

# Application of Low Field and Solid-State NMR Spectroscopy to Study the Liquid/Liquid Interface in Porous Space of Clay Minerals and Shales

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## Abstract

In petroleum research understanding displacement, redistribution, and adsorption of oil and water plays an important role. To study complex multi-component systems such as liquid/liquid/mineral interactions in the porous space of clays and shales we applied low field (2 – 15 MHz) and high resolution (300 MHz) NMR spectroscopy. The detailed NMR analysis shows that the results from low field NMR measurements are in good correlation with the solid-state data. Consequently the process of liquid/liquid displacement can be characterised by considering the relaxation times, signal amplitudes and chemical shifts together.

## Keywords

Low field NMR, solid-state NMR, shale, clay, wettability

## 1. Introduction

Low field NMR spectroscopy is widely used for the study of fluids in porous mediums such as rocks and minerals [1]. High resolution NMR methods also find application for the characterization of interactions between fluid and rock surfaces within the porous space [2]. In our research we combined low field NMR spectroscopy with high resolution NMR methods as well as wettability characterization [3] to investigate the effect of liquid adsorption on the wettability of porous rock depending on mineralogical structure and liquid viscosity.

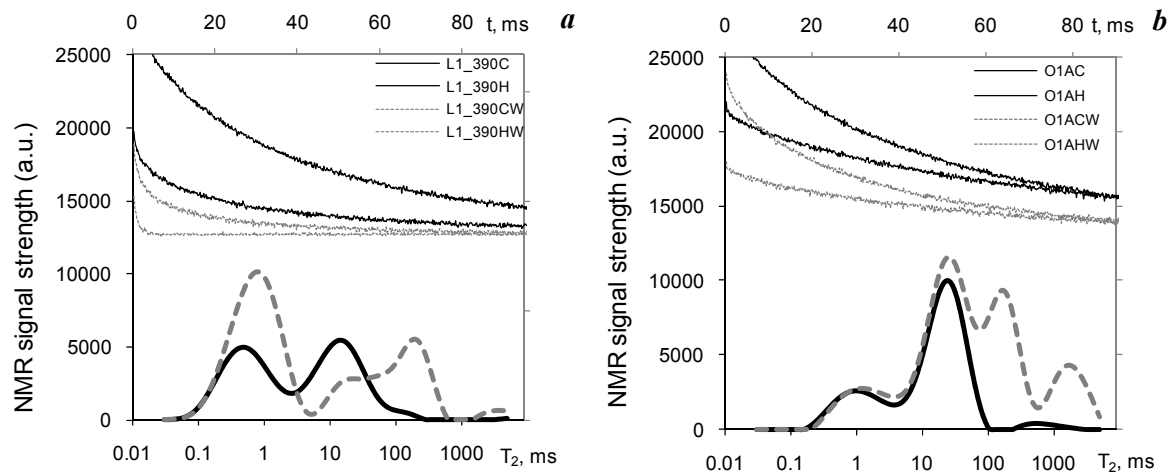
## 2. Samples and Methods

For our investigation we selected two shale minerals with distinctively different wetting behaviour [3]: hydrophobic O1A (Quartz 41%, Kaolin 42%, Mica 16%, Hematite <1%, Siderite <1%) and hydrophilic L1\_390 (Quartz 20%, Orthoclase 11%, Illite 49%, Chlorite 2%, Hematite 5%, Dolomite 13%). They were tested in dried, powdered state and then saturated with two different crude oils (C - light crude oil: 45 API; viscosity 3 mPas, and H - heavy crude oil: 20 API; viscosity 220 mPas at 20° C) and sea water (35,000 salinity).

The liquid distribution within mineral packs was studied by determination of the transverse nuclear spin relaxation time decay  $T_2$  using the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence on a Maran Ultra NMR spectrometer (2 MHz) and a Bruker NMR Surface Analyser MOUSE - MOBILE Universal Surface Explorer (15 MHz). High-resolution solid-state  $^{13}\text{C}$  NMR spectra were obtained on Varian Unity-plus 300 MHz NMR spectrometer by the use of magic-angle spinning (MAS) and  $^1\text{H}$  high-power dipolar decoupling (DD).

## 3. Results and Discussion

Detailed analysis of  $T_2$  relaxation times was performed using the spin echo (SE) decay measurement on the Bruker MOUSE NMR (Fig. 1). Comparison of the distribution of two different crude oils within shale packs shows that the heavier crude oil H has a stronger interaction with the surface and the amplitude of the NMR signal is higher. This distribution persists after re-hydration – the amplitude of the signal for heavier crude oil remains higher and only a small amount of oil was removed after hydration of hydrophobic O1A (Fig. 1). However for the hydrophilic sample L1\_390 the light crude oil C is nearly completely removed after re-hydration and only heavy crude oil remains on the surface of L1\_390HW.



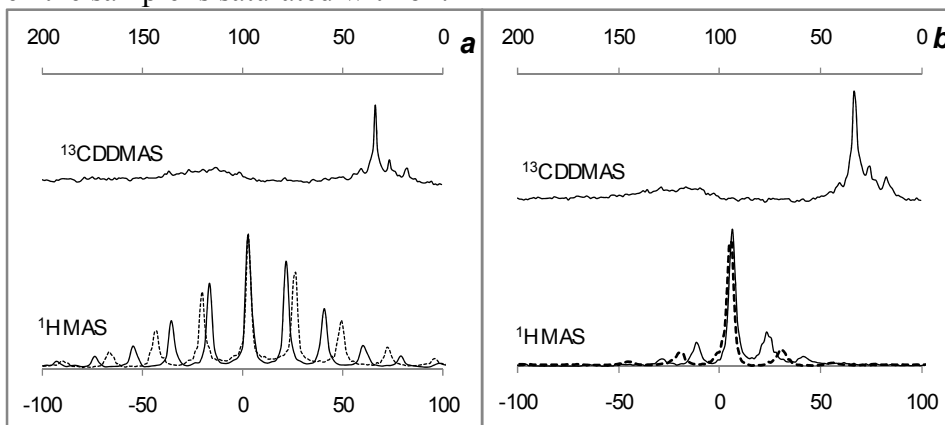
**Fig. 1:** Top part of figure shows SE decay measurement (using CPMG pulse sequence) on Bruker MOUSE NMR for L1\_390 (a) and O1A (b). Black curves for samples saturated with -H heavy crude oil and below it - C light crude oil; light grey lines for samples after following re-hydration -CW and -HW correspondingly. Bottom part of figure CPMG  $T_2$  distribution obtained on NMR Maran Ultra-2. Solid black curves for samples saturated with -C light crude oil L1\_390 (a) and O1A (b) and dashed gray -W after rehydration.

$T_2$  distribution for these two samples saturated with C light crude oil and water. Fig. 1 shows that oil saturation of shale mineral reveals two  $T_2$  peaks:  $T_2 = 10-100$  ms for oil within the porous space and  $T_2 = 0.1-1$  ms for oil adsorbed by clay. In the hydrophilic shale L1\_390 oil is quite evenly distributed between inter-granular pore space and clay bound state whilst in the hydrophobic shale it is preferentially located in the porous space. After exposure of shale to water the  $T_2$  peak of the clay-bound water becomes more distinct at  $T_2 \sim 1$  ms. It is much larger in the hydrophilic sample L1\_390-C in comparison to the hydrophobic O1A-C sample. However, water penetration into hydrophilic L1\_390-C results in a shifting of the peak at 10-100 ms to a longer  $T_2$  that reflects the displacement of the surface bound oil by the water. In

comparison, water penetration into hydrophobic shale O1A-C is accompanied by the appearance of water peaks at  $T_2 > 100$  ms, reflecting filling of inter-particle pore space, where water avoids the surfaces and does not cause liquid/liquid displacement.

High field NMR (Varian 300 MHz) was used to investigate and analyse the mobility and interaction of oil and water with the surface. The DDMAS spectra reveal the characteristic carbon resonances of mobile molecules. Thus the sharper and narrower peak in the case of L1\_390 is due to stronger interaction of some components of oil with the surface. However, the larger signal for O1A reveals a thicker oil layer on the surface of O1A (Fig. 2).

Solid-state proton NMR spectra of the two shales show different chemical shift anisotropy for samples saturated with light oil –C and heavy crude oil –H. In case of the hydrophilic shale L1\_390 we see stronger interactions of –C oil with the solid particles and therefore larger chemical shift anisotropy (more spinning sidebands – around 12 ppm to 22 ppm left and right from central resonance) than in case of the hydrophobic O1A shale. Intensive spinning sidebands indicate the large chemical shift anisotropy in both oil saturated –C and –WC water/oil saturated shale L1\_390 in contrast to O1A. Thus considering  $^1\text{H}$  MAS distribution we can see that shale L1\_390 has a surface that interacts strongly with water in contrast to O1A, which has weaker interaction that results in a strong hydrophobic behaviour when the sample is saturated with oil.



**Fig. 2:** Top part - Carbon DDMAS spectra of hydrophilic L1\_390 (a) and hydrophobic O1A (b) saturated with –C light crude oil. Bottom part: proton MAS spectra of L1\_390 (a), O1A (b) saturated with –C light crude oil (solid line) and water and then oil saturated–WC (dashed line).

#### 4. Conclusions and Outlook

We showed that the process of liquid distribution and liquid/liquid displacement in porous rock can be effectively characterised and analysed quantitatively using NMR spectroscopy. Low field NMR measurements are in good agreement with the solid-state NMR data: the intensity of the NMR detected signal and the signal relaxation time reflect differences in the oil adsorption on different shales, and highly variable mobility of the oil molecules due to different affinity to mineral surfaces is revealed in more detail by chemical shift spectra. The hydrophobic kaolinite-rich shale and hydrophilic illite-rich shale give fundamentally different NMR response. This case study demonstrates that a combination of low and high-field NMR spectroscopy can be used for the investigation of liquid distribution and mobility within the porous space of rocks of different wettability, and with complex clay mineralogy.

#### References

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