

## NMR of wetting - how to rock it despite of ageing

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Ageing is commonly related to a change in wetting behaviour. In reservoir rocks, the term “ageing” refers to extended exposition to crude oil; a typically water-wet sandstone will then gradually become oil-wet as a consequence of the deposition of insoluble fractions of oil onto the surface grains. Rocks can be aged artificially by subjecting them to oil at elevated temperature or pressure for weeks or months, possibly supported by centrifugation.

Experimentally determining the wetting status of a particular rock sample remains a challenging task since most rocks will show mixed-wet behaviour globally (properties will allow both water and oil to adsorb with finite probability) and locally (different grain materials or local residue concentrations). On a more subtle level, “oil-wet” can further be separated into specific interaction properties of aromatic and saturate molecules.

In this study, we discuss wettability as a means to investigate the effect of molecular interaction with surfaces onto their relaxation properties. Water and oil as the single phase in typical sandstone rocks were shown to follow qualitatively different NMRD features [1]. During coexistence, one of the two liquids will preferentially adsorb and the other will ideally behave bulk-like. By saturating native and aged sandstones and chalk we have found entirely different NMRD behaviour for water, benzene or alkanes. In order to separate the different relaxation contributions, we have studied perdeuterated and perfluorinated compounds and compared their relaxation with those of <sup>1</sup>H nuclei. Intra- and intermolecular contributions can thus be quantified. In a further step, microwave irradiation of radicals in the rock samples were employed to enhance the signal intensity of nuclei coming into close contact with these radicals. We observed that the radicals contained in the rock itself, such as Mn<sup>2+</sup> ions, may contribute to nuclear relaxation but are inefficient for DNP due to the extreme width of the EPR line; radicals embedded in the solid oil residues, on the other hand, led to significant DNP enhancement despite their overall much lower concentration [2]. The solid layer, containing predominantly asphaltenes and resins, thus has the double effect of altering the adsorption properties of maltene molecules and of providing additional relaxation sinks due to their content in stable radicals.

[1] J.-P. Korb, G. Freiman, B. Nicot, P. Ligneul, *Phys. Rev. E* **80**, 061601 (2009).

[2] B. Gizatullin, I. Shikhov, C. Arns, C. Mattea, S. Stapf, *Magn. Reson. Imaging* **56**, 63-69 (2019).