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In situ monitoring of the microstructure of detergent drops during drying using a rapid nuclear magnetic resonance diffusion measurement

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Abstract The application of a nuclear magnetic resonance (NMR) diffusion measurement suitable for monitoring, in situ, the evolution of microstructure in commercial surfactant-based detergent drops as a response to drying is demonstrated for the first time. We utilise pulsed field gradient (PFG) NMR diffusion techniques to observe variations in self-diffusion coefficient, surface-to-volume ratio and characteristic pore size by probing the water content of the drops. Previously, we quantified the evolution of microstructure in vials of detergent paste using conventional PFG techniques. Now we apply a rapid PFG technique to enable this measurement during the relatively fast in situ drying of a drop with spherical geometry, relevant to spray drying processes. A finer structure is seen to form in the drops compared to the paste in the vials.

Introduction

The end-use behaviour of commercial detergent powders (e.g. dissolution rate) is highly dependent on the internal microstructure that forms when the detergent paste is spray dried during manufacture. This internal microstructure is determined by both formulation (feedstock) and process conditions during spray drying [1]. The evolution of the microstructure also influences the drying kinetics and hence is critical to define the overall drying time and optimal manufacturing methods. Spray drying is an energy intensive process involving high operational costs: any information leading to optimised drying could provide significant financial and environmental rewards [2]. In the spray drying process, the detergent paste is dispersed into small drops to provide a much larger surface area for evaporation. Understanding the development of the microstructure in these individual drops is vital to improve drying efficiency in the future.

In recent years nuclear magnetic resonance (NMR) has become a popular technique for studying surfactants [3], emulsions [4], foams [5], and drops, thin films and interfacial layers [6] due to the range and versatility of the measurements available. In a basic NMR experiment, the resonance behaviour of sensitive nuclei in a strong magnetic field is observed by the application and detection of electromagnetic radio frequency (rf) radiation. It is typical to observe ^{1}H nuclei in water or organic compounds, as these nuclei have high NMR sensitivity and natural abundance. Here we focus on pulsed field gradient (PFG) measurements applicable to the characterisation of porous media [7]. Nuclear spins, when exposed to a magnetic field gradient, acquire a phase shift proportional to their position in the magnetic field. By applying two such gradient pulses, separated by a time interval Δ, it is possible to observe molecular motion and hence self-diffusion [8]. These measurements are both non-destructive and non-invasive, although the acquisition times of the required multi-dimensional data sets can be long. Recently, a rapid NMR diffusion measurement called Difftrain [9] was applied to the characterisation of microstructure in materials [10]. This technique has proven useful in studies of dynamic systems

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(e.g. measurements of advective dispersion [11, 12] or emulsion droplet sizing [13]), where conventional PFG measurements would not provide sufficient time resolution. Material characteristics determined using Difftrain have been validated against theoretical predictions for model porous media and excellent agreement was observed [10].

Conventional NMR PFG and relaxation techniques have been applied previously to monitor the evolution of microstructure in detergent pastes (as studied here) in vials [14], where the surface-to-volume ratio S/V and tortuosity κ of the pore structure was determined as a function of drying time by observing the mobility of the water in the paste. The deposition of solute material was observed additionally through NMR T_1 relaxation time measurements. The spatial distribution of water and drying kinetics of an individual detergent drop have been studied in situ previously using NMR imaging techniques [15], although the microstructure was not explored; this is the focus of the work presented here.

In this work, we demonstrate the applicability of Difftrain to the in situ study of the evolution of microstructure in individual detergent drops during drying, where conventional PFG measurements cannot provide sufficient temporal resolution due to the small sample volume and relatively rapid drying (compared to detergent paste in vials). This is preceded by a validation of the Difftrain pulse sequence by probing the microstructure in a vial of detergent paste during drying and comparing these results to those obtained previously with conventional PFG techniques [14].

Theory: NMR diffusion measurements

If the diffusion of a liquid is unrestricted, the free diffusion coefficient D_0 can be determined from NMR PFG measurements using the Stejskal–Tanner equation [8]:

$$M(g,\delta,\Delta) = M(0)\exp\left[-(\gamma\delta g)^2 D_0\left(\Delta - \frac{\delta}{3}\right)\right], \quad (1)$$

where M (g, δ, Δ) is the signal intensity (magnetisation) at a given magnetic field gradient strength g, applied for a time δ, after diffusion has occurred for a time Δ (the observation time), $M(0)$ is the signal at zero gradient strength and γ is the gyromagnetic ratio ($\gamma = 2.68 \times 10^8$ Hz T^{-1} for ^{1}H).

If the diffusion is restricted, say, by the walls of a pore with a surface-to-volume ratio S/V, the free diffusion coefficient in Eq. 1 will be replaced by an apparent diffusion coefficient D_{app}, determined by the properties of the confining geometry. For short values of observation time Δ, a relationship describing the behaviour of D_{app} as a function of Δ can be defined as [16]

$$D_{app}(\Delta) = D_0\left[1 - \frac{4}{9\sqrt{\pi}}\frac{S}{V}(D_0\Delta)^{1/2} - \frac{1}{12}\frac{S}{V}(D_0\Delta)C_s + \frac{1}{6}\frac{S}{V}\rho\Delta\right] + \mathcal{O}\left[\Delta^{3/2}\right], \quad (2)$$

assuming the interfacial surfaces are smooth with a mean curvature C_s, and allowing for surface relaxation as described by the surface relaxivity term ρ, where $\mathcal{O}$ represents negligible higher order terms.

Typically, for values of $\Delta < 40$ ms, Eq. 2 can be truncated to

$$D_{app}(\Delta) \approx D_0\left[1 - \frac{4}{9\sqrt{\pi}}\frac{S}{V}(D_0\Delta)^{1/2}\right] \quad (3)$$

without incurring significant errors. From this equation, S/V and D_0 can be determined through the measurement of D_{app} as a function of Δ. A schematic representation of a typical data set that can be fitted by Eq. 3 is shown in Fig. 1. According to Eq. 3, $D_{app}(0) = D_0$ and the initial slope of D_{app} plotted against $\Delta^{1/2}$ (at A in Fig. 1) provides S/V. If the sample contains a network of connected pores, then at the long-time limit as $\Delta^{1/2} \to \infty$, the apparent diffusion coefficient reaches an asymptotic limit (at B in Fig. 1) that describes the tortuosity κ of the connected pore network as

$$\lim_{\Delta^{1/2}\to\infty}\left[\frac{D_{app}}{D_0}\right] = \frac{1}{\kappa}. \quad (4)$$

In a standard PFG experiment, the apparent diffusion coefficient is obtained by incrementing the strength of the applied magnetic field gradient g in successive measurements such that

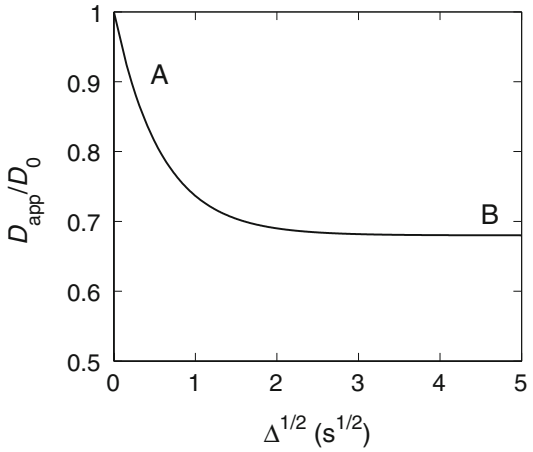

Fig. 1 Schematic representation of normalised apparent diffusion coefficient D_{app} as a function of the square root of observation time $\Delta^{1/2}$. The initial slope at A can be fitted according to Eq. 3 to obtain the surface-to-volume ratio S/V. The asymptotic limit at B provides a measure of tortuosity κ from Eq. 4

$$D_{\text{app}} = -\frac{\ln[M(g)/M(0)]}{(\gamma\delta g)^2(\Delta - \delta/3)} \quad (5)$$

where the gradient duration δ and observation time Δ remain constant. To obtain measurements of D_0, S/V and κ, it is then necessary to repeat the determination of D_{app} across a range of Δ to obtain data equivalent to Fig. 1. When using Difftrain, this second stage is inherent in the measurement since signal intensities are acquired at various Δ, as explained in section "Experimental". A plot of D_{app} as a function of Δ is then obtained simply by incrementing the gradient strength g in successive Difftrain experiments. Thus, the Difftrain protocol offers a considerable reduction in experimental time when determining D_0, S/V and κ compared to conventional PFG techniques.

Experimental

The initial detergent paste is a mixture of three phases—surfactant, aqueous and solids—that are separable by centrifuge. The constituent components in the phases can be seen in Table 1. The surfactant is a sodium salt of linear alkylbenzene sulphonate (LAS). The LAS contains molecules with a range of positional isomers of the aromatic ring, and molecular weights due to variations in the length of the alkyl chains. Distributions of typical LAS components and impurities can be found elsewhere [17, 18].

For validation purposes, 17-mm diameter vials of detergent paste were dried and the evolving microstructure monitored with both conventional pulsed gradient stimulated echo (PGSTE) [19] and Difftrain pulse sequences. Surface-to-volume ratios obtained from PGSTE experiments have been validated previously using samples with known pore size [10]. Due to the low temporal resolution of the PGSTE measurement, a set of identical vials were dried in an oven at 60 °C to provide a range of pastes with known water content (determined by gravimetric analysis) [14]. These vials were sealed to prevent evaporation and placed inside a 7.1 T vertical bore superconducting NMR magnet. A 25-mm diameter rf birdcage coil resonator, tuned to a Larmor frequency of 300 MHz for ^{1}H, was used to accommodate the vials. The NMR experiments were conducted using a Bruker DMX spectrometer. For the Difftrain measurements, a single vial was dried in situ inside the NMR magnet. To dry the paste, air heated to 60 °C was passed through the magnet for 50 h. The in situ air temperature was calibrated using NMR methanol thermometry [20], as explained elsewhere [14].

To determine the structural evolution of individual detergent drops during drying, a drop suspension carriage, see Fig. 2 [15, 21, 22], was used to retain the detergent drops in the magnetic field for the entire duration of the experiments. A 10-µl drop (diameter $d_x = 1.6$ mm) was pipetted onto a 50-µm diameter glass filament at the base of the carriage. This drop diameter corresponds to the maximum drop size formed typically during the manufacture of detergent powders. Using a Perspex guide, the carriage was lowered into the top of the vertical bore magnet. The carriage rested on a 15-mm diameter rf birdcage coil resonator so that the drop was positioned in the centre of the coil. To dry the drop, air heated to 60 °C was passed through the magnet bore for 100 min. The Difftrain measurements were repeated on seven different drops to establish the reproducibility of the data. Data were acquired every 4 min until no further variation in the signal intensity was observed, at which point it was assumed the drop was dry. Spin echo profiles were acquired before and after each Difftrain measurement to allow the relative water content of the drop (where relative water content = absolute water content/initial water content) to be determined.

The vial of detergent paste provided an improved rf coil filling-factor, higher signal-to-noise ratio S/N, and a

Table 1 Initial formulation of surfactant (LAS)-based detergent paste indicating the component fractions in the surfactant, aqueous and solids phases prior to drying

	Component content (wt%)		
	Surfactant	Aqueous	Solids
LAS	9.0	–	–
Water	3.9	25.1	–
Polymer	–	2.8	–
Sulphate	0.7	7.8	26.3
Zeolite	–	–	24.4

The total water content is 29 wt%

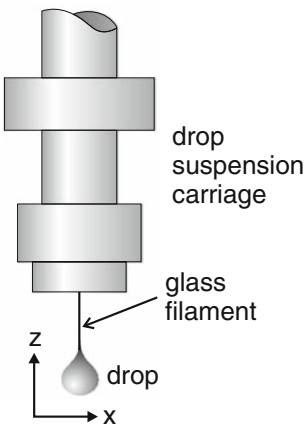

Fig. 2 Schematic diagram of the suspension carriage for holding a detergent drop in the rf coil during non-invasive in situ drying and absorption experiments. Additional design details can be found elsewhere [15, 21, 22]

significantly longer drying time compared to the individual drops. To reach a relative water content of 0.1 (compared to the initial water content) the drops required, on average, 50 min of drying time, whereas the vials required at least 20 h of drying to achieve an equivalent relative water content. The microstructural evolution of the detergent paste in the vial was therefore much easier to determine than for the individual drops.

Difftrain is based on the alternating pulsed gradient stimulated echo (APGSTE) sequence [23], except small tip angle α rf pulses are employed (where $\alpha \approx 10^{o}$) allowing a train of $n = 8$ stimulated echoes, each with a different observation time Δ_n (rather than a single echo with a fixed Δ) and intensity M_n (g, δ, Δ_n) as defined by Eq. 1, to be acquired with a minimum of 2 scans. The Difftrain pulse sequence is shown in Fig. 3, where $\Delta_n = 2\tau + T_{start} + (n-1)T_{inc}$. In this implementation of Difftrain, magnetic field gradient durations of $\delta = 2$ ms and strengths of $g = 1$, 10, 20, 35, 55 and 80 G cm^{-1} were used in successive experiments, where stimulated echoes were acquired at encoding times of $2\tau = 5$ ms and observation times of $\Delta_{1-8} = 10$, 18, 26, 34, 42, 49, 57 and 65 ms in every measurement. From these measurements it was possible to determine diffusion coefficients, surface-to-volume ratios and characteristic pore sizes in the detergent drops, as described in section "Theory: NMR diffusion measurements". Each set of Difftrain measurements, with 16 repeat scans to improve S/N, was acquired in 200 s ($\approx$3.5 min). An equivalent set of PGSTE measurements, with only 2 repeat scans, had an experimental duration in excess of 4 h. Regardless of the PFG measurement technique utilised, each set of NMR diffusion data was analysed to provide a surface-to-volume ratio S/V and characteristic pore size r_{char}, where $r_{char} = 3/(S/V)^{-1}$.

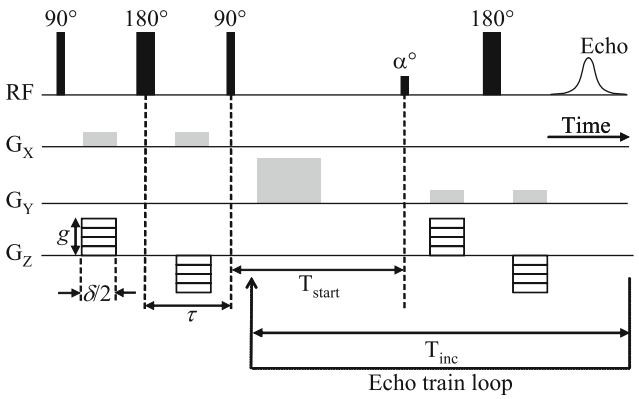

Fig. 3 The Difftrain pulse sequence. *Grey rectangles* represent homospoil gradients. The diffusion encoding gradients are ramped on the z-axis (*striped rectangles*). The observation time $\Delta_n = 2\tau + T_{start} + (n-1)T_{inc}$. For the special case of $n = 1$ and $\alpha = 90°$ this sequence is identical to the APGSTE pulse sequence [23]

Results and discussion

The aim of this work is to demonstrate the application of Difftrain to the characterisation of the evolving microstructure in an individual detergent drop due to drying. First, we validate the rapid diffusion measurement against the conventional PGSTE technique by observing microstructural changes in vials of detergent paste as a function of drying time. The change in the unrestricted diffusion coefficient D_0 during drying is shown in Fig. 4a. Good agreement is observed between the Difftrain and PGSTE results. More data are available from the Difftrain measurements, where a single vial was dried in situ, compared to the PGSTE measurements where a set of identical vials were pre-dried prior to the acquisition of the NMR data. As the relative amount of mobile water decreases from 1 to 0.14 (where a relative water content of 1 $\equiv$ 29 wt% of water), the unrestricted diffusion coefficient decreases from an initial value of $D_0 = 9.8 \times 10^{-10}$ m^2 s^{-1} to

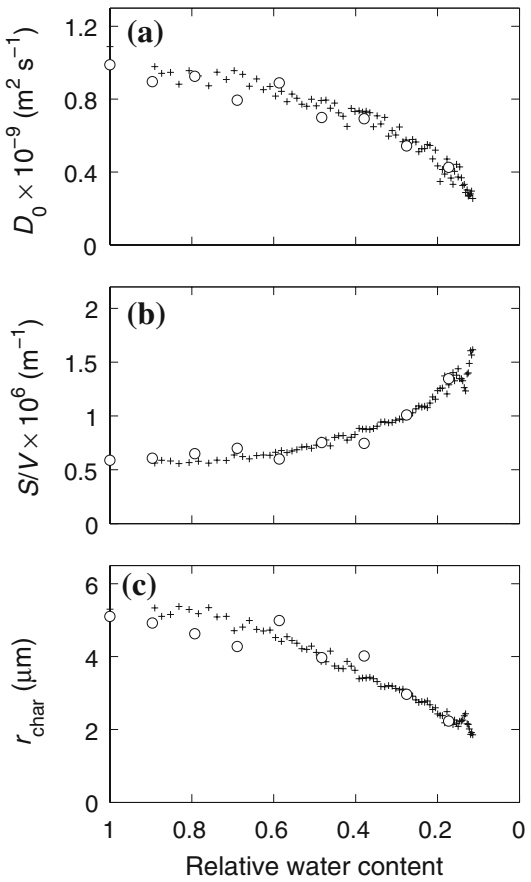

Fig. 4 **a** Unrestricted diffusion coefficient, **b** surface-to-volume ratio and **c** characteristic pore size determined as a function of relative water content for detergent paste in vials using conventional APGSTE (*open circle*) and rapid Difftrain (*plus*) measurements. In all cases the two techniques provide equivalent results, although only the Difftrain data can be acquired during in situ drying. The APGSTE data have been published previously [14]

2.5×10^{-10} m^2 s^{-1}. This is consistent with a relative change in solute concentration as the water content is reduced: a larger proportion of the water is restricted by, and bound to, the LAS and polymer molecules.

In Fig. 4b the variation in surface-to-volume ratio throughout the drying period is shown. The surface-to-volume ratio increases from $S/V = 0.56 \times 10^6$ m^{-1} to a value of 1.62×10^6 m^{-1} as the water content decreases. The corresponding decrease in characteristic pore size from 5.3 to 1.9 μm, Fig. 4c, is determined from the surface-to-volume ratio, assuming spherical pore geometry. This reduction in apparent pore size is caused by residual moisture remaining in smaller pores due to preferential wetting. Also, as the detergent mix dries, the polymer, LAS and sodium sulphate will come out of solution and crystallise on the edge of the pores causing an additional reduction in porosity. Again, excellent agreement is seen between the static PGSTE and the dynamic Difftrain measurements.

The variation in the microstructure of detergent drops during drying is shown in Fig. 5 for a—free diffusion coefficient D_0, b—surface-to-volume ratio S/V and c—characteristic pore size r_{char}, determined using Difftrain. Data from seven identical drops have been overlaid. The solid lines are smoothed polynomial fits to the data in Fig. 4 and are shown for comparison. The relatively narrow distribution of data points shows the experiment is reliable and reproducible. The scatter in the data is a direct consequence of the small sample size that results in a low S/N. The average free diffusion coefficient can be seen to decrease from an initial value of $D_0 = 9.8 \times 10^{-10}$ m^2 s^{-1} to a final value of 1.0×10^{-10} m^2 s^{-1}. The average surface-to-volume ratio increases from an initial value of $S/V = 0.6 \times 10^6$ m^{-1} to 30×10^6 m^{-1}, corresponding to a reduction in the characteristic pore size of $r_{char} = 5$ to 0.1 μm. These overall trends are consistent with the drying of detergent paste in a vial (c.f. Fig. 5, solid lines) and are indicative of a change in mobility as the free water content is reduced leading to a relative increase in the LAS and polymer concentrations and to the deposition of soluble sodium sulphate onto the pore walls. The evolution of the initial microstructure of the drops agrees well initially with the bulk (vial) samples. It should be noted that the values for D_0 and S/V obtained at low relative water contents (<0.2) exhibit more scatter due to the very low S/N of the raw data. Nevertheless, it is possible to conclude that the final values of D_0 and r_{char} are lower in the dry drops compared to the dry bulk paste with an equivalent relative water content of 0.1 (corresponding to a drying time of 50 min for the drops and 20 h for the vials). This difference suggests the formation of a finer microstructure in the dry drops, likely as a result of more uniform drying than in the bulk detergent paste, and possibly as a result of less geometric restriction on shrinkage.

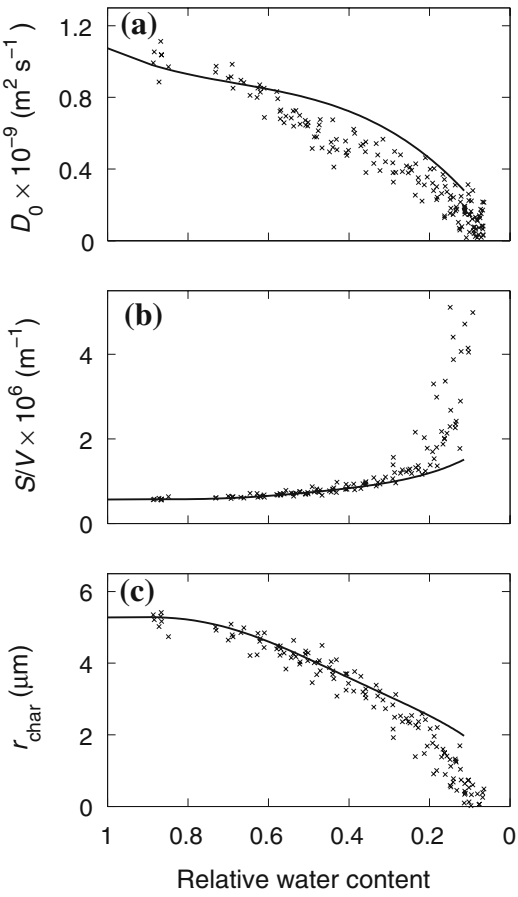

Fig. 5 Difftrain data showing variations in the **a** free diffusion coefficient, **b** surface-to-volume ratio and **c** characteristic pore size during the in situ drying of detergent drops. Values acquired from seven separate individual drops have been overlaid to give an indication of the spread and reproducibility of the data. The *solid lines* indicate the trends observed in the Difftrain measurements of detergent paste in a vial determined from Fig. 4

The microstructural information presented here is difficult to attain by any other method. Optical techniques are limited by the opaque nature of the samples, and hence provide only a surface interpretation that is not necessarily indicative of the structure at depth into the sample. However, the microstructure measurements can be complimented with techniques that probe the nanostructure of the detergent (i.e. molecular arrangement of the LAS), for example X-ray diffraction [17] or NMR spectroscopy [24].

Conclusions

Rapid NMR Difftrain diffusion measurements have been used for the first time to observe microstructural changes during the drying of individual detergent drops. Despite the

low S/N and short duration of these experiments, variations in the dynamic microstructure were monitored successfully and the surface-to-volume ratio was seen to increase as water was evaporated, leading to the deposition of crystalline sodium sulphate in agreement with similar studies on larger volumes of detergent paste. These experiments provide insights into the behaviour of individual drops and could lead to improved energy efficiency during the drying process.

This work shows the feasibility of studying the microstructure of individual detergent drops in situ using non-invasive NMR diffusion measurements. The methodology could be enhanced in the future through the use of a specialised rf probe and magnetic field gradient coil geometries. If these experiments were to be implemented routinely in an industrial environment, low-field magnets with optimised geometry [6] could provide a cost effective and safe alternative to the high-field system used here.

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