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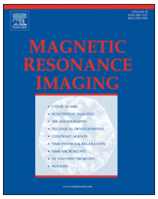

Original contribution

Investigating mobility of crude oil adsorbates on mineral surfaces by NMR

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ABSTRACT

We have applied diffusion and relaxation Nuclear Magnetic Resonance experiments to investigate the translational and rotational mobility of adsorbents on quartz and calcite mineral surfaces. On both surfaces it was found that water is the dominant molecule. On the quartz surface the majority of water molecules have a relatively high degree of both rotational and translational mobility, while a minor fraction of water molecules, and all hydrocarbon molecules, have a significantly lower mobility. On the calcite surface the translational mobility is very low for all the adsorbed molecules, while there is a large diversity in rotational mobility, indicating that the hydrocarbon molecules are strongly attached to the surface, but that some part of each molecule still have a large degree of rotational mobility. Diffusion and relaxation experiments give a detailed description of both the molecular mobility of adsorbed species on these mineral surfaces, which leads to new insight with respect to aging processes on a molecular level.

1. Introduction

Synthetical wettability alteration through enhanced oil recovery methods requires a detailed understanding of the mechanisms responsible for this process. It also requires insight into the naturally occurring process of altering the originally water-wet reservoir rock toward more oil-wet. This natural phenomenon begins when oil migrates into the reservoir pore network and replaces parts of the water fraction, a process known as primary drainage. Adsorption of polar components from crude oil onto reservoir rock surfaces is considered to be an important mechanism for the naturally occurring change in wetting properties from water-wet to more oil-wet.

Adsorption of different acids from acid/decane model oils onto calcite surfaces of varying specific surface areas has previously been researched in detail [1-4]. However, in order to further understand petroleum reservoir processes, it is necessary to obtain a detailed understanding of more realistic systems. The complex composition of crude oil can make contributions to an aging process that cannot be mimicked by a model oil. In a previous study from our group [5], solid state Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy was used to identify the molecular structure and investigate the arrangement of molecules from a high acid crude oil adsorbed onto calcite and quartz surfaces. These minerals are among the most commonly encountered in petroleum reservoirs. It is generally accepted that only a third of the petroleum in known reservoirs is economically recoverable with established technology [6]. Understanding aging processes on a molecular level will aid in designing more effective methods for enhanced oil recovery.

In the current study, we have performed static (non-spinning sample) diffusion and relaxation experiments to investigate the mobility of the adsorbents on the surface of the same samples as used in the solid state MAS experiments described above [5]. We show that the combination of solid state MAS and static diffusion/relaxation NMR experiments results in a detailed description of both the molecular structure and mobility of adsorbed species on these mineral surfaces, which leads to new insight with respect to aging processes on a molecular level.

2. Experimental

2.1. Sample preparation

Precipitated calcium carbonate crystals from the BioUltra series ($\geq 99.0\%$), produced by Sigma-Aldrich, were used as the calcite model. The calcium carbonate powder has a specific surface area of $0.99\,m^2\,g^{-1}$. NC4X quartz crystals, produced by The Quartz Corp, were a generous gift from Equinor ASA. The quartz sand has a specific surface area of $0.089\,m^2\,g^{-1}$. The crude oil sample used for aging of both surfaces originates from a sandstone reservoir n the Norwegian continental shelf (Grane field). The oil has a density of $0.93\,g\,cm^{-3}$, an API gravity of 20, and a total acid number (TAN) of $2.0\,mg\,KOH\,g^{-1}$. The asphaltene content is low.

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Details of the sample preparation can be found in Ref. [5], so only a brief description is given here. Dry powder was placed in a humidity chamber along with a saturated K_2SO_4 solution for 14 days. This condition gives a humidity of 97%, which produces a thin film of water on the surface of the powder. This surface pretreatment has previously shown to increase the efficiency of fatty acid adsorption from model oils on calcite surface by nearly 100% [7]. The powder was then placed in 50 g Grane crude oil for an aging period of 24 h(80 °C) under constant stirring. The suspension was centrifuged and the powder was separated from the supernatant. Excess crude oil was removed from the powder surface by dispersing it in decane, decaline and heptane. The powder was left to dry in a fume hood over night and then packed in a 4 mm MAS rotor. After obtaining solid state NMR data, which was presented [5], the MAS rotors were placed inside 5 mm NMR tubes, followed by diffusion and relaxation experiments.

2.2. NMR experiments

All NMR experiments were performed at 25 °C on a Bruker AVIII 500WB spectrometer, using a commercial probe from Bruker Biospin (DiffBB). Diffusion experiments were performed using the 13-interval bipolar sequence [8]. The diffusion time was 20 ms, the sine-shaped gradient pulse length was 0.8 ms, and the gradient strength was varied linearly between 0 and 16 T m^{-1} in 32 steps. Correlations between the longitudinal (T_1) and transverse (T_2) relaxation times were measured using a combined Inversion-Recovery - Carr-Purcell-Meiboom-Gills (IR-CPMG) sequence. The inversion time was varied in 32 steps between 1 ms and 15 s, and the CPMG echoes were collected with an echo time of 0.2 ms and a total of 10,240 echoes. The obtained diffusion data was analysed using Topspin 3.5 and Dynamics Center 2.2 from Bruker Biospin. The $T_1 - T_2$ correlation data was analysed using 2D-ILT software [9].

3. Results and discussion

3.1. Diffusion

NMR spectra from the quartz and calcite samples at different diffusion weighting are shown in Fig. 1. In the quartz sample (Fig. 1a) there are two signals with different diffusivities. The main signal is located at 4.7 ppm, corresponding to the chemical shift of water. A quantitative diffusion analysis reveal that the main signal has a diffusion coefficient of $1.0 \cdot 10^{-9}$ m^2 s^{-1}. The other minor signal is observed at higher diffusion weighting and is located at 2–3 ppm, which corresponds to the chemical shift for the aliphatic chain $(-(CH_2)_n - CH_3)$ in hydrocarbons. This signal has a diffusion coefficient of $5.0 \cdot 10^{-11}$ m^2 s^{-1}. These diffusivities indicate a relatively high translational mobility.

In the calcite sample (Fig. 1 b) there is only one signal, and the spectra obtained at different diffusion weighting indicate a very low diffusivity. A quantitative diffusion analysis reveal that this signal has a diffusion coefficient of $3.0 \cdot 10^{-15}$ m^2 s^{-1}, and thus it has very low translational mobility. It should be noted that the diffusional signal decay was relatively low in this analysis, leading to a high degree of uncertainty in the diffusion coefficient, and this value should thus be considered as an upper limit.

These results correspond very well with our previously obtained solid state MAS NMR results on these samples [5], which showed that water is the dominant adsorbent on both surfaces, with fractions of respectively 0.92 and 0.75 for quartz and calcite surfaces. Furthermore, spectra obtained at decreasing temperatures revealed that a significant fraction of water on the quartz surface freezes at 243 K, indicating that these water molecules are not strongly confined to the surface [10], and thus have higher mobility (Fig. 9 in Ref. [5]). The remaining, broader signal, is located around 2–3 ppm, which is the same position as in our diffusion weighted spectra. The corresponding NMR spectra from the calcite surface at decreasing temperatures (Fig. 6 in Ref. [5]) did not show the same phase transition for any of the adsorbed molecules, indicating that all molecules are strongly confined to the surface [10], and thus a low translational mobility of all surface species.

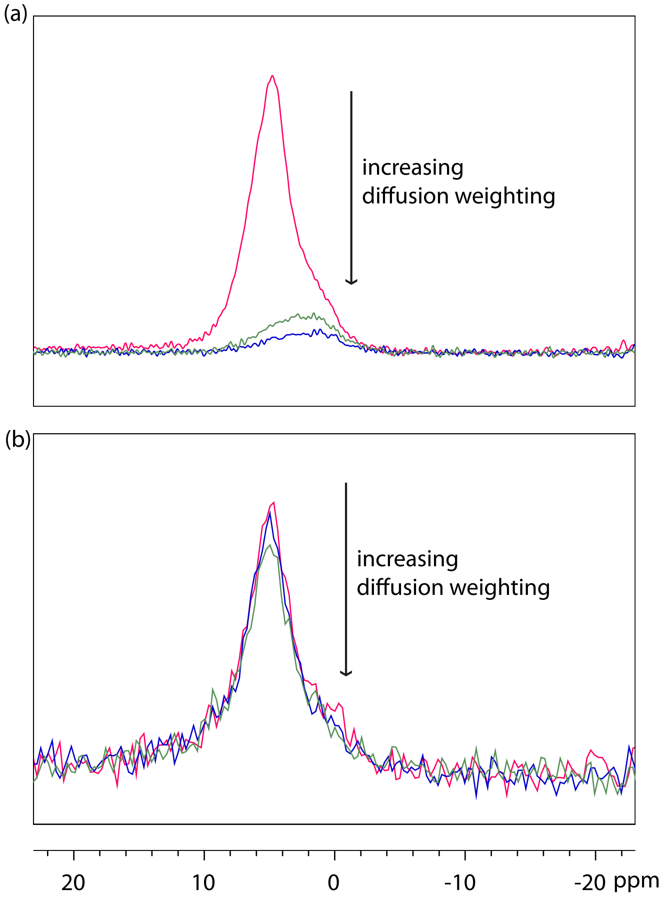

Fig. 1. NMR spectra from the quartz (a) and calcite (b) sample at different diffusion weighting. Diffusion b-factors (s^2 m^{-1}): $2.67 \cdot 10^9$, $2.84 \cdot 10^{12}$, $6.75 \cdot 10^{13}$.

3.2. Relaxation

The results from the relaxation measurements were interpreted using a simplified qualitative version of Bloembergen-Purcell-Pound (BPP) theory [11]. For highly mobile liquids, where the correlation time is short, the system is in the motional narrowing limit, and the two relaxation times are very similar. T_1 becomes longer than T_2 when the mobility is very low and the correlation time becomes very long. The obtained $T_1 - T_2$ correlations are presented in Fig. 2. In the quartz sample (Fig. 2a), there is one main signal with $T_1 \approx 400$ ms and $T_2 \approx 40$ ms, resulting in $T_1/T_2 \approx 10$. This indicate a relative moderate rotational mobility for the main part of the adsorbed molecules. In the lower part of the signal $T_1/T_2 \approx 40$, indicating a lower rotational mobility for some molecules. This is in correspondence with the results from the diffusion analysis on this sample, where two fractions with different translational mobilities were detected.

In the calcite sample (Fig. 2b) the $T_1 - T_2$ correlation is very different, with a large range of both T_1 and T_2 values. Part of the signal is located relatively close to the diagonal, with $T_1 \approx 700$ ms and $T_2 \approx 150$ ms, resulting in $T_1/T_2 \approx 5$. This indicate a relatively high rotational mobility for the molecules that give rise to this signal. This observation seems not to be in agreement with the results obtained in the diffusion analysis, that indicated that all molecules have a very low translational mobility. However, it is possible that even though the

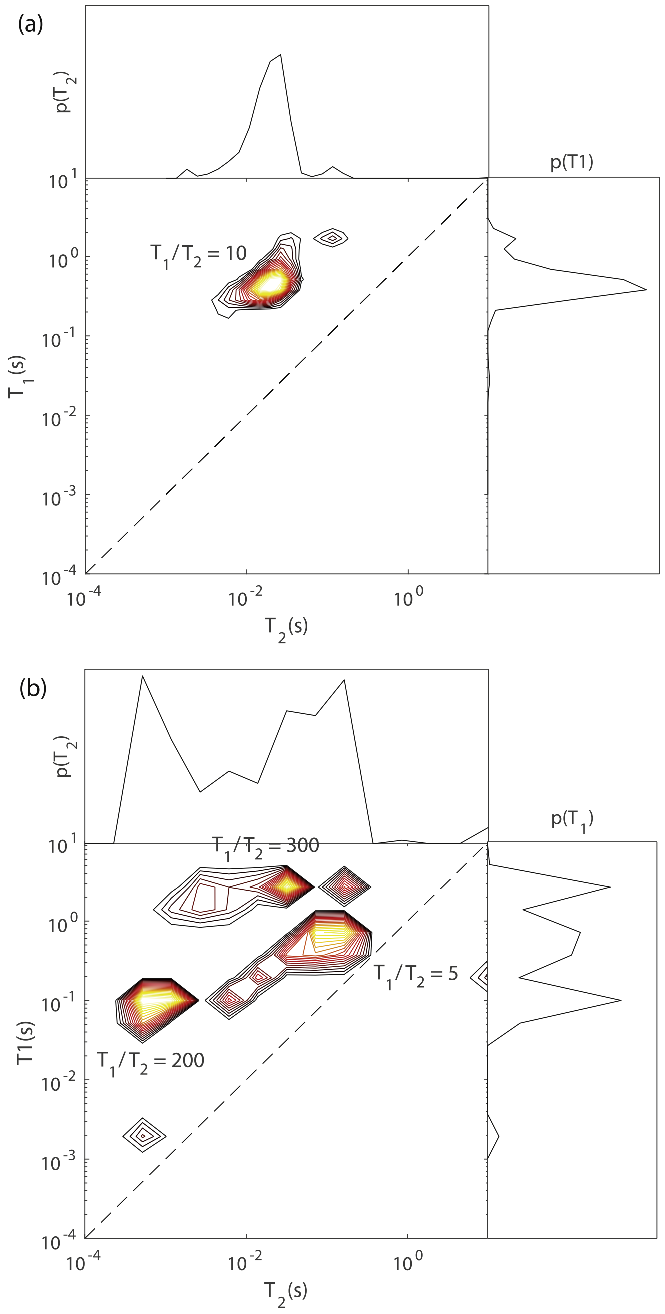

Fig. 2. $T_1 - T_2$ correlations obtained in the quartz (a) and calcite (b) samples. The dotted line indicates the diagonal where $T_1 = T_2$.

molecules have a low translational mobility, the rotational mobility can be relatively high, but this detail should be followed up in future studies. Another part of the signal is located at $T_1 \approx 100$ ms and $T_2 = 0.5$ ms, resulting in $T_1/T_2 \approx 200$. This indicate a relatively low rotational mobility for these adsorbed molecules. The last part of the signal is located at $T_1 \approx 2700$ ms and $T_2 = 10$ ms, resulting in $T_1/T_2 \approx 300$, indicating a very low rotational mobility. These two fractions of adsorbed molecules, having T_1/T_2 in the range of 200–300, correspond well with the results obtained in the diffusion analysis.

In our previous study [5], T_1 was measured in solid state MAS NMR experiments, which makes it possible to determine T_1 for the different chemical species in a chemical shift resolved spectrum. In addition, T_2-measurements were performed on static samples. In the quartz sample, it was found that water had a T_1 of around 100 ms, and the hydrocarbon signals had T_1-values in the range 100 to 1500 ms. The T_2-measurements revealed 3 components, having values of 12 ms (surface water), 60 ms (non-surface water), and 370 ms (hydrocarbons), and with relative fractions of respectively 0.14, 0.78 and 0.08. This range of T_1 and T_2-values correspond well with the values found in the same range in Fig. 2a.

For the calcite sample, it was found that water had a T_1 of around 1400 ms, and the hydrocarbon signals had a T_1-value of approximately 3400 ms. The T_2-measurements revealed 3 components, having values of 2 ms (surface water), 60 ms (acid headgroup), and 370 ms (aliphatic part of hydrocarbon chain), and with relative fractions of respectively 0.74, 0.22 and 0.04. This corresponds to the signals found above $T_1 = 1000$ ms in Fig. 2 b. However, there are also a significant amount of signal found below $T_1 = 1000$ ms, which was not observed in the solid state MAS NMR experiments. We do not know the reason for this discrepancy, but this will be a focus in future investigations of these type of samples in our research group.

3.3. *Mobility of adsorbed molecules*

In our previous study [5], it was concluded that on the quartz surface adsorbed hydrocarbon acid molecules are totally dissolved in a relatively thick layer of water molecules. On the calcite surface the adsorbed hydrocarbon acid molecules are electrostatically attached to the calcite surface, with the polar head group orientated toward the surface in an relatively thin inner layer of water molecules in close contact with the surface. The diffusion and relaxation data obtained in the current study supports these conclusions, but also gives an additional insight to the translational and rotational mobility of the adsorbed molecules. On the quartz surface the majority of water molecules seems to have a relatively high degree of both rotational and translational mobility, while a minor fraction of water molecules, and all hydrocarbon molecules, have a significantly lower mobility. On the calcite surface the translational mobility is very low for all the adsorbed molecules, while there is a large diversity in rotational mobility, indicating that the hydrocarbon molecules are strongly attached to the surface, but that some part of each molecule still have a large degree of rotational mobility.

4. Conclusion

We have shown that diffusion and relaxation NMR experiments gives a detailed description of the translational and rotational mobility of water and hydrocarbon molecules adsorbed on quartz and calcite mineral surfaces. The results show that the mobility of adsorbed molecules is very different on the two surfaces, indicating a significant difference in adsorption mechanisms. On the quartz surface, all molecules have a high rotational and translational mobility, indicating that molecules are relatively weakly adsorbed on this surface. On the calcite surface the translational mobility is very low for all the adsorbed molecules, while there is a broad range in rotational mobility, indicating that the hydrocarbon molecules are strongly attached to the surface, while each molecule still have a reasonably large degree of rotational mobility. Diffusion and relaxation experiments clearly give a new insight with respect to aging processes on a molecular level that may occur on these mineral surfaces.

Acknowledgments

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