

In Situ NMR Analysis of Fluids Contained in Sedimentary Rock

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Limitations of resolution and absorption in standard chemical spectroscopic techniques have made it difficult to study fluids in sedimentary rocks. In this paper, we show that a chemical characterization of pore fluids may be obtained *in situ* by magic angle spinning (MAS) nuclear magnetic resonance (NMR), which is normally used for solid samples. ¹H MAS-NMR spectra of water and crude oil in Berea sandstone show sufficient chemical shift resolution for a straightforward determination of the oil/water ratio. © 1998 Academic Press

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Chemical information such as the quantity and nature of the residual hydrocarbon content of rock cores is a vital part of reservoir evaluation. Analysis of pore fluids, for this purpose, is usually performed after a distillation extraction process (1), due to the lack of a simple, reliable spectroscopic technique which can be used *in situ*.

¹H nuclear magnetic resonance (NMR) spectra of pore fluids inside sedimentary rock cores typically consist of a broad featureless line. Trace amounts of paramagnetic metals in the rock result in a significant magnetic susceptibility mismatch between the rock and the pore fluid. The resulting nonuniform magnetic field in the pore space broadens the NMR resonance. Linewidths vary over a wide range, with 50 ppm being typical for sandstones, and 5 ppm more typical for carbonates (2).

However, NMR relaxation times have proven to be an important noninvasive probe of the physical geometry of porous media. Since the relaxation of nuclear spins occurs predominantly through contact with paramagnetic sites on the pore walls, relaxation times may be related to the collision rate of spins with the pore walls, which in turn is related to the pore size (3). Recently it has been shown that geometric quantities such as the surface-to-volume ratio may be extracted with pulsed gradient techniques (4, 5). Such geometric information is valuable for both oil recovery and hydrology, since pore size is the factor that most directly determines the flow properties of fluids in porous media (6). The development of “inside out” NMR instrumentation which can be lowered into boreholes has therefore been a significant development for the well logging industry (7).

Inferring the chemical nature of pore fluids from the kind of

NMR measurements just described requires *a priori* information. Relaxation times in part reflect molecular weight, but are strongly affected by pore geometry. Measurement of hydrocarbon/water ratios requires comparison of the total ¹H signal with the total ¹³C signal. The latter is very weak due to low natural abundance, gyromagnetic ratio, and the large NMR static linewidth. Furthermore there is the potential of signal originating from the rock material itself.

In this paper we demonstrate that the susceptibility broadening in rocks can be dramatically reduced (by a factor of 40 for the sample chosen here) by the use of magic angle sample spinning, making it possible to resolve the chemical shifts of proton resonances of pore fluids. The magnetic field \mathbf{B}_{dip} at a position \mathbf{r}' in the pore space due to paramagnetic impurities in the rock, (see Fig. 1), is given by

$$\mathbf{B}_{\text{dip}}(\mathbf{r}') \cdot \hat{z} = \frac{B_{\text{ext}}}{4\pi} \int \chi(\mathbf{r}) \frac{(3 \cos^2 \theta - 1)}{|\mathbf{r}' - \mathbf{r}|^3} d\mathbf{r}, \quad [1]$$

where $\chi(\mathbf{r})$ is the local magnetic susceptibility in the rock, and the external magnetic field, \mathbf{B}_{ext} , has been taken in the z direction. It is well known that a dipolar field, such as that given in Eq. [1], averages to zero under magic angle spinning (MAS), in which the axis of the rapidly spun sample is inclined at an angle of $54.7^\circ = \cos^{-1}(1/\sqrt{3})$ with respect to the external field. We note that two assumptions are built into Eq. [1]: that $\chi(\mathbf{r}) \ll 1$ and that $\chi(\mathbf{r})$ is isotropic. To the extent that either of these assumptions is invalid, it can be shown that \mathbf{B}_{dip} will only be partially averaged.

MAS is routinely used in solid state NMR to average out chemical shift anisotropy and internuclear dipolar interactions (8). The potential of MAS to narrow susceptibility broadening and residual anisotropy in solid composite and “soft” systems has been appreciated for some time (9, 10); recent examples include resins, lipids, and gels (11–13).

Figure 2 shows the effect of MAS on NMR spectra of Berea sandstone saturated with water. The Berea sample used is a quarried stone with a measured susceptibility of 30.7×10^{-6} and porosity of 22.4%. Under MAS the water spectra exhibit spinning sidebands, spaced at multiples of

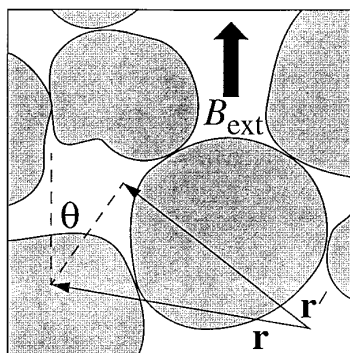


FIG. 1. Sketch of sandstone showing the geometric parameters in Eq. [1].

the rotor frequency, demonstrating that the static spectrum is indeed inhomogeneously broadened. Under these experimental conditions, we find that MAS narrows the NMR linewidth by about a factor of 40, from about 6 kHz to 150 Hz, fwhh, at a static field of 4.25 T.

The cause of the residual line width under MAS is not fully determined. T_1 measurements indicate that it is too large to be dominated by surface relaxation (3). Possibilities include relaxation by diffusion in field gradients and residual broadening from magnetic susceptibility anisotropy. The residual line-

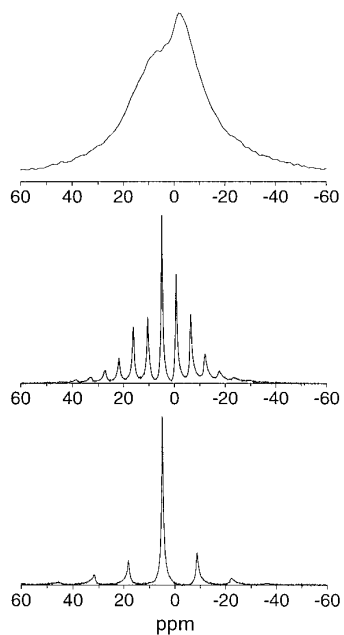


FIG. 2. The effect of MAS on ^1H NMR spectra of Berea sandstone saturated with water. The spectra from top to bottom are the results of spinning the sample at 0 Hz, 1 kHz, and 2.5 kHz, respectively. Spectra were recorded at 300 K on a Chemagnetics Infinity spectrometer operating at 4.2 T, using a home-built MAS probe. The rock samples were saturated with fluid under vacuum and sealed into vespel capsules with an epoxy putty. The vespel signal has been subtracted from all spectra. The capsules were machined to fit precisely into 7-mm zirconia rotors. Typical 90° pulse lengths were $5 \mu\text{s}$. The chemical shift is referred to tetramethylsilane at 0 ppm.

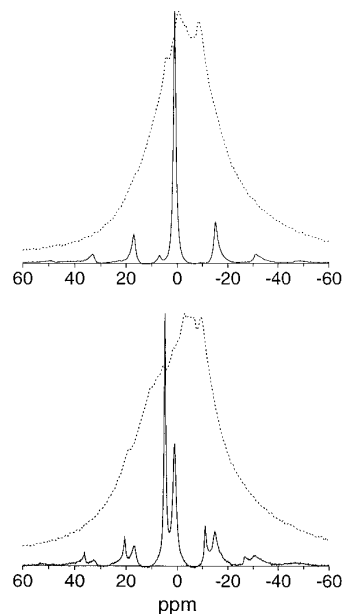


FIG. 3. ^1H MAS-NMR spectra of Berea sandstone saturated with a light crude oil (top), and a mixture of crude and water (bottom). The spinning speed was 2 kHz in both cases. The dotted line shows the spectra with a static sample in each case. Other experimental conditions are as in Fig. 2.

width of the center band shows a slight increase with increased spinning speed. Further measurements at a higher field (7.1 T) did not yield significant improvement in resolution, since the residual linewidth increased roughly linearly with increasing chemical shift. A further unresolved issue, relevant to the more shaly sandstones, is the extent to which MAS reduces the linewidth in any "clay-bound" portion of the fluid.

Figure 3 shows NMR spectra of Berea sandstone saturated with a light crude oil, viscosity 12 cp, and with a mixture of the same crude oil and water. The spectrum of oil alone shows a large peak in the aliphatic region and a small peak in the aromatic region, as expected in a light crude. Such information concerning mixture components clearly is not accessible from the NMR spectrum of a static sample. The spectrum of crude oil and water exhibits the aliphatic oil peak, and an intense water peak. The smaller aromatic peak is obscured by the base of the water line. From the data presented in Fig. 3, we calculate that the oil:water ratio within the sample is 0.95:1.0 \pm 0.1, by volume, taking the density of ^1H to be equal in oil and water (14). This indicates that the rock was preferentially water wet, since the sample was prepared by emersion in a mixture with an oil:water ratio of 3:1.

Our experiments show that chemically resolved NMR data are possible in a sedimentary rock such as Berea sandstone. While an obvious application is chemical analysis of the contents of the rock pore space, new kinds of geometric information should also become available, by combining chemical resolution with existing relaxation measurements. Hydrocarbon relaxation times, for example, provide a good estimate of

oil viscosity (15). Another possibility is the use of chemical shift-resolved relaxation data to distinguish which of the fluids, or possibly which fraction of the crude, is preferentially wetting the pore walls and thus relaxing more efficiently. The geometry of the nonwetting phase could be explored using chemically resolved pulsed gradient spin echo measurements (4, 5). There has also been significant interest in the use of NMR imaging to provide spatial maps of fluid phases. (See for example Refs. (16–20)). The choice of fluids and rocks has been limited by the challenge of resolving separate phases. The recent advent of NMR instrumentation (21), which combines field gradients with MAS, has opened the door to generalizing these studies. Further information about the proximity of fluid constituents might be extracted from nuclear Overhauser measurements (22). Other high resolution NMR techniques such as multiple quantum spectroscopy and two-dimensional NMR should also be applicable (22).

Finally, we note that when a mixture of fluids is present in the pore space, rapid spinning will tend to centrifuge the heavier components to the periphery of the sample. In such circumstances, techniques such as magic angle turning (23), or possibly rotation of the external field, may be more appropriate (24).

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