

CHARACTERIZATION OF INTERACTION BETWEEN OIL/BRINE/ROCK UNDER DIFFERENT ION CONDITIONS BY LOW FIELD SOLID-STATE NMR

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ABSTRACT

For the foreseeable future, water flooding will still remain the most economical and the most efficient way for oil field development and production. Apart from the conventional purpose of water flooding, which is to supplement energy into reservoirs and to support formation pressure, how to extend the function of water flooding is a key to enhance oil recovery while keeping the cost low enough. Currently, ions tuning water flooding (ITWF), with its function to adjust the ion strengths amongst ions of reservoir oil, clay minerals and injected fluid, rises as a hot-spot add-on that helps detach the crude oil from surfaces of clay minerals, hence enhances both micro and macro oil displacement efficiency. Quantitative investigation and evaluation of the microscopic mechanism of ITWF on oil/water/mineral is the key to the technical breakthrough. In this work, we suggested to use low field solid state NMR to evaluate the interaction between model oil compounds and inorganic rock interface under different ions tuning water. The fully refocused FID changed according to different water and ion used. Adding certain amount water weaken the interaction between model oil compounds and inorganic rock interface. However, ions strengthen the interaction between model oil compounds and inorganic rock interface, which played a negative role. The results could well guide our further application of ITWF.

INTRODUCTION

Ions Tuning Waterflooding (ITW) is a promising improved oil recovery (IOR) technology. According to our recent research work, the EOR-effect of ions tuning waterflooding is not only dependent on the low salinity but closely related to the ionic content and ionic types. Therefore, the principle of ions tuning waterflooding is not only

to dilute the salinity of the injection brine but also to adjust the salinity and composition of the injection brine[1].

In recent years, several mechanisms were proposed to account on how the ions tuning waterflooding to recover additional oil. (1) Fines migration and clays swelling caused by ions tuning waterflood are the main mechanisms of improved oil recovery[2-3]. (2) Multi-component ionic exchange between the rock minerals and the injected brine was proposed to be as the major mechanism to enhance oil recovery[4-5]. (3) Expansion of the double layer to be as the dominant mechanism of oil recovery improvement[6]. The general agreement among researchers is that ions tuning waterflooding causes reservoirs to become more water-wet[7-9]. Even though different mechanisms have been proposed to explain the wettability alternation, the primary mechanisms of which are still uncertain. Several mechanisms have been proposed to be the dominant reason to improve oil recovery by ions tuning waterflooding. Moreover, the wettability change is claimed to be the dominant reason for incremental oil recovery. However, what the main causes (electrical double layer expansion, multi-component exchange and fines migration) to improve the wettability are still uncertain. Therefore, the main objective of this paper is to investigate the fundamental mechanisms to enhance oil recovery of ions tuning waterflood by Low Field Solid-state NMR, which is established as a powerful technique to observe structure and segmental dynamics of polymers at the molecular level. [10] In principle, molecular mobility can be deduced from simple FID signals where a fast or slow decay indicates the presence of rigid or mobile components, respectively.

In this work, we suggested to use low field solid state NMR to evaluate the interaction between model oil compounds and inorganic rock interface under different ions tuning water. The results show that ions strengthen the interaction between model oil compounds and inorganic rock interface, which played a negative role, which may guide our further application of ITWF.

EXPERIMENTAL SECTION

Preparation of Samples: Desired amounts of model oil (nonanoic acid and 2-methyl quinoline), model rock (SiO_2 sphere with diameter of $10\ \mu\text{m}$ and tunnel diameter of $17\ \text{nm}$) and deuterated water (D_2O) were combined by first dissolving the model oil in purified chloroform and then adding the model rock and D_2O .

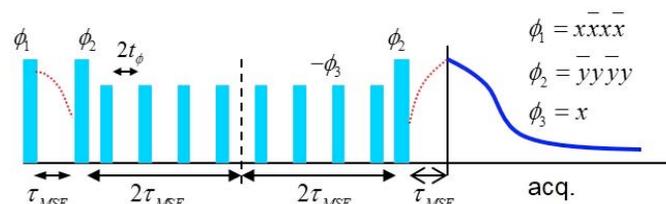


Figure 1: Magic-sandwich echo (MSE) pulse sequence for refocusing the loss of rigid-phase signal due to the dead time. [11-14].

^1H NMR experiments: The measurements were performed in a Bruker Minispec mq20 low-field spectrometer at 20 MHz proton resonance frequency with a typical $\pi/2$ pulse length of about 3 μs and receiver dead time of about 13 μs . Magic-Sandwich Echo (MSE, shown in Fig. 1a) could well refocus the initial FID signal, which gets lost in the single pulse experiment due to the dead time problem of the spectrometer. A Hahn Echo pulse sequence could well eliminate magnetic field inhomogeneity as well as refocus chemical shift anisotropy. We combined the MSE FID at short acquisition time ($\sim 80 \mu\text{s}$) with ^1H Hahn Echo decay signal at long echo time ($80\sim 10^6 \mu\text{s}$) to obtain a fully recovered FID.

RESULTS AND DISCUSSIONS

The interaction of model oil and rock results in heterogeneous mobility of the mixture: relative rigidity on the surface and mobility away from the surface. Such molecular mobility differences show up in simple FID signals. A fast decay indicates the presence of rigid components, while a slow decay is the response of mobile components. In the single pulse experiment, the spectrometer loses the initial part of the FID signals due to a long dead time and the recorded fraction of rigid components would be under-estimated in the final FID decomposition analysis. To overcome this, a MSE sequence was used to refocus the missing initial FID signals. A problem also arises at long acquisition times where the magnetic field inhomogeneity may result in a decay of FID and, thus, would obscure our analysis. Herein, Hahn echo was also utilized to record the FID signal decay with increasing echo time ($80\sim 10^6 \mu\text{s}$), as it was able to well eliminate the magnetic field inhomogeneity and refocus the chemical shift anisotropy. A fully refocused FID with complete shape could be obtained through a combination of MSE FID and Hahn echo decay. Figure 2 shows fully refocused ^1H NMR FID of nonanoic acid / model rock with different nonanoic acid contents at 30 °C. With increasing nonanoic acid amount, the FID decays more and more slowly. The same thing happens in fully refocused ^1H NMR FID of 2-methyl quinoline / model rock with different 2-methyl quinoline contents.

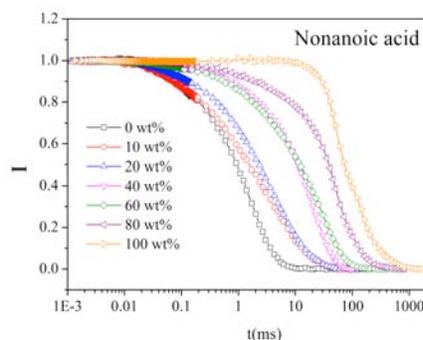


Figure 2: Fully refocused ^1H NMR FID of nonanoic acid/model rock with different nonanoic contents at 30 °C

To eliminate the influence of ^1H in water, we used D_2O instead in all the following NMR experiments with 20 wt% amount of model oil. When different amount water added, the FID curves changes differently with nonanoic acid and 2-methyl quinolone added. The FID decays more slowly with increasing amount of water, as show in figure 3a. (1.0D means 1.0 amount to corresponding model oil amount) when more than 2.0D is added the FID no longer changes. On the contrary, the FID curves change very slightly in 2-methyl quonoline / model rock when different amount of water added, as shown in figure 3b. More water added only slightly increases the slowly decayed component.

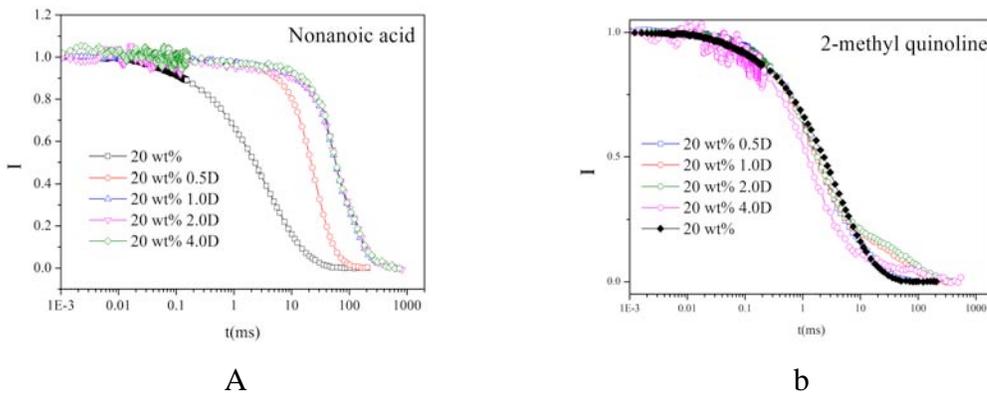


Figure 3: Water added in (a) nonanoic acid/model rock (b) 2-methyl quinoline/model rock

When small amount of ions (Ca^{2+} for example) added, we can see nearly on change of FID curves in nonanoic acid system, as shown in figure 4a. If the amount is very large, 5 eqv for example, the FID decays faster than others. In 2-methyl quinolone system, the FID decays faster with increasing ions amount, as shown in figure 4b. This suggests that ions play a negative effect.

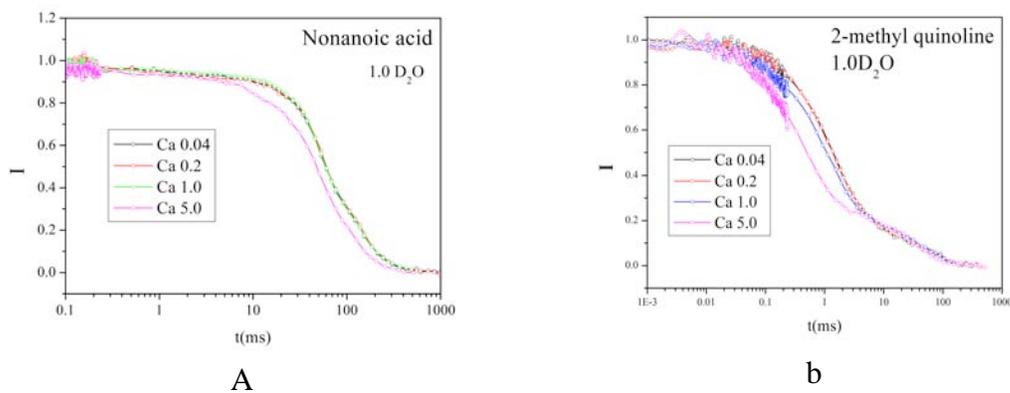


Figure 4: Ca^{2+} added in (a) nonanoic acid/model rock (b) 2-methyl quinoline/model rock

CONCLUSION

In this work, the low field solid state NMR suggested a sensitive method to evaluate the interaction between model oil compounds and inorganic rock interface under different ions tuning water. The fully refocused FID changed according to different water and ion used. Adding certain amount water weaken the interaction between model oil compounds and inorganic rock interface. However, ions strengthen the interaction between model oil compounds and inorganic rock interface, which played a negative role. The results could well guide our further application of ITWF.

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