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Original contribution

On the influence of wetting behaviour on relaxation of adsorbed liquids – A combined NMR, EPR and DNP study of aged rocks

Bulat Gizatullin[a], Igor Shikhov[b], Christoph Arns[b], Carlos Mattea[a], Siegfried Stapf[a,*]

[a] FG Technische Physik II/Polymerphysik, Technische Universität Ilmenau, D-98684 Ilmenau, Germany
[b] School of Petroleum Engineering, Univ. of New South Wales, Sydney, Australia

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ABSTRACT

The influence of wettability modification in natural rocks has been studied by means of NMR relaxation dispersion of water and several organic liquids, employing ^{1}H, ^{19}F and ^{2}H relaxometry. Berea, Bentheimer and chalk were aged with a bitumen solution, altering the samples from water-wet to mixed-wet. Relaxation measurements were supported by EPR and DNP experiments which are sensitive to bulk radicals and interfacial radicals, respectively. The effect of ageing on relaxation was found to be twofold: first, the change from water-wet to oil-wet affects the dynamics of molecules differently, in particular their immediate interaction with the surface, which is reflected in their relaxation times; second, the bitumen cover includes paramagnetic impurities which act as additional relaxation sinks to all molecules. EPR was used to confirm the amount of deposited material and the total radical content of the rock samples, whereas DNP revealed a small but significant signal enhancement due to the surface-bound bitumen containing stable radicals. The DNP enhancement is dominated by the Solid Effect despite the low viscosity of the interacting fluids.

1. Introduction

The wettability of rock surfaces constitutes one of the most important parameters for the optimization of oil recovery, but also for the understanding of water and contaminant transport. In a simplified picture, rock is either water-wet or oil-wet, which results in preferential adsorption properties for either of the liquids in a mixture and strongly affects fluid transport under an external pressure gradient. In reality, mixed-wet properties are common, either as a consequence of the particular surface chemistry or due to its spatial heterogeneity. In addition, the interaction with the individual molecules in crude oil can be quite variable, since oil contains aromatic and aliphatic, polar and nonpolar, acidic and basic components. In the NMR picture, parameters such as pore size distribution, metal content, surface wettability and molecular interactions add up to a complex relaxation behavior that often precludes straightforward identification of individual fluids. However, assessing the wettability conditions of reservoir rock remains one of the main tasks of NMR oil-well logging.

Information about rock wettability is frequently obtained from the relaxation time distribution of adsorbed fluids, i.e. water and model oils separately saturating the pore space, or water/oil mixtures where surface properties lead to a preferential redistribution of the two immiscible liquids. Under reservoir conditions, the coexistence of both fluids is the more probable scenario. Due to the possible overlap of relaxation times distributions, two-dimensional acquisition methods have turned out advantageous since they allow the distinction of the typical properties of water and oil: the transverse relaxation time T_2 and the self-diffusion coefficient D are probably most suitable for assigning the spectrally unresolved signal to the individual constituents [1,2]. Combinations of T_1/T_2 or T_1/D have also been suggested and may show stronger contrast, depending on the magnitude of the magnetic field used in the study [3]. The diffusion coefficient itself is usually found to be insensitive to the surface wetting condition, except for two-phase saturation where the shape of a liquid's distribution in space, and hence its tortuosity, can be affected by the presence of preferential adsorption conditions. In a simplified approach of fully water-wet or oil-wet samples, the non-wetting phase is often attributed bulk-like behavior, while the wetting phase encounters enhanced relaxation due to its contact with the surface [4–6]. The nature of this process is mostly not taken into account in detail, and is summarized into the "surface relaxivity" ρ, which in turn is a field-dependent quantity at least for ρ_1, while a constant, field-independent transverse surface relaxivity ρ_2 is often approximated. In the literature, rocks are either imbibed with crude oil, or with a model substance, most likely a linear alkane of intermediate viscosity such as *n*-decane or *n*-dodecane. The behavior of the aromatic constituents in oil is usually neglected. Nevertheless, there

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[*] Corresponding author.
E-mail address: Siegfried.stapf@tu-ilmenau.de (S. Stapf).

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is experimental evidence that, in the presence of asphaltenes, aromatic molecules show much reduced T_2 relaxation times and a strongly pronounced T_1 dispersion when compared to saturated molecules under identical conditions [7,8]. This has been tentatively explained by increased interaction of the aromatic maltene in analogy to $\pi - \pi$-stacking with the polyaromatic asphaltene cores, themselves existing as aggregates of a few molecules which slow down the overall tumbling time of the whole complex [9]. Aromatic maltenes are then thought to possess a longer interaction time to relax via the asphaltene's nuclei and, if present, radical electrons. The pore space generated by the interstitial space between the single asphaltene molecules and their dangling hydrocarbon side chains may provide further possibilities for increased residence times of small maltenes.

In rocks, or more generally: in a material with a large specific surface, the nuclear relaxation rate represents a sum of the bulk value and the result of additional mechanisms from interaction with the surface. These can be other unpaired electrons close to the interface, but also the motion along a curved surface itself was shown to lead to dramatically prolonged reorientational correlation times and a strong T_1 dispersion [10]. While the latter effect is pronounced in pores on the order of few 100 nm or below, unpaired electrons of low concentration can shorten relaxation relative to the bulk value even in coarse-grained rocks with large pore sizes on the order of 10 μm or above, such as sandstones. Surface relaxivity is likely a superposition of both contributions and is dependent on the relative properties of molecules and surfaces. For instance, polar liquids inside untreated silica glass with a high polarity (i.e., hydroxyl groups) were shown to have a broad correlation times distribution over several orders of magnitude and relaxation times reduced up to 1000 fold compared to the bulk, while non-polar molecules showed a much weaker effect [10].

Water and oil in rocks were demonstrated to possess different relaxation dispersion depending on the wettability situation [11]. In these studies, the presence of paramagnetic centres of a given average surface density was assumed and supported by electron paramagnetic resonance (EPR), which allows to estimate the density based on the assumption of an equal distribution of the centres in the rock. Note that, while EPR measures the total amount of unpaired electron spins in the volume, the fraction on the surface cannot be determined directly. Such information is only available via the interaction of the paramagnetic centres with liquid molecules in their immediate vicinity, either by fitting a model of surface diffusion as in [5], or by employing polarization transfer from the electrons to the nuclei (see below). Control over the surface electron spin concentration can be achieved either by cleaning the sample in acid, or by allowing the surface to be covered with a third, insoluble substance. The latter scenario corresponds to the temporal change of rock wettability as a consequence of prolonged exposition to crude oil in a reservoir, or by artificial treatment of the pore space, summarized under the general term *ageing*. Ageing renders an originally water-wet rock sample oil-wet. In the context of the discussion above, ageing both changes the interaction of molecules with the surface and, if the added component contains radicals, provides additional relaxation centres. It is therefore not straightforward to separate the two effects on the surface relaxivity and on the total relaxation dispersion of the maltene nuclei as a consequence of molecular reorientations close to the surface.

In this study, an attempt is made to obtain qualitative insight into the relative contributions to relaxation rates by measuring relaxation dispersion for native and aged rocks saturated with liquids of different properties. To this end, three well-defined and widespread rock types – Berea sandstone, Bentheimer sandstone, Liège chalk – were considered both in their native state and after thorough treatment with a defined bitumen solution that left, after repeated ultracentrifugation and washing, a surface-bound layer containing asphaltene. Cylinders of these materials were saturated with either water, D_2O, benzene, hexafluorobenzene, or decane, and the corresponding relaxation times distributions of the ^{1}H, ^{2}H and ^{19}F nuclei, respectively, were measured in the field range between 0.02 mT and 0.7 T. These liquids are expected to experience different wetting conditions, while the relaxation mechanisms differ for the three nuclei considered. Furthermore, the presence of unpaired electrons was quantified on an X-band CW EPR spectrometer, and DNP measurements were carried out in order to determine the amount of signal enhancement of liquid molecules by polarization transfer from the electrons immediately at the rock surface.

2. Experimental and theoretical models

Cores of 8 mm diameter and 21–23 mm length were cut from blocks of three types of rocks, Bentheimer sandstone (porosity 24%, average pore size 40 μm) [12], a Berea Buff sandstone (porosity 21%, average pore size 10 μm) and a Liège chalk (porosity 30%, average pore size 1 μm). The Bentheimer sandstone contained 1.6% kaolinite while the total clay content of the Berea sample was 9%. This lead to a significantly broad pore size distribution of Berea as obtained by Hg porosimetry, while the other two samples possessed comparatively narrow and unimodal pore size distributions.

Ten cores of each rock were cut where care was taken for obtaining identical, homogeneous samples without visible defects or inclusions. Five samples each were stored in their native state, while the remaining five were aged for a total of 10 days in a solution of bitumen (commercial grade C170), hexadecane and toluene [12] at a temperature of 333 K. Subsequently, the samples were stored in hexane for 6 days at room temperature and repeatedly flushed with hexane afterwards. It is assumed that the majority of hexane-soluble components were removed from the rock sample while most of the asphaltene, and possibly a fraction of resins, remained. The SARA analysis of the bitumen, carried out prior to the dilution stage according to the Energy Institute IP 469 standard, resulted in 12.9% saturates, 28.8% aromatics, 41.7% resins and 15.72% asphaltenes; the elemental analysis showed that vanadium is the dominating metal with a content of 408 ppm, or about one vanadium atoms per 100 asphaltene molecules. This suggests the possibility of vanadyl radical complexes in the sample (see below).

An analysis using weight increase and known specific surface [12] revealed that only about 30–40% of the surface of the Bentheimer sample was covered with the bitumen residue, with an average coverage layer thickness on the order of 60 nm. Therefore, the sample must be considered mixed-wet, with native and aged surfaces coexisting. Where the surface is covered, interactions with the original surface components are fully suppressed due to the thickness of the coverage layer which much exceeds the interaction distance between liquids' nuclei and surface nuclei or free electrons. Berea and chalk samples are likely also covered incompletely, although no exact numbers for the surface coverage could be obtained. In the subsequent discussion of relaxation properties, this variable surface condition needs to be considered, and any variation of the relaxation behavior will therefore be treated as a qualitative trend.

In order to study the relaxation dispersion of different fluids, 3% NaCl brine solutions of H_2O and D_2O, *n*-decane, benzene and hexafluorobenzene were selected, and each of the native and aged samples were saturated with one of these fluids, resulting in a set of 30 rock core samples in total. The motivation behind the choice of these fluids was (a) to distinguish between water-wet and oil-wet conditions; (b) to identify a possible specific type of interaction of aromatics vs. saturates as has been observed for maltenes in crude oil or in asphaltene solutions; (c) to study the relaxation dispersion of other nuclei, again in conjunction with earlier studies, and in particular to compare intra- and intermolecular relaxation components (see below). All organic fluids were purchased from Sigma Aldrich and were used without further purification. Bidistilled water was used for the brine solution, and D_2O was 99,8% isotopically pure.

The results presented in this work constitute relaxation dispersion measurements (i.e. $T_1(\omega)$) carried out at a Stelar Fast Field Cycling (FFC) relaxometer (Stelar, Mede, Italy) at magnetic field strengths between 0.02 mT and 0.7 T. For detection, the probes were tuned to 11 MHz (^1H and ^{19}F) and 3 MHz (^2H), respectively, with the detection field set at the corresponding strength of 0.26 T, 0.28 T and 0.46 T. Signal acquisition was realized with a CPMG pulse sequence. All signal decays were fitted to a monoexponential function. All experiments were carried out at room temperature (293 K).

The EPR spectra and the total concentration of unpaired electrons in the samples were acquired at X-band (9.7 GHz) with a Miniscope MS 200 ESR spectrometer (Magnettech GmbH, Berlin, Germany). Apart from the native and aged rock cores, a reference sample of the original bitumen was also investigated. An X-Band DNP setup [13] in combination with the above-mentioned field-cycling relaxometer was used for determining dynamic nuclear polarization (DNP) equilibrium enhancement factors the native and aged rock samples filled with n-decane saturating the rock sample.

A number of theoretical concepts exist for the NMR relaxation time, and specifically for its dependence on Larmor frequency, for spins of liquids in the presence of interfaces. In this work, a qualitative treatment is intended which is able to predict and explain the variation of relaxation dispersion upon ageing of the rock samples, and the differences between the various adsorbed liquids.

On the one hand, relaxation of molecules has been modelled by recurring visits to immobile paramagnetic centers on, or very close to, the surface; these centers are naturally contained in rock samples and are possibly the dominating reason for the observed surface relaxivity ρ which is frequently used for inverting relaxation data into pore size distributions, where a uniform relaxivity for all pores is assumed. Dispersion then depends on the average time spent between paramagnetic centers, and a characteristic interaction time of the molecule to remain near these centers; this can be related to a surface-specific residence time if one assumes that no particular mechanism exists that holds up the molecule in the vicinity of the unpaired electron. Should there be active nuclei on the surface, such as is found in silica-type materials, additional relaxation processes may take place, and hydrogen exchange with surface hydroxyl groups may constitute another mechanism that promotes relaxation. In the case of a dominating paramagnetic relaxation mechanism, a T_1 dispersion logarithmically depending on the Larmor frequencies of protons and electrons was found [5,11]. In water-wet rocks, this dispersion was much more pronounced for water than for the weakly-interacting oil. A weaker "binding energy" for model oils was used to explain the observed temperature dependence.

In the absence of unpaired electrons and effective dipolar interaction with surface nuclei, a strong relaxation dispersion can still exist if the reorientation of the molecules is modulated by the surface curvature. This observation is mainly determined by the existence of a preferential orientation of a – typically small – molecule relative to the surface normal, such as for water on a polar glass surface. Under these circumstances, the molecule will diffuse freely between adsorption sites and retain the same orientation upon adsorption, which leads to a slow reorientation as the molecule "jumps" along a curved surface. This effect called "Reorientations Mediated by Translational Displacements (RMTD)" has been shown to lead to strong T_1 dispersion down to the kHz regime of Larmor frequencies, and to an overall T_1 variation of up to three orders of magnitude between low and high fields in samples with a high specific surface area. Again, the effect is much weaker, or entirely absent, for non-polar molecules close to a polar surface [10,14]. The dominance of the RMTD process has been observed, for instance, in small pores and iron-free clay platelet suspensions [15]; in rocks, the rather large pore sizes and higher natural concentration of paramagnetic centers favor the first model. In principle, T_1 relaxation dispersion can be approximated by a sum of both concepts, where it is generally assumed that fast exchange of molecules between the bulk phase and the surface region lead to an averaged, single relaxation time for a given pore diameter:

$(T_1)^{-1} = f_1\,(T_{1,RMTD})^{-1} + f_2\,(T_{1,surf})^{-1} + f_3\,(T_{1,bulk})^{-1}$, where $f_1 + f_2 + f_3 = 1$.

Low-viscosity liquids in the bulk state are characterized by the absence of any T_1 dispersion within the experimentally accessible frequency window, introducing the bulk value as a constant parameter, though this is not a requirement for the validity of the models:

One further possibility for distinguishing between different processes is the mechanism of relaxation itself. While proton relaxation is a consequence of dipolar interaction with intra- and intermolecular contributions, quadrupolar nuclei such as deuterons are predominantly relaxing via modulations of the effective electric field gradient at the position of the nucleus, which is an entirely intramolecular process. Indeed, comparative studies of H_2O and D_2O in porous glass have shown that the T_1 dispersion is found to be identical, proving the validity of the RMTD process as a purely intramolecular mechanism, i.e. being affected only by the reorientation of the molecule itself [10,16]. In addition, other mechanisms such as scalar coupling and chemical shift anisotropy have been found to be relevant for different nuclei, ^{19}F being one of them.

One aspect of this study therefore is the comparison of H_2O and D_2O relaxation, with molecules showing almost identical interactions with the surface but their nuclei undergoing different relaxation mechanisms, and to compare benzene with hexafluorobenzene to study whether any difference in relaxation behavior becomes evident, where we are aware of the fact that substituting hydrogen nuclei by fluorine will also alter the interaction of the molecule with its environment.

Dynamic Nuclear Polarization (DNP) relies on the transfer of magnetization of unpaired electrons, saturated by microwave irradiation, to nuclei in the immediate vicinity. A significant enhancement is therefore indicative of physical contact of the radicals and the molecules carrying the polarized nuclei; for the case investigated in this study, unpaired electrons must be close enough to the rock surface to allow a joint transition of the electron and the nuclear spin state.

DNP is generally divided into different processes, depending on the nature of hyperpolarization and the relative linewidths. Overhauser enhancement (OE) [17] and solid effect (SE) [18] are those that are expected to be dominant under the conditions of liquid-filled porous rocks at room temperature. OE requires the condition $\tau\omega_e \ll 1$ to be met, i.e. the correlation time with which either the dipolar or the scalar coupling is modulated needs to be shorter than the reciprocal electron Larmor frequency, corresponding to about 17 ps at X-band. This condition is typically fulfilled in low-viscosity liquids; however, the interaction of liquid molecules with solid interfaces is – as has been mentioned in the context of relaxometry – often more complicated and requires the assumption of a broad distribution of correlation times, so that the conditions for OE are violated. SE will then dominate as long as the width of the electron spectral line is smaller than the corresponding nuclear Larmor frequency, i.e. 14.3 MHz in this study. SE constitutes a double-quantum transition of one electron spin and one nuclear spin and consequentially possesses maximum intensity at $\omega_e \pm \omega_n$ whereas OE is maximal at ω_e. In this study, only solid effect has been identified which must be attributed to the enhanced interaction times of the mobile molecules with the immobilized radical electrons. It should be noted that OE was found for liquids on other surface-active radicals such as those grafted onto surfaces [19], whereas SE was found for viscous oils even in the absence of solid interfaces, where radicals are located inside the asphaltene aggregates tumbling with sufficiently long correlation times [8]. Leblond et al. [20] already demonstrated that a transition from OE to SE in a liquid can be observed upon cooling, i.e. increasing the viscosity and therefore the correlation times. It is beyond the scope of this paper to discuss the magnitude of the DNP enhancement, which is related to the lineshape, fraction of polarized nuclei and the value of the transverse electron relaxation time as outlined in [21,22].

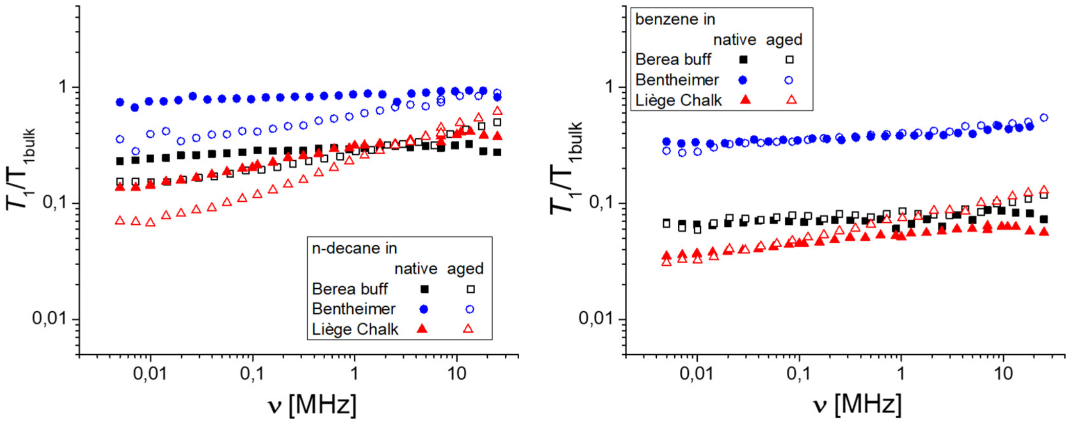

Fig. 1. Frequency dependence of the ^1H longitudinal relaxation time, $T_1(\omega)$, at room temperature (293 K), for liquids filling the pore space of native and partially aged rock samples. Actual relaxation times are normalized by the field-independent bulk values. Left: n-decane; right: benzene.

3. Results

3.1. NMR relaxation dispersion

Fig. 1 compares the T_1 dispersions for *n*-decane and benzene in all three rock types, native and aged. For better comparison, all data are normalized to the value in the bulk liquid; this representation aims at highlighting the difference in shape of the dispersion curves, but also gives insight into the relative contribution of the additional relaxation mechanisms in the rock porespace. In all rocks, dispersion of *n*-decane is weak or absent in the native sample, but becomes apparent in the aged sample. This is in agreement with the concept of the rock becoming oil-wet (or rather: partially oil-wet), thus increasing the interaction of the fluid with the pore surface in the presence of its hydrocarbon coverage. For untreated Bentheimer with its large pores and correspondingly low specific surface area, T_1 is very close to its bulk value, proving only minimal additional relaxation contributions of the solid interface. T_1 in Berea and chalk is significantly shorter than the bulk value. Interestingly, ageing leads to a *longer* T_1 at high frequencies in the latter two rock types; we are not aware of a report in the literature that has found an increase of T_1 upon ageing. This effect can phenomenologically be explained by short or intermediate reorientational processes, on the timescale of the reciprocal Larmor frequency, i.e. $< 10^{-7}$ s, becoming less relevant for relaxation in the bitumen-covered surface, whereas slower processes are dominating. The precise origin of this shift in timescales is currently not known.

For benzene, being another representative constituent of crude oil, a similar tendency during sample ageing would be expected. Indeed, save for an increase of dispersion in chalk and, to a lesser degree, in Berea Buff, the behavior is quite different to that of *n*-decane. With generally much shorter relaxation times compared to bulk, the dispersion is weaker. Once more, a prolonged T_1 after ageing is found at high fields, in particular for chalk. This would be the first indication that saturated alkanes such as n-decane or n-dodecane are not perfect “model oils” in the sense of relaxation dynamics, but that aromatics need to be considered separately.

Fig. 2 compares the T_1 dispersions for H_2O and D_2O. For light water, the ^1H relaxation is significantly shortened compared to the bulk, much more so than for *n*-decane but in the same order of magnitude as benzene, except for chalk. Dispersion is generally very weak and ageing does not change this frequency dependence. The same is true for the absolute value of T_1 with the exception of Berea sandstone where ageing results in a pronounced increase of T_1. One possible explanation for this observation could be the comparatively high clay content in Berea which corresponds to a tail of small pores in the PSD down to below 100 nm. Since only the average relaxation time was determined, loss of very short components by blocking of the smallest pores with the bitumen residues, where relaxation rates are orders of magnitudes higher than in the large pores, might account for the observed increase by a factor of three. The changes upon ageing found for water are thus in agreement with the expected behavior when the surface changes from water-wet to oil-wet, but the variation is exceedingly small and the dispersion being weaker than for n-decane is opposite to the findings by [5].

The deuteron nucleus in D_2O is an important marker for understanding molecular dynamics of water. As mentioned above, deuterons relax via intramolecular processes only, i.e. reorientation of the water molecule. Intermolecular interactions require dipolar coupling to other nuclei; since only deuterons are available, and the homonuclear relaxation rate is proportional to γ^{-4}, the corresponding relaxation rate is 1800 times lower than for the equivalent dipolar ^1H relaxation in H_2O. From comparing with the bulk ^2H relaxation in D_2O, the efficiency of the D-D dipolar coupling is about 10^{-4} times the value of the quadrupolar relaxation rate. The situation is somewhat different if relaxation occurs via nuclei in the interface or via electron spins, in this case the rate is $(\gamma_H/\gamma_D)^2 = 40$ times weaker than for protons. The effect can be estimated from the observed ^1H relaxation of water in rocks and is likewise shown to be negligible. The relaxation rates in D_2O relative to the bulk are in qualitative agreement with those of H_2O in the sense that rock ageing has little effect, again with the exception of the clay-rich Berea. However, their dispersion is much larger. This is at variance with the observation of light and heavy water in porous glass [10] where the ^1H and ^2H dispersions were identical, as is indeed expected for pure RMTD process relaxation. For ^1H, on the other hand, dipolar relaxation consists of intra- and intermolecular contributions as well as ^1H-electron dipolar relaxation from molecules visiting the paramagnetic centers. Assuming that H_2O and D_2O undergo essentially the same molecular dynamics, save for the slight difference in molecular mass, it is reasonable to conclude that the T_1 dispersion of D_2O is equivalent to the intramolecular, i.e. RMTD contribution of the H_2O dispersion, but being scaled by a corresponding prefactor which takes into account the differences between proton and deuteron relaxation. Therefore, the intermolecular and electronic contributions can be isolated from the total ^1H relaxation rate. As can be seen from the very weak dispersion in H_2O, the latter contributions must dominate for ^1H over the intramolecular part.

Finally, Fig. 3 presents the ^{19}F relaxation data for hexafluorobenzene. The fluorine nucleus possesses a gyromagnetic ratio similar to that of ^1H, and in many cases, relaxation has been found to be predominantly dipolar in nature, such as in viscous ionic liquids with protons and fluorine nuclei attached to either of two ionic species which showed very similar T_1 dispersion [23]. On the other hand, there is indication that ^{19}F is also significantly affected by non-dipolar mechanisms such as scalar coupling [24], in particular as interactions with

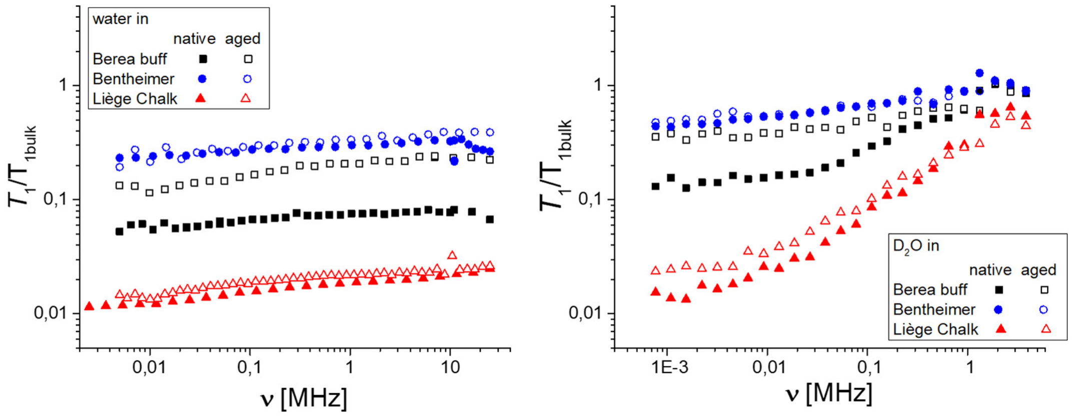

Fig. 2. Frequency dependence of the longitudinal relaxation time, $T_1(\omega)$, at room temperature (293 K), for water filling the pore space of native and partially aged rock samples. Actual relaxation times are normalized by the field-independent bulk values. Left: H_2O, relaxation of ^{1}H nuclei; right: D_2O, relaxation of ^{2}H nuclei.

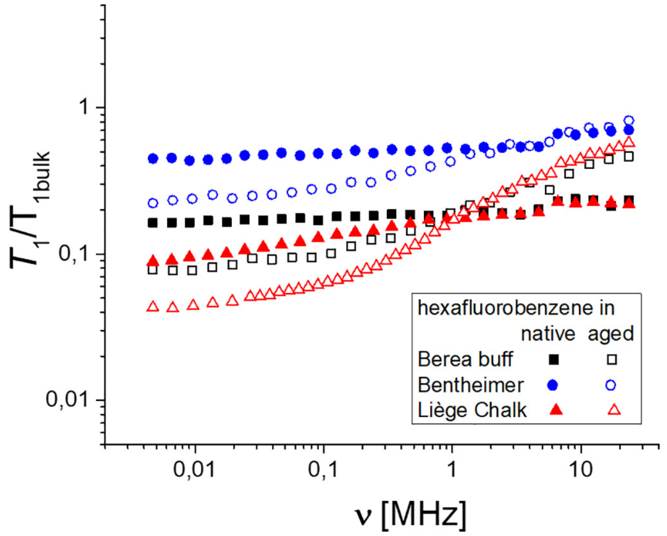

Fig. 3. Frequency dependence of the ^{19}F longitudinal relaxation time, $T_1(\omega)$, at room temperature (293 K), for hexafluorobenzene filling the pore space of native and partially aged rock samples. Actual relaxation times are normalized by the field-independent bulk values.

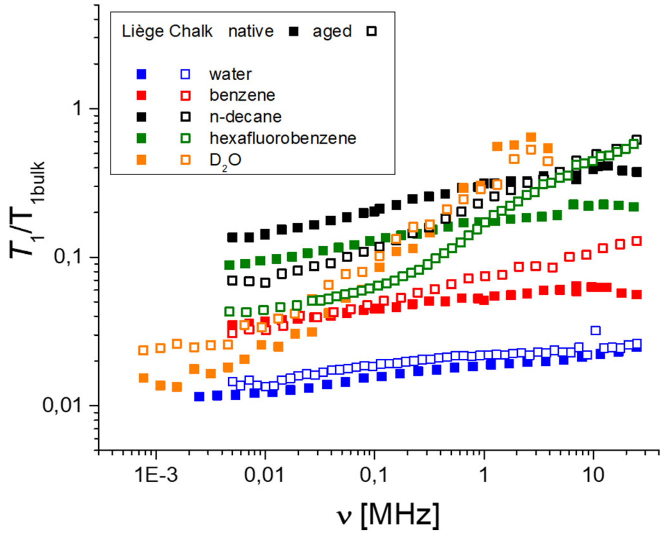

Fig. 4. Frequency dependence of the longitudinal relaxation time, $T_1(\omega)$, at room temperature (293 K), for liquids filling the pore space of native and partially aged Liège chalk samples. Data as described in Figs. 1–3 in comparison.

radicals are concerned. Note that scalar coupling is not modulated by molecular rotation alone but rather involves translational diffusion. Relaxation due to Chemical Shift Anisotropy (CSA), on the other hand, is usually negligible at the low magnetic fields used in this study.

Hexafluorobenzene in native rocks shows similar relaxation properties as benzene, i.e. hardly any frequency dependence but a somewhat less pronounced shortening compared to the bulk. In absolute terms, however, the additional relaxation rates inside the rock samples are almost identical to those for benzene. In aged samples, the low-field relaxation rate is about twice that for ^{1}H in benzene, whereas the main difference is seen in the much more pronounced dispersion for ^{19}F which goes along with a longer T_1 at high fields. Similar to the oil-contained *n*-decane and benzene, ageing the surface results in a weaker interaction of the hexafluorobenzene molecules, but the effect is much more obvious than for the other liquids.

With the exception of Berea Buff sandstone with its high clay content, the general trend of all liquids follows the expectation for a rock that is turned from water-wet to mixed-wet. (A more detailed study with completely oil-wet rock samples is currently under way). In Fig. 4, all relaxation data are shown for comparison for the case of chalk which has the highest surface-to-volume ratio and, as expected, the strongest dispersions and variations of the three samples under study.

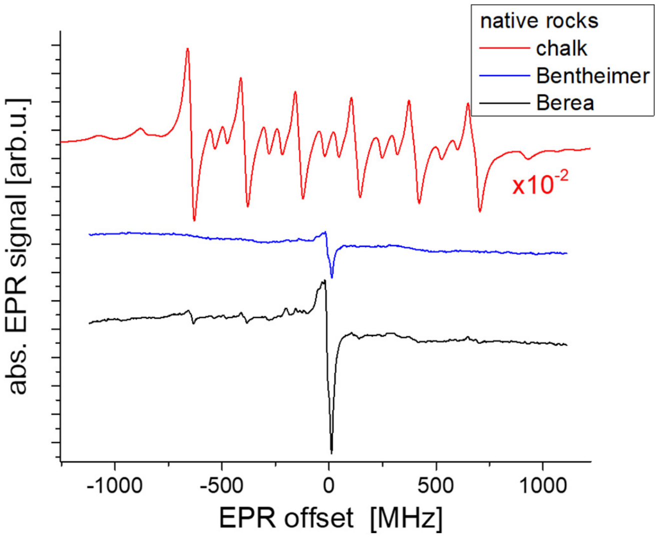

Fig. 5. EPR dispersion signal for dry, native rock samples obtained at X-band and room temperature (293 K). The signal from Liège chalk is multiplied by 0.01; data are shifted vertically for better comparison.

3.2. EPR spectra

Electron Spin Resonance Spectra obtained at X-band (9.5 GHz) reveal the existence of unpaired electrons in all three rock types (see Fig. 5). In Berea and Bentheimer sandstone, the signal is dominated by a central peak of free radicals, with an admixture of Mn^{2+} ions in Berea. In Liège chalk, a strong signal of Mn^{2+} is observed in agreement with findings on similar materials (note the six lines due to hyperfine splitting by the $I = 5/2$ ^{55}Mn nucleus) [25]. In the aged samples, an increase of the free radical signal is seen in the sandstones while it is just barely identifiable in chalk against the Mn^{2+} background (data not shown). The multiplet according to the vanadyl (VO^{2+}) centres from the bitumen samples is too weak to be identified with certainty. When comparing the different EPR spectra one needs to keep in mind that the weight gain due to absorption of the bitumen residue amounts to between 0.1 and 0.3% per sample, and that the radical concentration and composition of the original bitumen before dilution need not be identical with the properties in the aged sample after repeated washing with hexane.

3.3. DNP experiments

While EPR measures the total amount of unpaired electrons in the volume, Dynamic Nuclear Polarization (DNP) senses only those radicals that are located immediately at the surface and thus are accessible by passing maltene molecules. They consist of contributions of the paramagnetic centres of the native rocks, inasmuch they are close to the surface, and the radicals of the bound bitumen residue which possesses a much higher concentration. Under the mixed-wet conditions found in these samples, part of the native paramagnetic centres becomes covered by bitumen and are therefore unavailable for DNP.

Within experimental accuracy, carrying out DNP experiments in the native rock did *not* lead to any DNP enhancement. This is despite the fact that a certain number of centres are expected to reside close to the surface since they are likely responsible for the enhanced surface relaxivity observed in the relaxation measurements. One possible reason why no DNP was found even in chalk may be the large linewidth of the Mn^{2+} EPR spectrum which makes polarization transfer to maltene nuclei highly inefficient.

Aged samples, however, show significant DNP enhancement which is on the same order of magnitude for Bentheimer, Berea and chalk. As an example, Fig. 6a presents the result for X-band DNP of *n*-decane at a microwave power of 1.5 W and room temperature; in Fig. 6b, the power dependence of the maximum enhancement is shown. The signal is enhanced approximately twofold and follows the solid effect which is characterized by maxima at the microwave frequencies $\omega_e \pm \omega_n$. It is dominated by free radicals but also features a small contribution at one of the frequencies of the vanadyl complexes (peak on the left-hand side). These results demonstrate that a significant amount of radicals, which is similar between the different rocks, is available close to the bitumen surface, with its radicals associated to the asphaltenes present, so that the distance of closest approach and the contact times of *n*-decane molecules are suitable to favor solid effect DNP. The same observation, with somewhat different maximum enhancements, was observed for other liquids in these rocks. The fact that solid effect (SE) was found as opposed to Overhauser effect (OE), which would be expected for low-viscosity liquids, is somewhat surprising but appears to be corroborated by other observations of solid effect DNP of maltenes interacting with asphaltene aggregates in crude oil or in solution [8,26]. The duration of interaction with the radical seems to be sufficiently long to favor double quantum transitions which are required for SE, although a small mixture of OE cannot be excluded from the experimental data.

4. Discussion and conclusions

The determination of pore-size distributions (PSD) in reservoir rocks can be called the bread and butter business of oil-well logging by NMR. It relies on having a reasonable estimate about the surface relaxivity, possibly being obtained by calibration prior to the logging experiment, for a given test liquid such as water. While it is obvious that the relaxivity is linked to the mineralogy of rock, and therefore unavoidably is a distributed property within the grain structure of rocks, and while it is accepted that relaxivities depend on the type of liquid, providing an option to probe wettability properties of rocks, a suitable working hypothesis assumes an average value throughout the sample. The transverse component ρ_2 is then considered a more useful parameter since it is generally larger than ρ_1 – as required by theory – and T_2 can be measured in much shorter times, but the ratio T_1/T_2, which indirectly probes the timescales of molecular reorientations in the pore space, has occasionally been considered as a refined tool for assessing pore morphology and mineralogy [27]. Because T_2 is proportional to the zero-field limit of T_1, in essence, T_1/T_2 approximates the limiting values of the dispersion function $T_1(\omega)$ which reproduces, at least in principle, the full spectrum of molecular reorientations and surface interactions. Often, ρ_1 and ρ_2 are considered material constants for practical reasons, while a number of studies have shown their correlation with the concentration of paramagnetic centers in the rocks. Very low relaxivities are found for "clean" sandstones with essentially pure quartz surfaces [28].

Measuring relaxation dispersion provides an opportunity towards an in-depth understanding of molecular interactions; employing

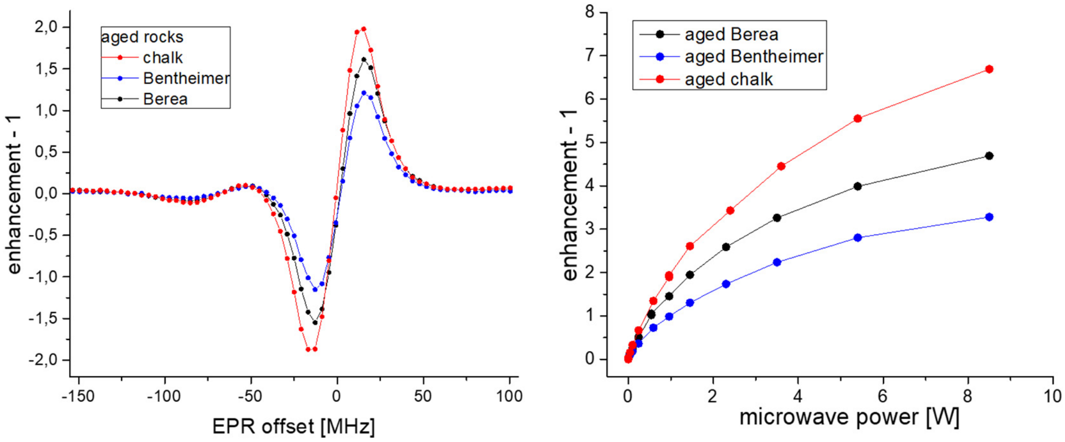

Fig. 6. Left: DNP enhancement factors of the ^{1}H signal of n-decane in partially aged rock samples at a microwave power of 1.5 W. Right: maximum of the DNP enhancement factor plotted as a function of microwave power. Experiments were carried out at room temperature (293 K).

different types of bulk liquids allows to separate dominating interaction contributions at least on a qualitative level. In this study, aged rock samples were shown to confirm the phenomenological correlation between surface interaction and wetting behavior, with several significant deviations occurring on a more detailed level. Rock samples aged by a bitumen solution turn from water-wet to partially oil-wet [12,29], thus decreasing water interaction and increasing oil interaction with the surface. The latter is confirmed by a more pronounced dispersion, being equivalent to a larger T_1/T_2 coefficient, for the examples of decane, benzene and hexafluorobenzene, though the effect is almost masked by a general increase of relaxivity for benzene. On the other hand, water and D_2O show only small variations bar a significant decrease of relaxivity for a clay-rich Berea sandstone. In this first-ever NMR dispersion study on deuterons in rocks, the dispersion for deuteron nuclei in D_2O was found to be much more pronounced than the equivalent for protons in H_2O, suggesting that a strong intermolecular contribution exists that only occurs for protons and that possesses only weak frequency dependence. This contribution may be attributed to efficient relaxation with surface-attached paramagnetic centers, which is negligible for deuterons the relaxation of which is dominated by quadrupolar terms. It is further noted that upon ageing, relaxivities for organic liquids are observed to decrease above a certain field strength which depends on the rock type but is typically below 100 mT. In general, all observed trends qualitatively correlate with surface-to-volume ratio.

All rock types in this study contain paramagnetic centers as was determined by EPR spectroscopy. Ageing the samples, despite leading to a weight gain of only between 0.1 and 0.3% in the form of bitumen residues, increased the EPR signal strength at least twofold with the exception of chalk which was characterized by a two to three orders of magnitude higher concentration of Mn^{2+} ions. Even for chalk, no detectable DNP enhancement was found for different liquids in the native material, while aged samples led to similar solid effect DNP enhancements for all three rocks, suggesting that the surface concentration of unpaired electrons was significantly increased by the deposition of bitumen. According to a more detailed study, this work finds the samples still in a relatively early stage of ageing where polar asphaltenes strongly dominate this surface deposit [12,29]. In the simplified picture of surface relaxivity, this could be interpreted by a necessary increase of relaxivity of ρ_1 and ρ_2. The findings in this study contradict this picture since (a) relaxivity for water is actually decreased after ageing, and (b) relaxivity for organic and fluoroorganic compounds is decreased at intermediate and high fields while it is increased at low fields. Relaxation is a complex superposition of intra- and intermolecular processes, nucleus-electron and possibly also nucleus-nucleus interaction with the surface, each possessing individual T_1 dispersion properties. The comparison of proton- and deuteron-containing molecules has the potential for separating these components; the comparison of H_2O and D_2O relaxation represents a first step in this direction.

The results of this study find their foremost application in the distinction of two-component liquids, which is of outstanding importance since water-oil mixtures are regularly present in reservoir rocks: not only can the shape of the T_1-dispersion potentially resolve the question about wettability conditions and their heterogeneities, but enhancing the near-surface fluid component selectively by comparing signal magnitude in a comparative DNP experiment with and without microwave irradiation is able to quantify wettability directly.

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