\dagger e^{-\mathbf{\Lambda}(\Delta + \delta)} \mathbf{v}}, \quad (4)$$

in common with the gpd and sgp models, there is only one free parameter, *i.e.* the droplet size a . Since the above equation refers only to a single droplet size (a), it is necessary to invert the signal attenuation data using regularization techniques²⁶ to obtain the emulsion droplet size distribution (*DSD*). While it is common practice to avoid this regularisation-step when using bench-top NMR apparatuses by assuming a priori a log-normal distribution, this is not universally appropriate. In this work the emulsion *DSDs* are extracted using Tikhonov regularisation with general cross validation (GCV) to choose the regularisation parameter, see Hollingsworth and Johns²⁶ and Lingwood *et al.*³⁹ for further detail.

An alternate approach to obtain the emulsion *DSD* has been demonstrated by Aichele *et al.*²⁰ using a combined PFG and CPMG pulse sequence known as the PFG-Diffusion Editing technique for simultaneous 2D measurement of diffusion and T_2 ; this technique circumvents relaxation time contrast limitations by mapping the T_2 relaxation time against droplet size allowing separation of restricted water from crude oil. This technique is however time consuming when compared with the technique presented in this paper and relies on a complex 2D Laplace Inversion which often leads to results that are difficult to interpret.

MATERIALS

The crude oil samples used were sourced from active oil fields (A, B and C) located across Western Australia. For reference purposes, a paraffin oil sample was also considered (Sigma Aldrich, $\geq 98.5\%$ purity, density of 0.827-0.890g/mL at 20°C, dynamic viscosity of 110-230mPa.s). The crude oil samples were characterized using a gas chromatograph (GC) (7890A, Agilent Technology) with a mass spectrometer (5975C, Agilent Technology). The oils were diluted in hexane, the GC flow was 1mL/min Helium, the inlet temperature (T_{inlet}) was 330°C.

The GC oven was heated from 50°C to 320°C at a rate of 10°C/min and held for 10 minutes at 320°C, resulting in a mass spectrum of 30 to 550 atomic mass units (amu). The resulting spectra are shown in figure 2, along with the carbon number mass distributions calculated from the measured spectra. Table 1 presents a range of physical and chemical properties measured for the crude oil samples.

Water-in-crude oil emulsions were prepared at 5, 10 and 20 wt% water in crude oil. Only crude oils B and C have sufficient natural surfactants to produce stable emulsions and hence were progressed to emulsion droplet sizing using NMR. The stability of crude oil emulsions was initially determined by using a bottle test, where changes over time were qualitatively observed, with further investigation conducted using PFG experiments on the emulsions over a week. These indicated that crude oil A was stable on a time scale of the order of minutes, while crude oils B and C were stable over several days, with neither emulsion fully separating into water and oil components, rather forming a density gradation which has not detectably changed over six months since the experiments were conducted. The emulsion samples were prepared in 50 mL volumes and sheared for two minutes at a shear rate ($\dot{\gamma}$) of 28,000 s⁻¹ using a homogeniser (Micra D8, ART-moderne Labortechnik, Germany). Sample volumes were then transferred via pipette to 5 or 10 mm NMR tubes with all measurements occurring within two hours of emulsion preparation.

EQUIPMENT AND PROCEDURE

NMR Measurements (T_1 and emulsion DSD distributions) were performed using a 20 MHz permanent magnet bench-top NMR instrument (Minispec mq series, Bruker, Germany –

Figure 3(a)) whose sample compartment was maintained at 20°C. The NMR experiments performed were:

- (i) T_1 inversion recovery measurements (Figure 1(a)) using 50 points spaced logarithmically from 5 to 5000ms with repetition time (T_R) of 15 seconds, total experimental time (T_{exp}) of 53 minutes and four averages (N_{avg}).
- (ii) Inversion recovery PFG-STE experiment (Figure 1(b)) with a gradient duration (δ) of 2ms, maximum gradient (g_{max}) of 4 T/m, 32 gradient increments, a variable observation time (Δ) (typically ≥ 0.2 second, optimised below), inversion time (T_{inv}) of 0.01 to 0.40 second (sample dependant, optimised below), $N_{\text{avg}} = 8$, $T_R = 10$ seconds and $T_{\text{exp}} \sim 43$ minutes.

We also employed a 43 MHz Halbach array magnet (Magritek, New Zealand – Figure 3(b)) featuring a unique 1 T/m gradient, able to accommodate 5 mm NMR sample tubes. This system features sufficient magnetic field homogeneity that oil and water signals in the NMR spectra acquired with this instrument can be unambiguously separated based on their chemical shift characteristics and hence individually analysed. Emulsion *DSDs* were also determined using a PFG-STE pulse sequence (no need for inversion recovery given the chemical shift resolution) that employed similar parameters to those used on the Bruker Minispec. All resulting data were processed using the regularisation procedure³⁹ detailed above using Matlab v.7.12 to obtain the T_1 and droplet size distributions presented in this work. For the interested reader examples of attenuation data obtained before inversion and the NMR spectrum with chemical shift resolution (as a function of imposed magnetic field gradient) are shown in the supplemental section.

RESULTS AND DISCUSSIONS

Figure 4 presents T_1 distributions measured for the three crude oils (as well as for paraffin oil and water for comparison purposes). The crude oils studied have been categorised according to their physical properties (Table 1) and GC measurements (Fig. 2) as a mixed chain light oil (crude oil A), a mixed chain medium crude oil (crude oil B) and a waxy linear chain light crude oil (crude oil C) which exhibits thixotropic behaviour. This allowed for the examination of oil systems presenting a range of NMR relaxation characteristics. What is immediately obvious is the very broad multi-modal distribution of T_1 values for the crude oil phases. As with the paraffin oil, this reflects the range of components within the oils, with shorter T_1 relaxation times being typically indicative of longer chain hydrocarbons. This breadth of the oil's T_1 distribution means that a single inversion time (T_{inv}), as per equation 1, is not able to suppress the entire oil NMR signal. A similar difficulty has previously been observed by Métais and Mariette²⁴ when studying complex food emulsions.

To suppress the entire oil NMR signal, it is more effective to select a value of T_{inv} which suppresses the oil peak with the longest T_1 value. It is then possible to select a sufficiently long observation time (Δ) such that the oil signal associated with shorter T_1 values is effectively suppressed. This methodology is demonstrated in figure 5 which shows the change in the T_1 distributions for a sample of 20 wt% water-in-crude oil C as the time between signal excitation and detection (t and thus effectively Δ) is increased. The shorter T_1 peaks are progressively suppressed until only the largest oil peak remains which can be suppressed using T_1 nulling. To successfully apply this method for effective oil signal suppression during emulsion droplet sizing it is necessary to select the appropriate T_{inv} and Δ values. This is accomplished by using the following optimisation routine.

The signal attenuation of each phase (oil or water) is dependent on the time (t) between the signal excitation and detection,

$$S_{o/w}(t) = HI \frac{(1-x_w)}{x_w} \frac{\exp\left(-\frac{t}{T_o}\right)}{\exp\left(-\frac{t}{T_w}\right)} \quad (5)$$

where $S_{o/w}$ is the oil signal to water signal ratio, HI is the hydrogen index of the oil, x_w is the water cut (volume fraction of water to total liquid produced) and T_o and T_w are the NMR relaxation times (T_1 or T_2). In the current experiments we use a PFG-STE experiment with an inversion pulse so we can explicitly write,

$$S_{o/w}(t) = HI \frac{(1-x_w)}{x_w} \left[\frac{\sum_i f_i \exp\left(-\frac{2\tau_E}{T_{2,o,i}}\right)}{\sum_i f_i \exp\left(-\frac{2\tau_E}{T_{2,w,i}}\right)} \right] \left[\frac{\sum_j g_j \left(1 - 2 \exp\left(-\frac{T_{inv} + t_{delay}}{T_{1,o,j}}\right)\right)}{\sum_j g_j \left(1 - 2 \exp\left(-\frac{T_{inv} + t_{delay}}{T_{1,w,j}}\right)\right)} \right] \quad (6)$$

where f_i and g_j are the fractional contribution of each discrete point i (or j) (*i.e.* $\sum_i f_i = 1$ and

$\sum_j g_j = 1$) in the T_2 and T_1 distributions characterising the oil phase. We are able to

independently measure the T_1 and T_2 relaxation distributions of the crude oil and water phases in the emulsion system using CPMG⁴⁰⁻⁴¹ and T_1 inversion experiments (figure 1(a)) respectively; HI and x_w are known. Consequently, as indicated by Eqn. 6 we are able to optimize (minimise) the value of $S_{o/w}$ by adjusting the value of T_{inv} and $\Delta (= t_{delay} + \tau_E)$. The resultant values of $S_{o/w}$ are consistently below 0.025 for all the crude oil samples that we have considered. This corresponds to the application of no magnetic field gradients; $S_{o/w}$ will decrease as magnetic

field gradients are applied during the inversion recovery PFG-STE measurement as the oil phase's diffusion is comparatively unrestricted. This optimisation of the experiment parameters is constrained by the requirement that the signal to noise ratio (SNR) for S_w be at least 10; generally we aim for an order of magnitude attenuation of the emulsion droplet (water) NMR signal between zero and maximum gradient strength as employed during the PFG measurements.

A sample result obtained using this optimization procedure is shown in figure 6 for a 20 wt% water-in-crude oil C emulsion. The most dramatic difference between the *DSDs* derived from the various NMR measurements is seen when comparing the case for measurements made using optimised inversion time parameters ($T_{\text{inv}} = 268\text{ms}$, $\Delta = 500\text{ ms}$) with measurements made without using an inversion pulse (*i.e.* using a PFG-STE pulse sequence). The latter case results in an erroneous bimodal distribution due to the convolution of NMR signal attenuation from restricted water inside droplets and free diffusing crude oil. When an inversion pulse is used with a non-optimal inversion time (*e.g.* $T_{\text{inv}} = 100\text{ms}$ vs. $T_{\text{inv}} = 268\text{ms}$) then an erroneous bimodal distribution also results where the contribution from the crude oil is only partially suppressed. An additional effect of the erroneous crude oil signal contribution on the emulsion *DSD* seen in figure 6 as a subtle shift of the lower end of the measured water *DSD* towards higher values. This results from the contribution of the freely diffusing oil phase to the NMR signal attenuation at higher gradient values. It is also worth noting that these erroneous oil effects would not be evident a log-normal shape were assumed *a priori* with respect to the emulsion *DSD* as opposed to the regularisation techniques employed here.

The optimised measurement procedure discussed above was subsequently applied to various water-in-crude oil emulsions, with their T_1 relaxation time distributions shown in figure 7. As the water component (longest T_1 component) is distinct and separate from the crude oil component for these emulsions it is possible to directly recover the water content by taking a ratio of the water peak area to that of the total area. Figure 8 shows the observed NMR signal contribution ratio (%) versus the wt% of water in the container; the good agreement indicates that the hydrogen index (HI) for these is in the range $HI = 0.95 - 1.04$, which is consistent with the expected range of 0.79 to 1.11 for most crude oils⁴².

To unambiguously confirm that the resultant signal obtained using the optimised inversion pulse is solely from the water component of the emulsion, the DSD of the emulsion was also measured using the Halbach array magnet, as described above. The Halbach system preserves chemical shift resolution of the oil and water signals in the emulsion, and via analysis of the signal peak in the acquired spectra corresponding to the chemical shift of water, an unambiguous analysis of the water phase diffusion is possible. A sample result of this comparison between the optimised inversion and chemical shift methods is shown in Figure 9; the typical difference in $\langle a \rangle$ across the six samples tested was less than 5%, and all samples had a monomodal log-normal type distribution, as is expected for a fully sheared sample⁴³.

While the results from using the spectrally resolved bench-top NMR systems (*e.g.* ACT Halbach array) seem to negate the requirements for an inversion suppression pulse added to a PFG-STE pulse sequence as applied when using the Bruker Minispec, practical limitations currently motivate the continued use of the Bruker Minispec system. It can accommodate larger

samples, is readily and widely available in industry (whereas the Halbach array system is a prototype), currently it allows the application of stronger magnetic field gradients (enabling the detection of a wider range of droplet sizes) and most poignantly it is much less susceptible to system and sample temperature fluctuations.

Figure 10 shows the results of obtaining *DSD* using the optimization procedure on six emulsion samples (Crude oils B & C at 5%wt, 10%wt and 20%wt water content). The results shown in figure 10 indicate similar droplet size distributions for the 5%wt and 10%wt water in both emulsions, while the 20%wt water in oil emulsions have slightly higher mean droplet size. In general the droplet size range is between 1 and 6 μ m indicating tight crude oil emulsions, a result of the high shear ($\dot{\gamma} \approx 28,000 \text{ s}^{-1}$) homogenization used in their preparation, while the distribution shapes are approximately log-normal indicating that the emulsions were well-mixed. Slightly smaller droplets were presented by Emulsion B despite it having a lower asphaltene content. Due to optical opaqueness and droplet concentration of the samples it was not feasible to directly compare the NMR results with optical measurements. It was however possible using the same equipment, sample preparation and experimental procedure, using a non-opaque water-in-paraffin oil system, to obtain a favourable size comparison between NMR and light microscopy droplet sizing results (maximum error of 10% in mean droplet size), these results had similar droplet size precision to those previously observed by Denkova *et al.*⁴⁴.

CONCLUSIONS

This study has demonstrated the feasibility of using an inversion recovery pulse to suppress the oil signal for water in crude oil emulsions before the application of a standard PFG-

STE pulse sequence. An optimisation routine was implemented to ensure no erroneous contribution to the measured emulsion DSD due to the oil signal. The methodology was implemented on a standard bench-top NMR apparatus and validated using a prototype NMR spectrometer which can unambiguously differentiate the oil and water (droplet) NMR signal based on chemical shift differences. It was applied to range of local crude oils and successfully measured the DSDs of various water-in-crude oil emulsions.

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SUPPORTING INFORMATION AVAILABLE

Figure S1 shows examples of NMR signal attenuation data. This information is available free of charge via the Internet at <http://pubs.acs.org/>

FIGURE CAPTIONS

Figure 1. NMR timing diagrams (pulse sequences) for (a) the inversion recovery pulse sequence and (b) the PFG-STE pulse sequence with an inversion pulse. These are respectively used to obtain the emulsion T_1 and droplet size distribution (DSD). Symbols used are defined in the text.

Figure 2. The gas chromatographs obtained for the different crude oils studied. Also Shown are the mass fractions based on carbon number obtained from the GC chromatographs.

Figure 3. Photographs of NMR equipment used in this work (a) 0.5T Bruker Minispec q20 system and (b) 1T Halbach Array ACT system. The relative magnet compartment size is also indicated.

Figure 4. The measured T_1 distribution of the crude oils (A, B and C), with water and a paraffin oil also included for comparison. To obtain these inversion results the T_1 quadrature was linear and all inversion parameters were kept constant to enable comparison between data.

Figure 5. Shows the effects of increasing the time from signal excitation to signal detection (t) on the relaxation time distribution of a 20%wt water-in-crude oil C emulsions.

Figure 6. The droplet size distribution of a 20%wt water-in-crude oil C emulsion; The effect of using an inversion pulse and not optimizing the inversion time (*i.e.* using $T_{inv} = 100\text{ms}$) are compared with using an optimized inversion time (*i.e.* $T_{inv} = 268\text{ms}$) and the case when no inversion pulse is used at all. The erroneous contributing peaks of the crude oil diffusion are clearly marked. The effect of the crude oil contribution also increases overall signal attenuation causing water droplets to appear erroneously larger.

Figure 7. The T_1 distributions obtained using inversion recovery pulse sequences for (a) water in crude oil B emulsions and (b) water in crude oil C emulsions.

Figure 8. The %wt water in crude oil in the sample compared with the measured water signal contribution to the total signal obtained using the T_1 relaxation time distributions.

Figure 9. The DSD obtained using a PFG-STE pulse sequence on a spectrally resolved bench-top NMR instrument (*i.e.* ACT Halbach Array) versus using the inversion pulse weighted PFG-STE pulse sequence on a non-spectrally resolved NMR instrument (*i.e.* Bruker Minispec q20). The plot is on a linear scale to clearly demonstrate differences.

Figure 10. The water droplet size distributions (DSD) of water in crude oil emulsions B & C at various water concentrations (5%wt, 10%wt & 20%wt) obtained by using optimised inversion recovery PFG-STE pulse sequence.

TABLES

Table.1. Measured physical (and NMR) properties of the crude oils investigated.

	Crude oil A	Crude oil B	Crude oil C	Water
Density (g/mL)	0.82	0.90	0.82	1.00
Asphaltenes (% wt)	0.12	0.42	1.74	0.00
Diffusion coefficient at 25°C (m ² /s)	1.64 x 10 ⁻¹⁰	3.42 x 10 ⁻¹¹	2.15 x 10 ⁻¹¹	2.26 x 10 ⁻⁹
$T_{1,avg}$ (ms)	752	85	183	2412
$T_{2,avg}$ (ms)	736	62	102	2060

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10