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Filtration of Emulsions

Part 2

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REPORT OF ANALYSIS

Date: 02.02.2015

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1 SUMMARY

Low field NMR was used to characterize water droplets before and after filtration through frits with 20 μm pore size. The filtration had low impact on droplet sizes in w/o emulsions stabilized by Span 80, however more clusters of droplets were formed after filtration. The new NMR software made it possible to analyse the emulsion in situ in both frits and synthetic plugs, showing that the droplets were stable in the filter plugs for days.

Filtration of oil or water through synthetic plugs prepared from silica suspension in water, showed that added pure oil replaced water from the plug and pure water replaced oil. W/o emulsions prepared at high mixing speed with small droplets seemed to pass through the silica plug similar as for the frits. W/o emulsions with larger droplets seemed to be affected by filtration, resulting in changes in the droplet size distribution, and also in the clustering.

Different techniques to prepare silica plugs were developed in order for these to mimic reservoir samples. The adopted procedure involves a preparation of the plug from a solid suspension, the porosity of which was adjusted by compressing the suspension with a piston in the syringe. In order to stabilize the plug the top and the bottom was sealed with 20 μm frits. The porosity, pore dimensions and connectivity of the plugs were determined by NMR.

2 INTRODUCTION

This laboratory study is part II of the collaboration between IRIS and Ugelstad Laboratory. Part I involved study of the transport ability of emulsion droplets with different sizes through porous solid materials (glass filters) with different pore size. It was concluded that droplets larger than the pore size of the porous material could pass the pores without affecting the emulsion. In this continuation the goal was to determine the effect of filtration in different porous media. The average droplet size (volume based) and the droplet size range

(half value range) of water in oil, oil in water emulsions and polymer system were investigated by NMR. The porous medias used were frits (sintered polyethylene) or prepared from silica suspensions. In order to determine the size distributions of emulsion samples and characterize porous media NMR procedures were used which involved development and optimization of new NMR procedures. In order to obtain more information of the behavior of emulsions in porous media, droplet dimensions were analyzed before, in situ and after filtration through stacks of frits in a syringe.

In this report the effect of filtration on w/o emulsions, o/w emulsions and polymer solutions through commercially available frits and silica plugs prepared from silica suspensions was investigated. Finally, the porosity and connectivity of plugs was investigated by NMR.

3 SAMPLES

Primol

Span 80

Tween 80

3.5 % NaCl in water (Brine)

MilliQ water

Synthetic Amorphous Silicon Dioxide Silica (particle size is 320 μ m)

4 EXPERIMENTAL

4.1 Experimental Procedure for Filtration of W/O Emulsions through Frits

Emulsions with 15 % and 30 % water cut (WC) were prepared. First 0.5 % Span 80 solution was prepared. Then 30 mL of brine and oil were mixed with an Ultra Turrax (IKA, T18 with a 10 mm head) with speeds up to 24 000 rpm to create small droplets. The samples were shaken horizontally at 300 rpm for 30 min on a horizontal shaker to create larger droplets.

The emulsions were filtered through a stack of 9 frits on top of each other inside a syringe (Figure 1). Most of the syringe tip and top were removed to fit the NMR tube. The stack of frits had a diameter of 12.5 mm and a height of ca 18 mm (max height in the NMR instrument), and consisted of sintered particles of poly ethylene, with mean pore size 20 μ m in a multidirectional channel system. The emulsions were analyzed by NMR and microscopy before filtration, after filtration and in situ in the filter (Figure 2-4). All samples were run in minimum two parallels.



Figure 1: Syringe with frits used to filter emulsions.

1.

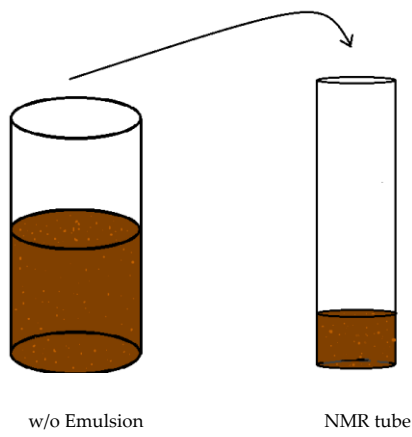


Figure 2: Characterization by NMR of emulsion directly after preparation

2.

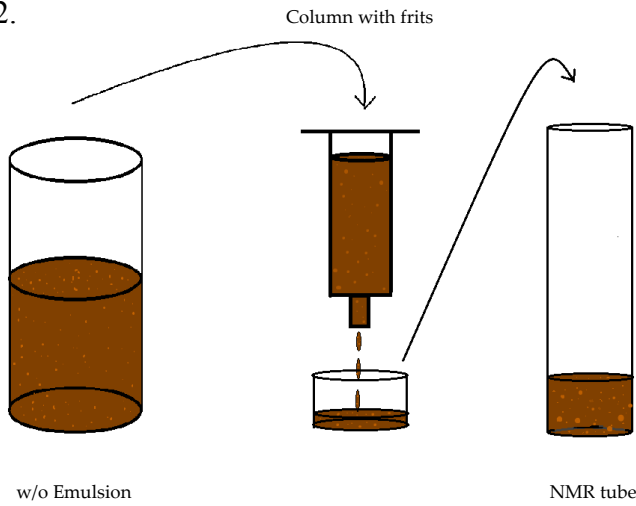


Figure 3: Characterization of emulsion by NMR after filtering through frits with mean pore size 20 μm .

3.

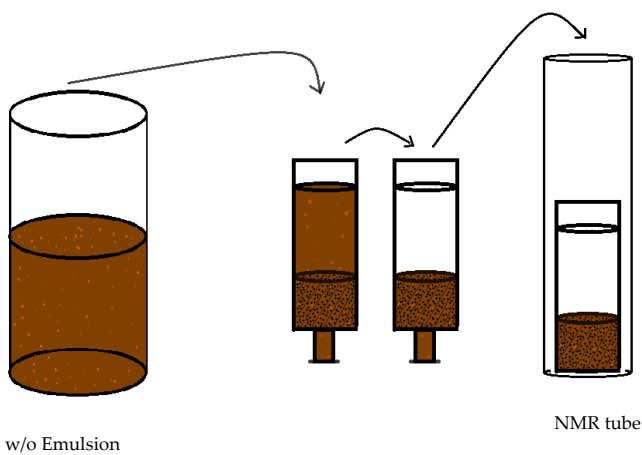


Figure 4: Characterization of emulsion by NMR in situ. The frits should be soaked with emulsion. (Most of the syringe tip were removed.)

4.2 Experimental Procedure for Filtration of W/O Emulsions through Silica Plugs

Similar emulsions as in chapter 4.1 were filtered through a silica plugs. 0.57 g of Synthetic Amorphous Silicon Dioxide Silice (particle size is 320 μ m) was added on top of a frit and the silica was soaked with 3 mL MQ water. The syringe piston was used to push the water through, and to pack the silica particles in-between two frits. The diameter of the silica plug was 12.5 mm and the height was ca. 18 mm. The emulsions were filtered through the plug and analyzed by NMR and microscopy before and after filtration. All samples were run minimum twice.

Additional analyses were performed with silica plugs in syringes which were sonicated for 10 min before the water was pushed out with the piston. Solution of Primol/Span 80 was filtered through the plug and analyzed by microscopy.

4.3 Experimental Procedure for Filtration of Polymers

Solutions of partially hydrolyzed polyacrylamide (HPAM) and brine were filtered through both frits and silica plugs. Two HPAMs with different molecular weight were tested; Floopam 3630S with higher molecular weight (around 20 million Dalton) and Floopam 3230S with a lower molecular weight (6-8 million Dalton).

4.4 Oil in Water Emulsions

Oil in water emulsions were prepared by stirring a solution of 10 % Primol and 4 % Tween 80 in brine for 2 min at 24 000 rpm.

4.5 NMR

4.5.1 NMR – Brine Profile

Figure 4.2.1 shows the NMR sequence used for measuring the water profile. Initially, the NMR signal contains a crude oil and water contribution. Because of a significantly lower transverse relaxation time for the crude oil, one may use the C1 loop to suppress the contribution from the crude oil. (The C1 loop is a preparatory sequence used to resolve brine from water signal.) The first gradient echo is then from water only, and a Fourier transform of this echo yields a water profile. The second loop is used to measure a gradient echo at an even longer observation time, which gives another water profile. These two profiles may then be used to correct for transverse relaxation of the water signal, ending with a third water profile, which is unaffected by transverse relaxation processes. This profile is proportional to the water content along the sample, and by calibrating with a sample that contains 100% water; one can measure the water content along the height of the emulsion. C_1 is determined by measuring the signal for pure oil phase and determining at which C_1 value the entire oil signal has vanished.

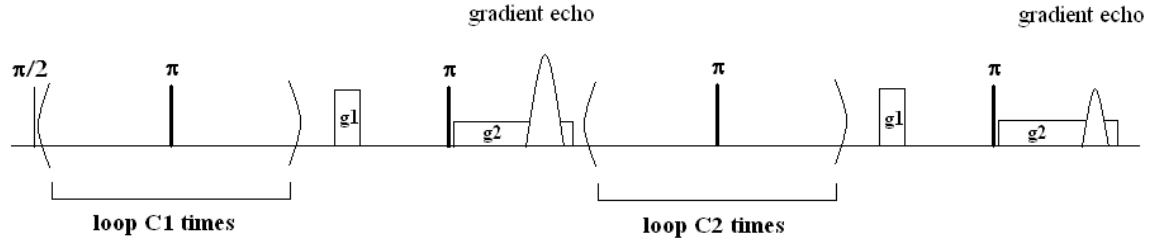


Figure 4.2.1: NMR sequence used for acquiring the water profile.

The NMR measurements were performed with a low field NMR spectrometer supplied by Anvendt Teknologi AS. The magnetic field is 0.48 T, capable of delivering a gradient strength up to 4 T/m. The duration of the sinusoidal gradient pulse is 0.8 ms, and the direction of the gradient is along the length of the tube. The NMR sample tubes of 18 mm diameter were filled with ~4 mL of the emulsion.

Details about the NMR procedure are given in Opedal et al. "Emulsion Stability Studied by Nuclear Magnetic Resonance (NMR)", Energy & Fuels, 2010, 24, 3628-3633 and in Simon et al. "Separation Profile of Model Water-in-Oil Emulsions followed by Nuclear Magnetic Resonance (NMR) measurements: Application Range and Comparison with a Multiple-light Scattering Based Apparatus", Journal of Colloid and Interface Science 356, 2011, 352–361.

4.5.2 Droplet Size Distributions (DSD) by NMR

There is a situation where the surface relaxation term is absent in the solution of the diffusion propagator, i.e. the short time expansion. By assuming piecewise smooth and flat surfaces and that only a small fraction of the particles are sensing the restricting geometries, the restricted diffusion coefficient can be written as

$$\frac{D(t)}{D_0} \approx 1 - \frac{4}{9\sqrt{\pi}} \sqrt{D_0 t} \frac{S}{V} + \varphi(\rho, R, t) \quad [1]$$

where $D(t)$ is the time dependent diffusion coefficient, D_0 is the unrestricted diffusion coefficient, in bulk fluid, and t is the observation time. The higher order terms in t , $\varphi(\rho, R, t)$, hold the deviation due to finite surface relaxivity and curvature (R) of the surfaces. At the shortest observation times these terms may be neglected such that the deviation from bulk diffusion depends on the surface to volume ratio alone. In a porous system a large span in pore sizes must be assumed, and thus eq. 1 must be expected to be valid also for a heterogeneous system. If ξ_i is the volume fraction of the droplets with surface to volume ratio $(S/V)_i$, eq. 1 can be expressed as

$$\sum_i \xi_i \frac{D_i}{D_0} \approx \sum_i \xi_i \left[1 - \frac{4}{9\sqrt{\pi}} \sqrt{D_0 t} \left(\frac{S}{V} \right)_i \right] = \left(1 - \frac{4}{9\sqrt{\pi}} \sqrt{D_0 t} \left(\overline{\frac{S}{V}} \right) \right) \quad [2]$$

Measurements of the early departure from bulk diffusion combined with a linear fit of the experimental data to the square root of time will thus result in a value for the average surface to volume ratio $\overline{(S/V)}$.

Transforming a T_2 distribution to a droplet size distribution

Assuming that the water molecules are probing the droplets within the sample, there is a simple relation between T_2 values and the droplet sizes

$$T_2 \approx \frac{V}{S\rho} \quad [3]$$

This couples the surface to volume ratio to the surface relaxivity, ρ , and makes it difficult to assign the T_2 distribution to a (V/S) distribution. However, if we make the assumption that eq. 3 holds for any droplet size, with ξ_i being the volume fraction of droplets with surface to volume ratio $(S/V)_i$ and corresponding relaxation time T_{2i} , we may write

$$\sum_{i=1}^n \xi_i \frac{1}{T_{2i}} = \sum_{i=1}^n \xi_i \rho_i \left(\frac{S}{V}\right)_i \approx \rho \sum_{i=1}^n \xi_i \left(\frac{S}{V}\right)_i = \rho \overline{\left(\frac{S}{V}\right)} \quad [4]$$

Here we have made the basic assumption that the surface relaxivity ρ is independent of droplet size.

The left hand side of eq. 4 is the harmonic mean $\overline{1/T_2}$ of the T_2 -distribution weighted by the fraction ξ_i of nuclei with relaxation time T_{2i} and n is the number of subdivisions of droplet sizes. This average can be calculated from the T_2 -distribution obtained in a CPMG measurement where the magnetization attenuation $M^{obs}(t)$ is converted to a T_2 distribution by solving an inverse problem using e.g. an Inverse Laplace Transform (ILT) routine. Then the surface relaxivity ρ can be calculated from eq. 4 if the average surface to volume ratio $\overline{(S/V)}$ is already found from the diffusion experiment. Finally, the measured T_2 -distribution can be transformed into an absolute droplet size distribution (V/S) by means of the relationship inherent in eq. 4.

To sum up, the procedure for deriving absolute droplet size distributions is as follows:

- 1) The average surface to volume ratio $\overline{(S/V)}$ is found from fitting eq. 2 to a set of diffusion measurements at short observation times.
- 2) The average (S/V) can be correlated to the average $(1/T_2)$ found from a CPMG experiment. From eq. 3 eq. 4 can then be written as

$$\left(\overline{\frac{1}{T_2}}\right) \approx \rho \left(\overline{\frac{S}{V}}\right) \quad \Rightarrow \quad \rho = \left(\overline{\frac{1}{T_2}}\right) \times \left(\overline{\frac{S}{V}}\right)^{-1} \quad [5]$$

Hence we find the relaxivity, ρ which then is assumed to be droplet size independent.

- 3) Under the assumption of droplet size independency of the relaxivity the value of ρ can then be used in eq 3 thus resulting in a linear relation between T_2 and the volume to surface ratio which is a measure of the droplet size. By multiplying the T_2 distribution by the calculated surface relaxivity the distribution is normalized to a droplet size distribution in absolute length units.

4.5.3 Separation of High Viscosity Oil and Water Signal

There are several ways to separate the NMR contribution of the oil and water components. The most straightforward way is when the viscosity of the oil is much higher than that of the water phase. Then the longitudinal and/or the transverse relaxation times will be significantly different, and one may store the NMR signal for full recovery of the crude oil signal back to thermal equilibrium while the water signal still can be measured. In figure 4.2.2 we have displayed the T_2 distributions of water in oil emulsion system for short and long z -storage (Δ) intervals. By increasing the duration of the z -storage one can thus omit the oil signal. The two peaks at short Δ correspond to the oil signal (left peak) and water signal (right peak).

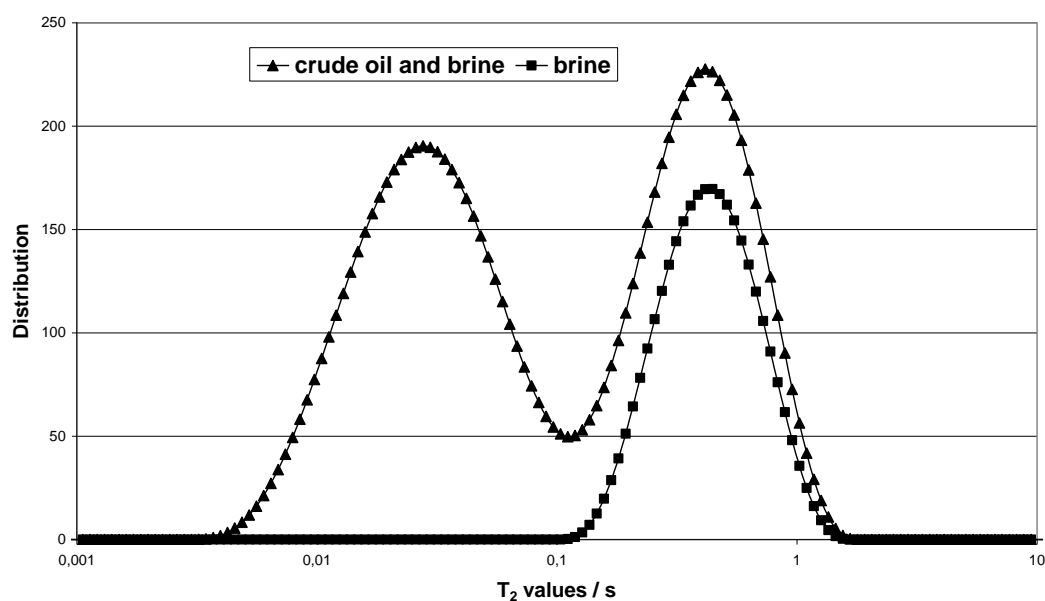


Figure 4.2.2: The effect of using z -storage delay Δ to obtain the T_2 distribution of water alone.

As the crude oil is relatively high viscous it turns out that this is the best way of resolving the water signal from the oil signal. Further details and references may be found in Sørland et.al [http://www.uni-leipzig.de/diffusion/pdf/volume5/diff_fund_5\(2007\)4.pdf](http://www.uni-leipzig.de/diffusion/pdf/volume5/diff_fund_5(2007)4.pdf) and Dynamic Pulsed-Field-Gradient NMR, <http://link.springer.com/book/10.1007%2F978-3-662-44500-6>

A good indication of the range of droplet sizes in the emulsion is to find the range of the width at half maximum. This is given by the difference between the two extreme values of the droplet size at which the distribution intensity is equal to half of its maximum value, i.e. the half value range.

4.6 Optical Microscopy

The emulsions were investigated by microscopy in order to visually compare the change before and after filtration with the NMR data. Nikon Eclipse ME 600 digital video microscope together with Image Pro Plus 5.0 software was used to acquire pictures of the water droplets. The lens used was the CFI LU Plan Epi 10X with an N.A. (numerical aperture) of 0.30. With the wavelength of the light source being 0.55 μm , the resolving power of this lens was 0.91 μm . A CoolSNAP-Pro cfw 4 megapixel cooled CCD camera (monochrome) from Media Cybernetics® was used to digitalize the images. (This camera incorporates a CCD (charge-coupled device), a 12-bit scientific digitizer and low-noise electronics to produce 36-bit digital monochrome images at greater than 100 \times 1000 resolution.)

5 RESULTS AND DISCUSSION

5.1 Filtration through Stacked Frits

DSD and brine profile of w/o emulsions, prepared by mixing at two speeds and two water cuts filtered through frits, were analyzed by NMR. Preparing the emulsion at lowest mixing speed, 300 rpm, resulted in larger droplets. The average droplet sizes were largest at highest water cuts (Table 5.1.1). Due to some uncertainties with the largest droplet sizes, the half value ranges and average DSD were reported instead of the total range of size distribution. This uncertainty is mainly due to the validity range of the model leading to the DSD when the droplets are rather big ($> 100 \mu\text{m}$).

Table 5.1.1 compares the average droplet diameter and half value range of the emulsions before and filtration. The average droplet size as well as the half value range was more or less unchanged during filtration, considering the uncertainty in this NMR program (5 %).

The NMR showed slightly larger droplets in situ, with 7 to 9 μm as the average DSD for the emulsions prepared at 24 000 rpm and 13 to 15 μm for emulsions prepared at 300 rpm. It can be noticed that some of the droplets are larger than the pores. These results could be understood if the pores are polydispersed in size or if some droplets are deformed inside the pores. The largest droplet sizes of the emulsions prepared at low mixing speeds were above 100 μm . The NMR program assumes that all droplets are spherical. The DSD is measured in one direction, the direction in which the droplets move amongst obstacles (making the droplet elongated), thus probably causing a slightly higher value in situ than outside the pores.

Table 5.1.1: Average droplet size distribution and half value range of emulsions before filtration, in situ and after filtration through dry frits.

MIXED BY ULTRA TURRAX 24 000 rpm	Before filtration		In situ		After filtration	
	Half value range [μm]	Average droplet size [μm]	Half value range [μm]	Average droplet size [μm]	Half value range [μm]	Average droplet size [μm]
15 % WC P1	3 - 12	6	3 - 19	8	Not measured	Not measured
15 % WC P2	4 - 9	6	4 - 12	7	Not measured	Not measured
15 % WC P3	4 - 9	6	Not measured	Not measured	4 - 9	6
15 % WC P4	4 - 9	6	Not measured	Not measured	4 - 9	6
30 % WC P1	5 - 14	9	5 - 14	9	4 - 13	8
30 % WC P2	5 - 13	8	5 - 15	9	5 - 13	8
MIXED BY SHAKER 300 rpm						
15 % WC P1	5 - 16	10	5 - 22	13	Not measured	Not measured
15 % WC P2	6 - 24	13	7 - 20	14	Not measured	Not measured
15 % WC P3	6 - 19	12	Not measured	Not measured	6 - 19	12
15 % WC P4	6 - 20	12	Not measured	Not measured	5 - 17	10
30 % WC P1	6 - 22	13	6 - 28	15	6 - 24	13
30 % WC P2	6 - 26	14	6 - 26	14	7 - 25	14

The water contents of the emulsions were the same before and after filtration. Hence there was no retention of water in the frits. Figure 5.1.1 shows the brine profile of w/o emulsion with 30 % WC, and similar profiles were obtained for all samples before and after filtration. The left-hand side of the curve refers to water concentration in the bottom of the syringe. The height of the sample was about 16 mm.

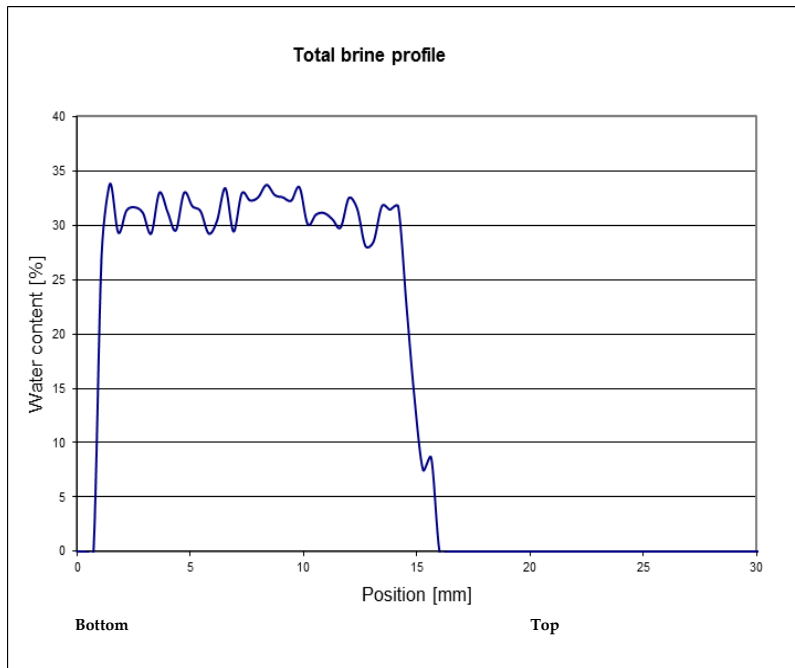


Figure 5.1.1: Water content as a function of position in the sample. (The left-hand side of the curve refers to water concentration in the bottom of the syringe.) Emulsion analyzed before filtration (30 % WC).

However, in situ the profile showed a front of a higher concentration of water droplets towards the bottom of the sample. This can be seen in the left part of the red curve in figure 5.1.2, where the water content (and thus the concentration of water droplets) increases up to 15 %. The blue curve in Figure 5.1.2 shows the porosity of the filter, which was 30 %.

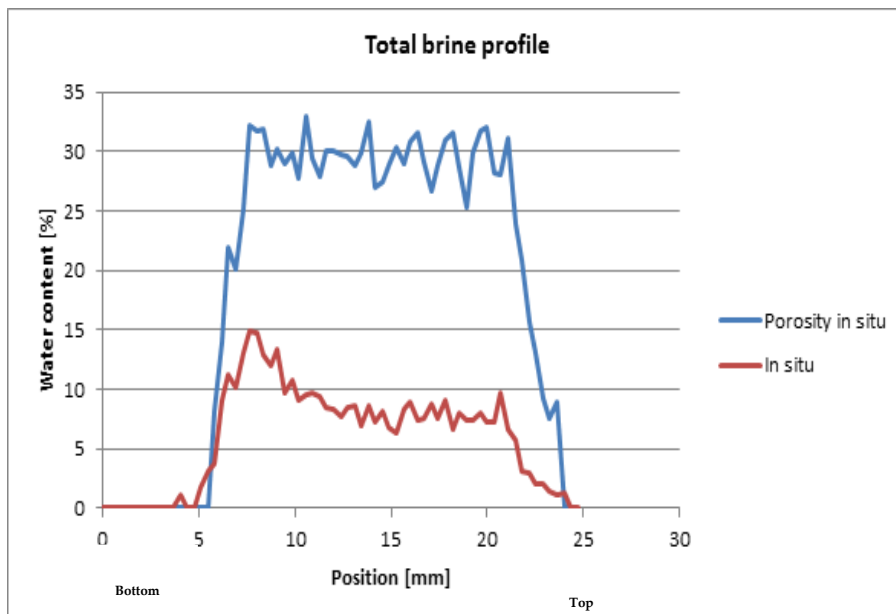


Figure 5.1.2: The red curve show water content in the w/o emulsion inside the frit (in situ) as a function of position and the blue curve shows the porosity of the frit. (The left-hand side of the curve refers to water concentration in the bottom of the syringe.) (Sample: 30 % WC, prepared with 300 rpm).

Effect of Aging In Situ

The effect of aging at room temperature showed little or no change in average droplet size or half value range in situ over a time period 5 days for emulsions prepared at 300 rpm (Table 5.1.2). A similar observation was made for emulsions prepared at 24 000 rpm and stored for 7 days.

Table 5.1.2: Average droplet size distribution and half value range of emulsions in situ immediately after preparation and up to 7 days.

	In situ	
	Half value range [μm]	Average droplet size [μm]
MIXED BY SHAKER		
30 % WC P1, directly after preparation	6 - 28	15
30 % WC P1, after 5 h	6 - 25	14
30 % WC P1, after 5 days	7 - 31	16
30 % WC P2, after 1 h	6 - 26	14
30 % WC P2, after 3 h	6 - 26	14
30 % WC P2, after 5 days	6 - 25	14
30 % WC P2, after 7 days	6 - 25	14
MIXED BY ULTRA TURRAX		
30 % WC P2, directly after preparation	5 - 15	6
30 % WC P2, after 7 days	5 - 14	6

Filtration of Emulsion through Initially Oil Saturated Frits

Filtration of pure water through frits saturated with pure crude oil or a solution of Primol/Span 80 showed that water replaced the oil and oil was eluted before the residual water. The filtration of w/o emulsion through oil saturated frits gave similar results as detected with filtration through dry frits and water saturated frits (Table 5.1.3).

Table 5.1.3: Average droplet size distribution and half value range of w/o emulsions before and after filtration through oil saturated frits.

MIXED BY ULTRA TURRAX FILTERED THROUGH OIL SATURATED FRITS	Before filtration		After filtration	
	Half value range [μm]	Average droplet size [μm]	Half value range [μm]	Average droplet size [μm]
15 % WC P1	4 - 9	6	3 - 9	6
15 % WC P2	4 - 8	6	4 - 10	6
30 % WC P1	5-14	9	5 - 14	9

Microscopy

All samples analyzed by NMR were also checked in microscope. The two methods cannot be compared directly since NMR is three dimensional and microscopy is two dimensional, but the microscope was used to visually observe what happens to the emulsion after filtration. Microscopy images of the emulsions before and after filtrations showed that clusters of droplets were formed after the filtration in the emulsions prepared at low speed (Figure 5.1.3). The filtration process seemed to promote a flocculation in the sample. Moreover, individual droplets seem to have the same diameter range before and after filtration. Span 80 is known to induce some flocculation of water droplets, but in this case there were a lot more clusters after filtration.

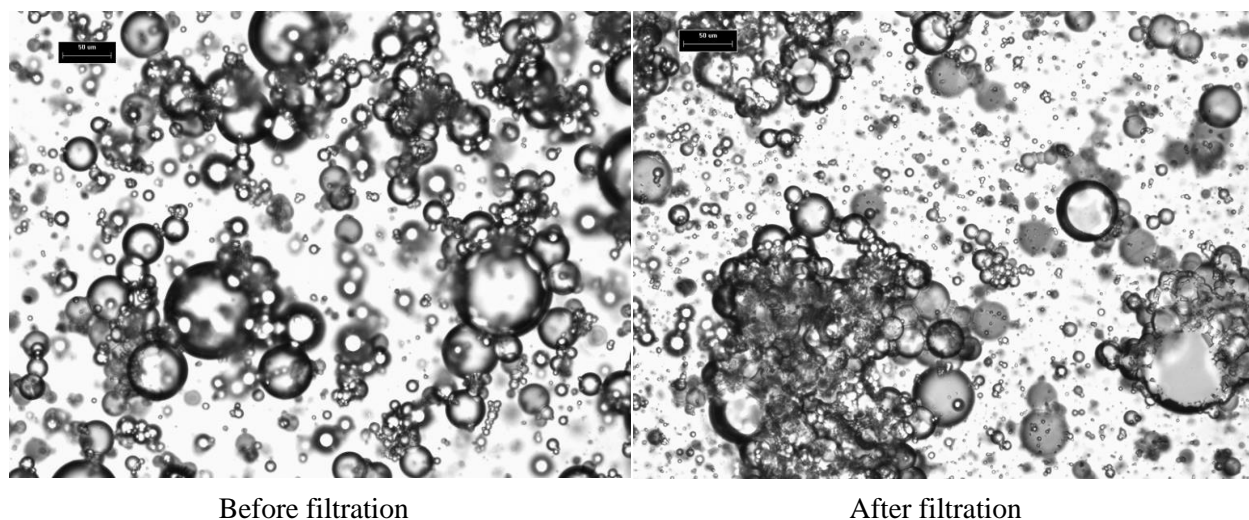


Figure 5.1.3: Microscope images of w/o emulsion before and after filtration. (15 % WC, prepared at 300 rpm.) The scale bar in the upper left corner is 50 μm .

5.2 Filtration through Silica Plugs

Similar emulsions as in chapter 5.1 were filtered through plugs prepared from silica suspensions (Figure 5.2.1), and analyzed by NMR. The average DSDs were similar after filtration of emulsion prepared at the highest mixing speed, with 6 and 7 μm for 15 % WC and 9 μm for 30 % WC, and the half value ranges showed only small variation.

The largest effect of filtration was observed in parallel one of both water cuts in the emulsions prepared at the lowest mixing speed, for which a decrease in average droplet diameter and the maximum droplet diameter (half value width) were detected after filtration. However this decrease was only marginal and only partially confirmed for the second parallel of WC 15 % and not confirmed by the second parallel of WC 30 %.



Figure 5.2.1: Syringe without silica plug (left) and modified syringe in NMR tube prepared with silica plug (right).

Table 5.2.1: Half value range and average DSD for water/Primol w/o emulsion before and after filtration through plugs prepared from silica suspensions.

MIXED BY ULTRA TURRAX 24 000 rpm	Before filtration		After filtration	
	Half value range [μm]	Average droplet size [μm]	Half value range [μm]	Average droplet size [μm]
15 % WC P1	4-11	7	4-10	7
15 % WC P2	4-9	6	4-11	7
15 % WC P3	4-10	7	4-11	7
30 % WC P1	5-16	9	5-20	10
30 % WC P2	4-16	9	5-16	9
MIXED BY SHAKER 300 rpm				
15 % WC P1	5-21	12	4-10	7
15 % WC P2	6-18	10	5-14	9
30 % WC P1	6-27	14	5-21	11
30 % WC P2	5-21	11	6-23	13

Filtration of Pure Oil and Pure Water

Filtration of pure crude oil or solution of Primol/Span 80 through the silica plug showed that the oil replaced the water in the plug before being eluted. Indeed, the first volume coming out of the syringe was water, which represented 10% of the water in the plug. The plug consisted of less than 1.5 mL water. After the water removal only pure Primol/Span 80 passed through the plug.

A test was also performed with filtration of pure water through silica plugs saturated with pure Primol. The first volume eluted was oil. However, due to air in the silica plug, which appeared when the piston was removed, also air bubbles were present in the oil droplets.

Microscopy

Microscopic images of the emulsions before and after filtrations through plugs of silica particles showed that clusters of droplets were formed after the filtration (Figure 5.1.3), which was similar to filtration through frits. In the emulsions prepared at lowest mixing speed a more narrow DSD, with a lot of clusters and very small droplets, were seen in microscope after filtration. However the droplets seen in emulsions prepared at the highest speed had a wider distribution after filtration, in addition to the clusters one could see a few droplets larger than before filtration (Figure 5.2.2). Emulsions with larger water droplets seem to be more affected by the filtration with changes in distribution parameters, and also in the clustering. For smaller water droplets the effects are much smaller. However, the overall effects are not large and they are not always reproduced by NMR.

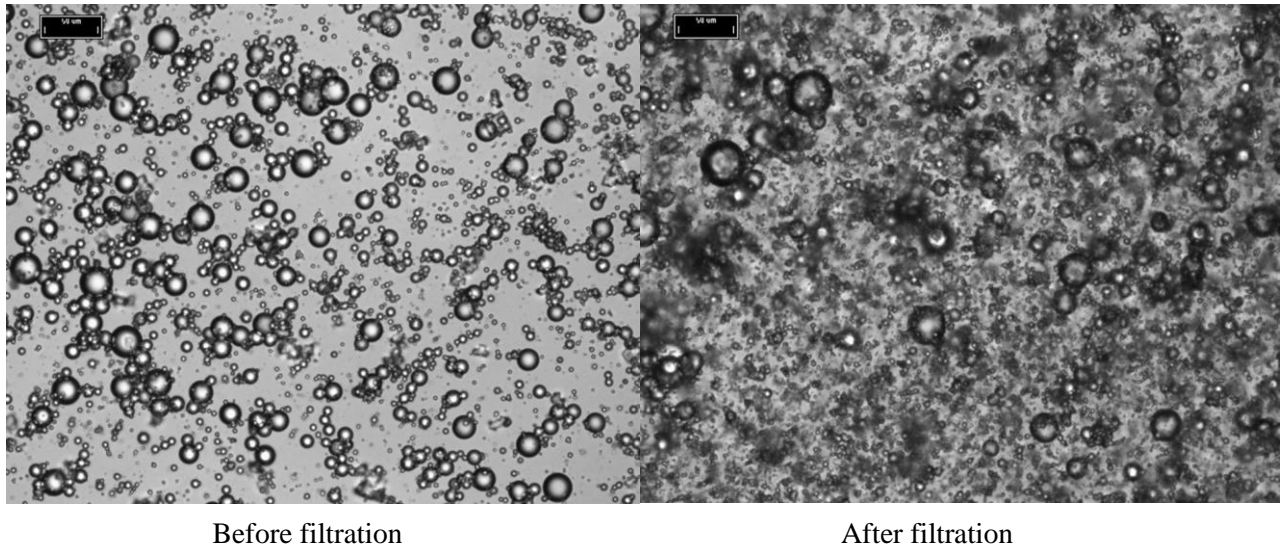


Figure 5.2.1: Microscopic image of w/o emulsion filtered through silica plugs prepared at 300 rpm before and after filtration (30 % WC). (The scale bar is 50 μm .)

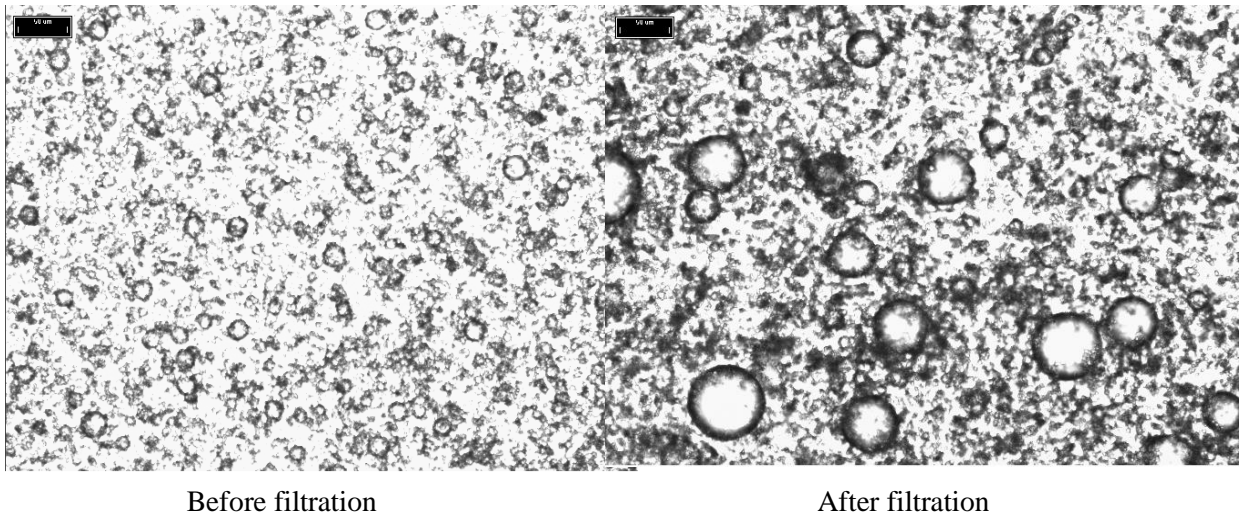


Figure 5.2.2: Microscopic image of w/o emulsion filtered through silica plugs prepared at 24 000 rpm before and after filtration (30 % WC). (The scale bar is 50 μm .)

Preparation of Silica Plugs

In the above experiments the silica plug was prepared directly in the syringe by placing a frit in the bottom of the syringe, adding the silica suspension, sonicating, and finally removing the residual water when pressing down a frit on top of the suspension with a flat bottomed cylinder. To create more dense silica plugs three modifications were introduced. The first was to centrifuge the silica suspension and transfer the sediment with a spatula to the syringe afterwards, compress and remove excess water. The first 10 droplets being eluted from the syringe when filtering pure oil were mainly water, while ca. 4 water droplets were filtered out when the plug was prepared directly in the syringe.

The second modification was performed by using vacuum to take out the water of the plug prepared directly in the syringe. The vacuum was immediately turned off when the water stopped dripping, to avoid drying the plug. The first 3 droplets filtered out were water.

The third modification was to use the syringe piston to compress the silica suspension on top of a frit inside the syringe. This modification made the plug so dense that it became impossible to filter liquid through, neither by hand nor with vacuum suction.

5.3 Filtration of Polymer Solutions

Solutions prepared from partially hydrolyzed polyacrylamide (Floopam 3230S and Floopam 3630S) were filtered through both frits and silica plugs. The filtration did not affect the 100 ppm Floopam 3230S solution, and the viscosities were more or less the same before and after filtration.

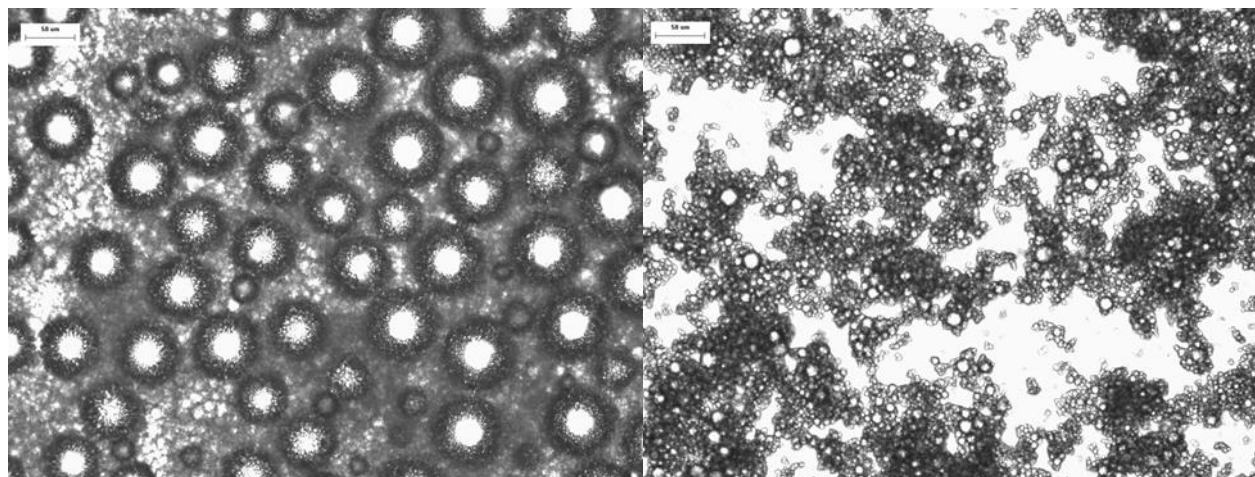
The viscosity for parallel 1 and 2 for Floopam 3630S did not give consistent results, however a third parallel confirmed the results of parallel 2, showing that there were no change in viscosity before and after filtration through frits and silica plugs, respectively.

Table 5.3.1: Viscosity (mPa s) of polymer solution before and after filtration through frits and silica plugs.

Viscosity of polymer solution [mPa s]						
	Before filtration	Filtered through frits		Filtered through silica plugs		
		Parallel 1	Parallel 2	Parallel 1	Parallel 2	Parallel 3
Floopam 3230S 100 ppm	1.18 ± 0.01	1.16	1.16	1.11	1.08	Not measured
Floopam 3630S 100 ppm	1.1 ± 0.04	1.14	1.04	1.29	1.07	1.05

5.4 Filtration of Oil in Water Emulsions

Oil in water emulsions were filtered through silica plugs. The emulsions were prepared with 10 % Primol and 4 % Tween 80 stabilizer in Brine. Figure 5.4.1 shows the microscopic images of the o/w emulsions before and after filtration through silica plugs. The filtration process seemed to affect both droplet size and the clustering more conspicuously than for w/o systems. The NMR characterization is still open.



Before filtration

After filtration

Figure 5.4.1: Microscopic image of o/w emulsion filtered through silica plugs prepared at 24 000 rpm before and after filtration (10 % Primol in water). (The scale bar is 50 μm .)

5.5 Long Range PFG-NMR Diffusion Measurements to Probe the Impact of the Porous Medium on the Emulsions

Pulsed Field Gradient NMR (PFG-NMR) may determine the root of the mean squared displacement (RMS) at various observation times. If the observation time is as long as ~ 1 second, bulk water may probe RMS distances of $100 \mu\text{m}$. For an emulsion of droplets of typically $10 \mu\text{m}$ in diameter, the RMS consequently approaches 0 as the observation time is increased beyond 1 second. Then the water inside the droplets is trapped in a very restricted region. This PFG-NMR measurement can be applied on bulk water, emulsions, and emulsions confined within a filter, and in the following the aim is to see whether the RMS changes for an emulsion being in a porous medium or as a single phase.

In order to measure the RMS distance over a distance that covers more than one pore, an observation time of 0.7 seconds was chosen. Then the RMS for bulk water is approximately $100 \mu\text{m}$. Any restrictions experienced by the water would then lead to a decrease in this value. The PFG-NMR sequence used is shown in figure 5.3.1.

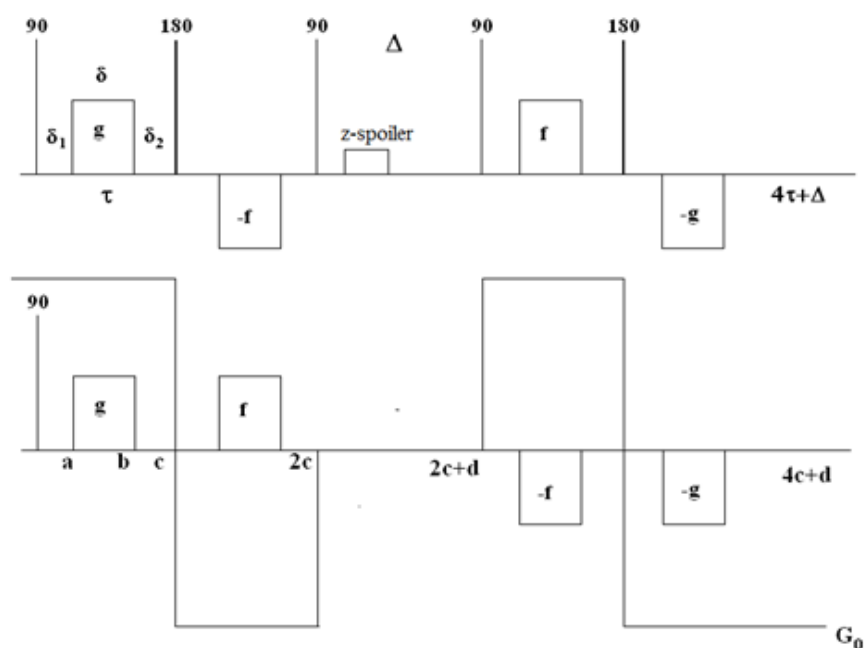


Figure 5.3.1: The 13 interval bipolar PFGSTE sequence with real (upper sequence) and effective (lower sequence) gradients. In the z-storage interval a short spoiler gradient pulse is applied to spoil unwanted signal.

Denoting $g = g_{cal}(i)$ and $f = g_{cal}(i-x)$, where g_{cal} is the calibrated gradient strength per arbitrary unit, and (i) and $(i-x)$ are the gradient amplitudes in arbitrary units, the equation is simplified to

$$I = I_0 e^{-\frac{4\tau}{T_2}} e^{-\gamma^2 g^2 (2\delta)^2 D \left[\Delta + \frac{3\tau}{2} - \delta/6 \right] \left[i - \frac{x}{2} \left(\frac{\Delta + \tau - \delta/6}{\Delta + \frac{3}{2}\tau - \delta/6} \right) \right]^2 - \gamma^2 D (2i-x) \delta (\delta_1 - \delta_2) (\tau) g_{cal} G_0 - \frac{4\tau^3 G_0}{3} + offset}$$

x provides the difference in applied gradient strength, and the offset is a small constant term due to this difference in amplitude of f and g .

Now the measured diffusivity may not be a single value but rather a distribution of values, depending of the heterogeneity of the sample. In addition a time dependence will be inherent, and as the observation time increases, the better is different systems resolved from each other.

5.5.1 Results, NMR

In figure 5.3.2 the attenuation from the sequence shown in figure 5.3.1 is applied on bulk water, a single emulsion (24000 rpm) and two emulsions in situ (within a porous system). The attenuation is produced by incrementing the applied gradient strength. The oil signal is suppressed due to its short T_1 relaxation time, so only the water signal of the emulsion is measured. Obviously the attenuation from the bulk water sample is the fastest, the second fastest is the emulsion in situ with the largest droplets (emulsion produced with 300 rpm), then the second slowest attenuation is from the emulsion in situ with the smallest droplets, and finally the single emulsion with the largest droplets.

Now, if the presence of the porous medium does not affect the cavities in which the water is found, one would expect the two slowest attenuations to coincide, but they do not. Thus, the presence of the solid matrix increases the RMS value of the water. In order to provide something more readably, the multi exponential attenuations are subjected to an inverse Laplace transform and the distributions are plotted as a function of the RMS value, as shown in figure 5.3.3.

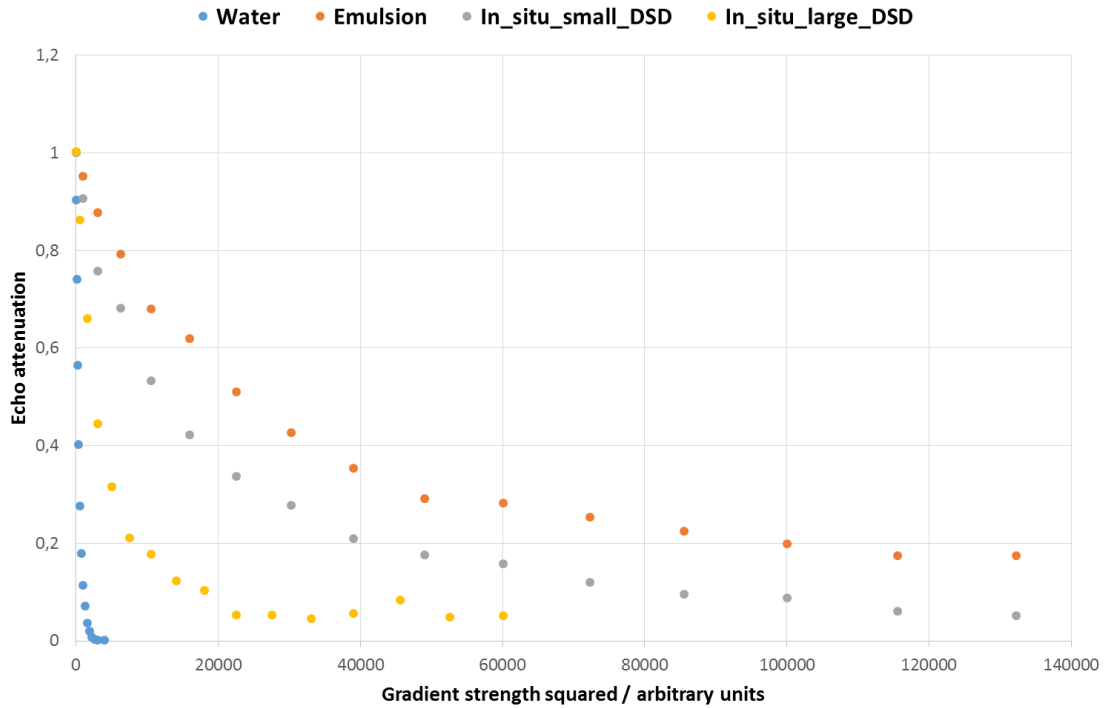


Figure 5.3.2: The attenuation of the NMR signal from a 13-interval PFGSTE applied on various samples.

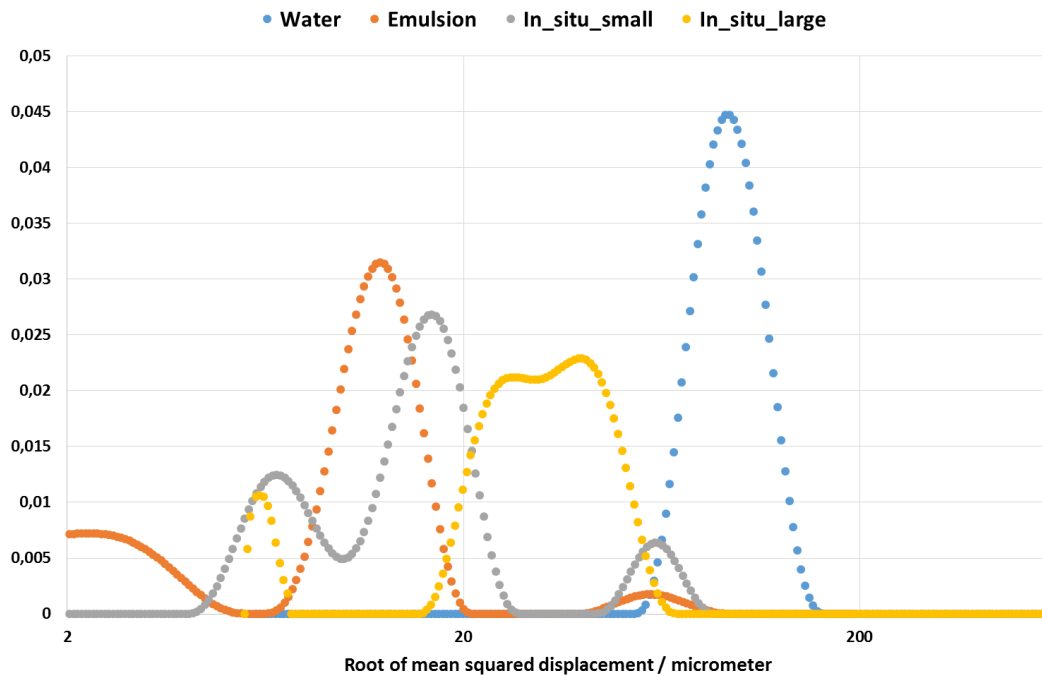


Figure 5.3.3: The inverse Laplace transform applied on the experimental data from figure 5.3.2, and the x-axis represented by RMS-values / μm

In figure 5.3.3 the distributions from the various samples as a function of their RMS value are shown. The bulk water shows up with a major peak around 100 μm while the distributions from other systems show up at RMS values smaller than 100 μm . When comparing the single emulsion (“orange”) with the same emulsion but in situ (“grey”), we see as already indicated in the raw data from figure 5.3.2, that there is higher RMS values in the presence of a porous medium. There is also a significant peak around 50 μm for the emulsion in situ, indicating that some of the water may traverse distances longer than the typical pore size of 20 μm .

The measurements shown here are preliminary measurements and not fully optimized. For example, the number of gradient steps is only 16, and to that, a number of 200 components are fitted to the distributions. Thus the number of gradient steps should be increased as well as the signal to noise ratio, both at the expense of measurement time. The current experiments took approximately 1 hour, even when using the spoiler recovery approach (a procedure to reduce measuring time) ([http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.399.6174 &rep = rep1&type=pdf](http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.399.6174&rep=rep1&type=pdf)).

However, the results shown in figures 5.3.2-3 demonstrate that the PFG-NMR measurements can be applied to monitor whether the emulsion is changed due to the presence of the porous medium. A plausible explanation is that the droplets are no longer spherical, but elongated in the direction of which the diffusion is measured by PFG-NMR (due to the construction of the porous medium, an isotropic diffusion propagator is not to be expected). By transforming the measured apparent diffusion to an RMS value, as the observation time is controllable and set in the PFG-NMR experiment, the distributions can be shown as a function of the RMS values. These preliminary tests show that it should be straightforward to judge whether there is something happening with the emulsion when it is located in situ or not.

5.6 PFG-NMR characterisation of the water saturated synthetic plugs

Two water saturated synthetic plugs were characterised by PFG-NMR in order to determine porosity, surface to volume ratio, which correlates to cavity dimensions, and to probe the connectivity. In figures 5.4.1-2 the porosity profile and its corresponding pore size distribution are shown for the Frits plug. The oscillation seen between 3-13 mm is due to partial drying of the sample, which is also observed visually.

When probing the connectivity, PFG-NMR diffusion measurements were conducted up to an observation time of 1.5 seconds. The result is shown in figure 5.4.3 where the reduction in mobility is the strongest in the beginning and tends to flatten out for the measurements conducted at the longest observation time. However, within the noise of the data points we cannot conclude that the connectivity limit has been reached at 1.5 seconds. At this observation time, the unrestricted root of the mean squared displacement is $\sim 100 \mu\text{m}$. As the average spherical pore size is as big as 55 μm , it is therefore not expected to reach the connectivity limit within 1.5 second.

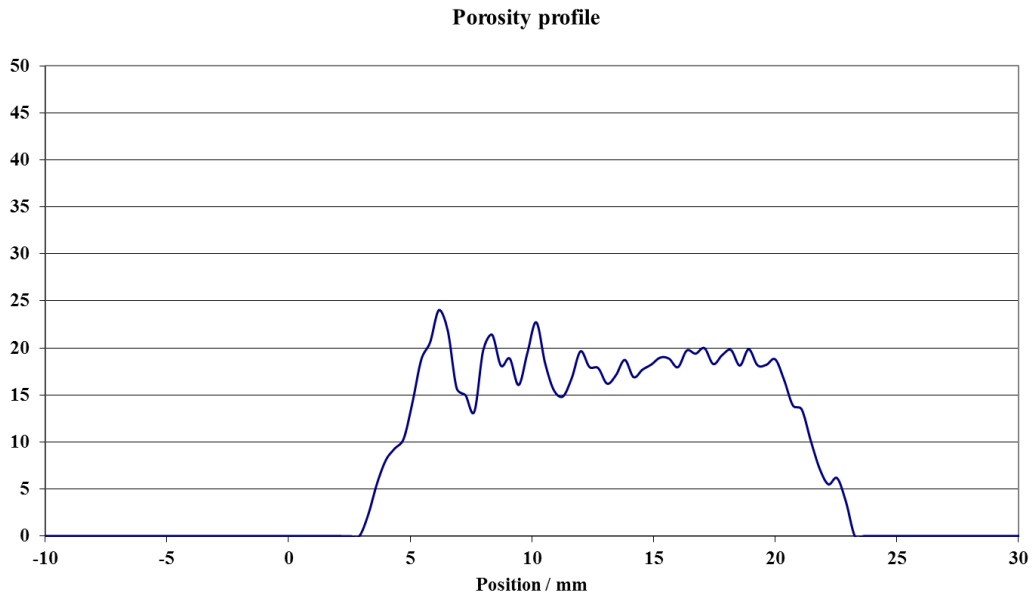


Figure 5.4.1: Porosity profile of water saturated frits sample.

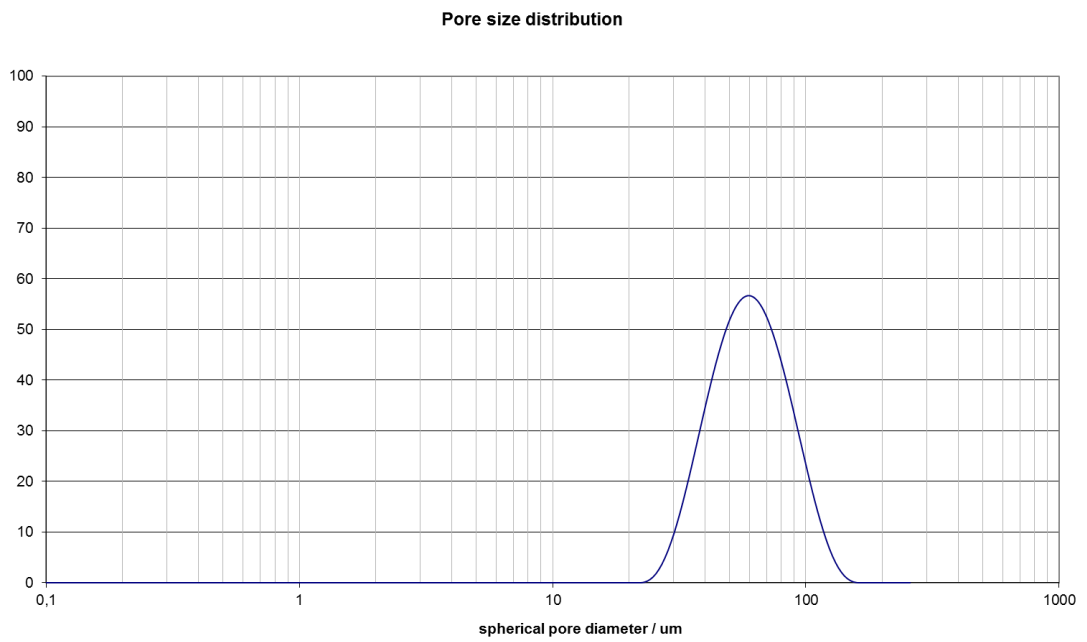


Figure 5.4.2: Pore size distribution arising from the frits sample, assuming spherical pores.

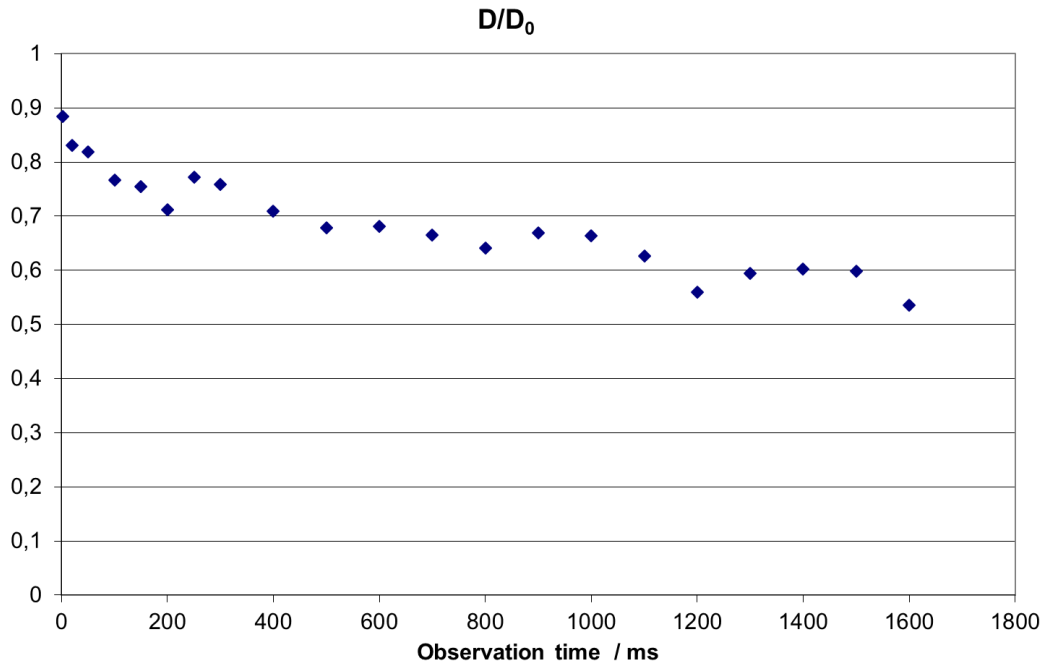


Figure 5.4.3: Probing the connectivity of the frits sample.

In figures 5.4.4-5 the porosity profile and its corresponding pore size distribution are shown for the silica plugs. While the porosity is significantly higher than for the Frits sample, the pore size distribution is smaller yielding an average spherical pore size of $\sim 30 \mu\text{m}$. However, when probing the connectivity there is hardly any attenuation of the apparent diffusion coefficient during the 1.5 seconds. That is, there is an initial decay due to the restrictions the silica plugs caused, and which makes it possible to determine a value for the surface to volume ratio. As the observation time increases up to 1.5 seconds the measured D/D_0 does not go below 0.80, and this confirms that the connectivity of the cavities within the silica plugs is very good, as compared to the Frits sample.

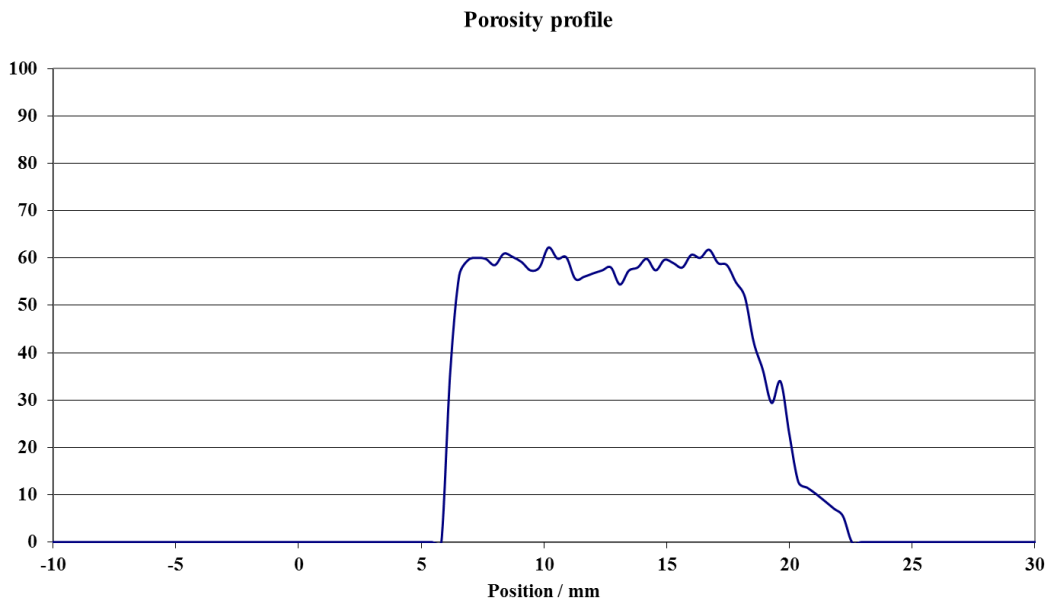


Figure 5.4.4: Porosity profile of water saturated silica plugs.

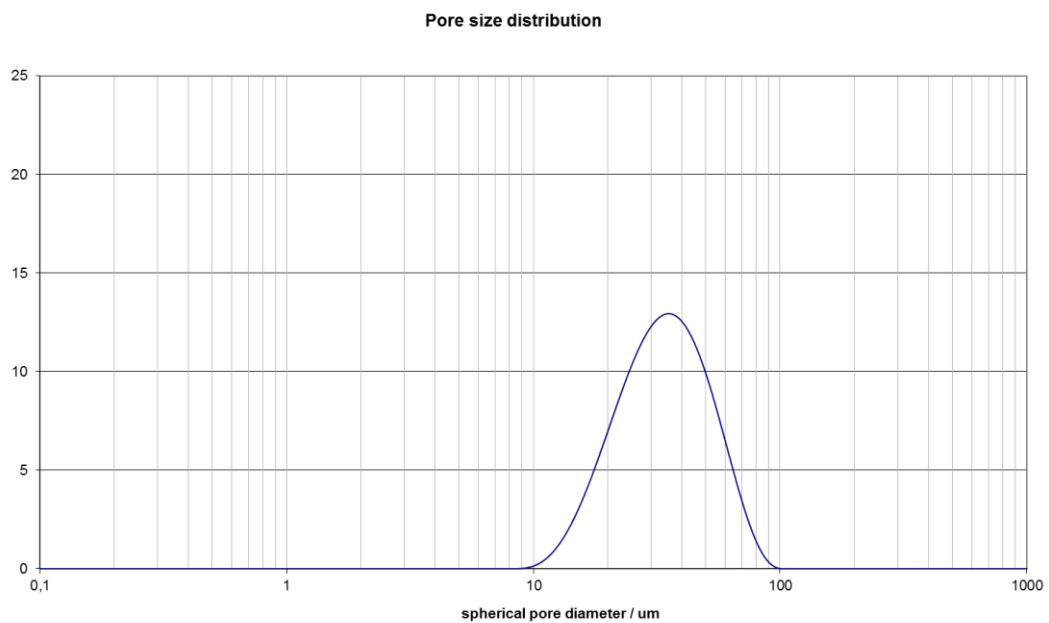


Figure 5.4.5: Pore size distribution arising from the silica plugs, assuming spherical pores.

6 CONCLUSION

Using the PFG-NMR technique it is possible to characterize the porous media when being water saturated (porosity profiles, pore size distributions and connectivity between pores). When an emulsion is present, the impact of the porous medium on the droplets can be probed, the concentration profile of the emulsion within the porous medium can be determined. Also asymmetrical changes in droplets seem to be able to be detected.

W/o emulsions prepared with smaller droplets were not affected by filtration through frits, to the same extent as larger droplets were changes in droplet sizes and clustering was more evident.

Synthetic plugs from silica suspensions were successfully prepared. It was possible to filter w/o emulsions with different droplet size through the these plugs. The filtration of emulsions prepared with smaller droplets did not affect the average droplet size or the distribution of the droplets, however more clusters were observed with microscopy after filtration. The emulsions with larger droplets seemed to be affected by the filtration; however this was only partially confirmed by the second parallel.

The filtration through frits of 100 ppm Floopam 3230S and 3630S did not affect the state of partially hydrolyzed polyacrylamide as judged from viscosities.

Oil in water emulsions were affected by filtration through frits. Obvious effects was seen from microscopy as regard to clustering and droplet sizes. The NMR study was not completed.

7 ACKNOWLEDGEMENT

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