PROTON T$_1$ AND T$_2$ RELAXIVITIES FOR CH$_2$ AND CH$_3$ PEAKS IN CRUDE OIL MEASURED BY 400 MHz NMR

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Abstract

Petroleum fluid has been extensively studied at low magnetic fields by Nuclear Magnetic Resonance (NMR) Spectroscopy, but high field NMR studies are rarely found in this area. The aim of this study is to determine the proton spin-lattice relaxation rate (1/T$_1$), T$_1$ relaxivity (R$_1$), proton spin-spin relaxation rate (1/T$_2$) and T$_2$ relaxivity (R$_2$) of paraffinic CH$_2$ and gamma CH$_3$ peaks. For this purpose, crude oil samples were taken from 3 separate wells in the Batman region. Using these samples, 3 different sets were prepared from a mixture of deuterated chloroform (CDCl$_3$) and crude oil. The total volume of each prepared mixture was 1 mL. The crude oil content in each set was changed from 0.05 mL to 0.20 mL in 0.05 mL steps. Special care has been taken to ensure the best shimming of the NMR spectrometer operating at 400 MHz. T$_1$ measurements were performed using an inversion recovery (IR) pulse sequence. 1/T$_2$ values were determined from the half-height line widths of CH$_2$ and CH$_3$ peaks. 1/T$_1$ and 1/T$_2$ rates and all relaxivities were found to vary from well to well. This change is due to the fluid composition of the wells. The 1/T$_2$ rates and R$_2$ relaxivities were found to be considerably greater than the 1/T$_1$ rates and R$_1$ relaxivities. R$_2$ relaxivities for CH$_3$ were also 2-5 times greater than for CH$_2$. The higher 1/T$_2$ and R$_2$ relaxivities compared with 1/T$_1$ and R$_1$ were attributed to the additional CDCl$_3$-mediated relaxation mechanisms. In conclusion, available data show that high 1/T$_2$ rates and R$_2$ relaxivities measured in the high field NMR laboratory can be applied to separate crude oil from other fluids in the oil field.

Keywords: CH$_2$ and CH$_3$, crude oil, 400 MHz NMR, 1/T$_1$ and 1/T$_2$ rates, R$_1$ and R$_2$ relaxivities
1. Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most important tools for crude oil studies. NMR spectroscopy has been used to study crude oil properties such as relaxivity, permeability, viscosity, water droplet size in a water-in-oil emulsion, diffusion coefficient, and changes in porosity and wettability [1-8]. NMR has also been used for reservoir fracture characterization, fluid characterization in reservoir rocks, and water and oil prediction in granular packing and rocks [9-11]. Thus, NMR logging for petroleum reservoir fluids is well established [12-15]. All these parameters were evaluated by means of NMR relaxation times.

On the other hand, low field NMR machines were used for the estimation well properties. Due to the sensitivity and high resolution capability, high field NMR spectrometers resolve NMR peaks well. Therefore, high field NMR spectrometers provide more information about molecular dynamics in petroleum fluids [16, 17]. However, high field NMR provides huge proton peaks that result in radiation damping [18]). Radiation damping can be removed by using a small amount of sample and a high amount of deuterated solvent such CDCl3 or D2O [19].

The increase in 1/T1 or 1/T2 values of the solution per unit concentration of ion or protein added to a solution is called ion or protein relaxivity [20, 21]. Paraffinic CH2 and gamma CH3 peaks in the high field NMR spectrum of crude oil are the highest, easily obtainable and relatively well separated [17]. On the other hand, surface relaxivity is intensively investigated in oil exploration studies [1, 22-27]. Since Surface oil fluids contain CH2 and CH3 molecules, the determination of the relaxivity of these molecules may contribute to the studies in this field.

T1 and T2 measurements are based on inversion recovery (IR) and Carr-Purcell-Meiboom-Gill (GPMG) methods. These techniques require the use of pulse repetition time (TR) and a large number of inversion delay times (ti) or echo times (te). Therefore, IR and CPMG are time consuming methods. It is desirable that NMR petroleum fluid measurements are not time consuming. For this, it is quite convenient to calculate the 1/T2 relaxation rate from the half-height line widths (LW) of the NMR peak. This approach takes very little time and is frequently seen in the literature in relatively recent years [28-31]. T1 cannot be measured from the peak half-line width, but measurement of T1 is also useful for checking the negligible effect of magnetic field inhomogeneity and the accuracy of 1/T2 values. The 1/T2 in deuterated solvents is known to take contributions from spin-rotation relaxation as well as dipolar broadening [32]. Therefore, 1/T2 measurements are expected to give high values.

The aim of this study is to determine the NMR T1 and T2 relaxation times of paraffinic CH2 and gamma CH3 peaks of mixtures containing low amounts of petroleum and high amounts of CDCl3. For this reason, crude oil samples were taken from three wells in the Batman region of TURKEY. Three sets of mixtures containing varying amounts of petroleum fluid and CDCl3 were prepared. T1 was measured by the IR method, while T2 was determined from the half-height line widths of the NMR peaks.

2. Materials and methods

Petroleum fluid samples were taken from Şelmo1, Şelmo 2 and Didan wells in the Batman region. Three sets of 5 mixtures containing CDCl3 and crude oil were prepared. The total volume of each mixture was 1 mL. The crude oil content in each set was altered from 0.05 mL to 0.2 mL in a step of 0.05 mL. The prepared mixtures were transferred to 5 mm diameter quartz NMR tubes. The NMR spectrum was obtained with Bruker Avance NMR spectrometer at 400 MHz.
MHz. The sample temperature was kept at \((20 \pm 1) ^\circ C\) by means of an automatic temperature controller unit.

A special care has been taken to achieve the best shimming. Before starting a single-pulse experiment, the NMR tube was always fixed at the correct position on the probe head using the white Teflon plate. Tuning and matching were made properly. After very careful shimming using the standard mixture (3% CDC13 in acetone), a resolution of 0.26 Hz was achieved. This corresponds to the best shimming [Avance NMR Systems ZUEP0102, Manuel P/N Z31369, and DWG-No.1077007]. The shims were re-adjusted each time when a new sample was inserted into the probe. Measurements were made without sample spinning. The CH2 and CH3 peaks are shown in Figure 1 [17].

![Figure 1](image)

**Figure 1.** 400 MHz NMR spectrum of a mixture containing 0.05 mL oil and 0.95 mL CDCl3

T1 measurements were performed using the inversion recovery (IR) pulse sequence \([(180-\tau_d-90)-T_R]\). Inversion delays (\(\tau_d\)) were changed from 1 to 5000 ms. 18 delay times were used for each data collection. Pulse repetition time (T_R) was selected as 25 sec. T1 was converted to \(1/T_1\) for estimations. The experimental error for the \(1/T_1\) was \(\pm 0.03\) s\(^{-1}\). Line width (LW) is the distance between the points at which the line drawn parallel to the base at the half height of the peak intersects the spectrum. \(1/T_2\) values were determined from \(1/T_2 = \pi \cdot \Delta \nu_{1/2}\) where \(\Delta \nu_{1/2}\) is the half-height line width of the CH2 or CH3 peaks [33]. This distance was measured by cursor. LW measurement was performed after the spectrum was sufficiently expanded. For each sample, the LW measurements were repeated 20 times, and the mean values were taken as data. The error in determining each LW was estimated as \(\pm 0.058\) Hz.
3. Results

The $1/T_1$ and $1/T_2$ values determined for each well are shown in Table 1 and Table 2, respectively. As can be seen, both $1/T_1$ and $1/T_2$ values of each peak vary from well to well. The relaxation rates also increase with the fluid content. Furthermore, $1/T_2$ values are much larger than $1/T_1$. This corresponds to the very short $T_2$ times reported in previous studies [34, 35].

Table 1. Proton $1/T_1$ rates (1/s) for the CH$_2$ and CH$_3$ peaks of the mixtures prepared with the crude oil taken from three wells in Batman region.

<table>
<thead>
<tr>
<th>Concentration (mL)</th>
<th>Şelmo 1</th>
<th>Şelmo 2</th>
<th>Didan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_2$-$1/T_1$</td>
<td>CH$_3$-$1/T_1$</td>
<td>CH$_2$-$1/T_1$</td>
</tr>
<tr>
<td>0.05</td>
<td>0.821</td>
<td>0.413</td>
<td>0.606</td>
</tr>
<tr>
<td>0.10</td>
<td>0.855</td>
<td>0.438</td>
<td>0.813</td>
</tr>
<tr>
<td>0.15</td>
<td>0.925</td>
<td>0.476</td>
<td>0.941</td>
</tr>
<tr>
<td>0.20</td>
<td>1.043</td>
<td>0.573</td>
<td>1.123</td>
</tr>
</tbody>
</table>

Table 2. Proton $1/T_2$ rates (1/s) for the CH$_2$ and CH$_3$ peaks of the mixtures prepared with the crude oil taken from three wells in Batman region.

<table>
<thead>
<tr>
<th>Concentration (mL)</th>
<th>Şelmo 1</th>
<th>Şelmo 2</th>
<th>Didan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_2$-$1/T_2$</td>
<td>CH$_3$-$1/T_2$</td>
<td>CH$_2$-$1/T_2$</td>
</tr>
<tr>
<td>0.05</td>
<td>21.28</td>
<td>53.25</td>
<td>23.11</td>
</tr>
<tr>
<td>0.10</td>
<td>23.11</td>
<td>60.35</td>
<td>24.87</td>
</tr>
<tr>
<td>0.15</td>
<td>24.36</td>
<td>67.45</td>
<td>26.62</td>
</tr>
<tr>
<td>0.20</td>
<td>26.62</td>
<td>78.12</td>
<td>31.97</td>
</tr>
</tbody>
</table>

The least squares fits of $1/T_1$ versus fluid content are shown in Fig. 1, whereas those for $1/T_2$ are shown in Figure 3.
Figure 2. The least squares fits of $1/T_1$ values versus fluid content.

Figure 3. The least squares fits of $1/T_2$ values versus fluid content.
All fits have a very significant correlation. Correlation coefficients range from 0.90 to 0.99 for 1/T1 and from 0.91 to 0.98 for 1/T2. The relationships between the relaxation rates and fluid content are as follows:

- **SHELMO 1**
  - CH2 - 1/T1: \( y = 1.472x + 0.7270 \)
  - CH3 - 1/T1: \( y = 1.036x + 0.3455 \)
- **DIDAN**
  - CH2 - 1/T1: \( y = 1.584x + 0.7565 \)
  - CH3 - 1/T1: \( y = 0.722x + 0.4285 \)
- **SHELMO 1**
  - CH2 - 1/T2: \( y = 34.54x + 19.525 \)
  - CH3 - 1/T2: \( y = 60.26x + 21.325 \)
- **DIDAN**
  - CH2 - 1/T2: \( y = 34.54x + 19.525 \)
  - CH3 - 1/T2: \( y = 60.26x + 21.325 \)

The slopes of the fits correspond to the relaxivities of the peaks. The relaxivity unit is given in 1/(mL.s). The relaxivities are shown in Table 3.

**Table 3.** Proton relaxivities (R1 and R2) for the CH2 and CH3 peaks of the mixtures prepared with the crude oil taken from three wells in Batman region.

<table>
<thead>
<tr>
<th>Relaxivity</th>
<th>SHELMO 1 CH2</th>
<th>SHELMO 1 CH3</th>
<th>SHELMO 2 CH2</th>
<th>SHELMO 2 CH3</th>
<th>DIDAN CH2</th>
<th>DIDAN CH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1.472</td>
<td>1.036</td>
<td>3.358</td>
<td>0.722</td>
<td>1.584</td>
<td>0.260</td>
</tr>
<tr>
<td>R2</td>
<td>34.540</td>
<td>163.420</td>
<td>56.660</td>
<td>116.920</td>
<td>60.260</td>
<td>227.320</td>
</tr>
</tbody>
</table>

4. Discussion and conclusions

High field NMR machines provide high sensitivity and very good shimming that minimizes the contribution of magnetic field inhomogeneity to dipolar broadening. For these reasons, calculating 1/T2 from half-height line widths of NMR peaks became more popular in the 2000s [28-31,36]. The linear relationships with the high correlation coefficients in Fig.3 confirm that magnetic field inhomogeneity is minimized for the current NMR measurements. Otherwise, such linear relations cannot be obtained. Current T1 values measured by IR are consistent with previous results [3, 5]. This means that the current 1/T2 rates and R2 relaxivities are quite reliable. Otherwise, the linear relationship between 1/T1 and fluid content could not be obtained.

Let's look at the effect of magnetic field inhomogeneity more quantitively. The smallest 1/T2 in Table 2 for CH2 is 21.28 seconds, and this corresponds to 6.77 Hz line width [LW = (1/T2)/\( \pi \)]. High values of 1/T2 are quite consistent with previous studies [34, 35]. According to the literature regarding to surface relaxivity, the relaxivity was used to investigate structural, interfacial, and colloidal properties of heavy oils and oil sands [37]. The low-field relaxometry was also used to estimate the viscosity and API gravity of Brazil crude oil [24]. As can be seen in Table 3, the relaxivities vary from well to well. In addition, CH3 has greater R2 relaxivity than CH2. On the contrary, the R1 relaxivity of CH2 is greater than that of CH3. These differences should be related to the composition of fluids and viscosity [3, 25, 38]. The previous literature on the use of relaxivity shows that the relaxivity values obtained at 400 MHz will be useful in determining the fluid type.

The high 1/T2 values and high R2-relaxivity values found for CH2 and CH3 are the important findings reached in this study. Since the current study is the first study performed at high NMR frequency and in the laboratory, it was not possible to compare the measured 1/T1 and 1/T2
values with other studies. However, the explanations made in the first 2 paragraphs of the
discussion section show that the high $\frac{1}{T_2}$ and $R_2$-relaxivity values in question are not related
to the magnetic field inhomogeneity, but due to the additional contributions caused by different
relaxation mechanisms. These mechanisms should be chemical exchange between H and D,
spin rotation, and the indirect involvement of quadruple relaxation [32, 34, 39-41]. The use of
CDCl$_3$ as a solvent in experiments allows different relaxation mechanisms to be involved [32].
Therefore, the high $\frac{1}{T_2}$ and $R_2$ values obtained at the 400 MHz NMR frequency are in line
with our expectations. Such extremely high $\frac{1}{T_2}$ and $R_2$ values are very advantageous results
for high field NMR studies performed in the laboratory. In addition, the current results are very
important as they will easily separate petroleum fluids from other liquids found in oil fields.
This means that the current method can be used in high field NMR laboratories for the
identification of crude oil. However, the petroleum fluids used in this study were taken from
wells. Instead this, examining the oil taken from the first natural source where it was born and
found may yield more interesting results. In addition, direct high-field NMR examination of
crude oil without the use of CDCl$_3$ may yield different results, too.

Various methods have been used in the investigation of petroleum liquid by NMR [2, 4, 8-11,
42]. These methods can give different values depending on the source from which the petroleum
fluid is taken, the frequency and temperature at which it is examined. The existence of such
different results is not a contradiction, as each one serves a specific purpose. Therefore, the
current 400 MHz NMR results add more information to previous NMR studies on petroleum
fluids.

In conclusion, the $\frac{1}{T_2}$ rates and $R_2$ as well as the $\frac{1}{T_1}$ rates and $R_1$ relaxivities vary from well
to well. $\frac{1}{T_2}$ rates are greater than $\frac{1}{T_1}$ rates, and $R_2$ relaxities are significantly greater than $R_1$
relaxivities. In addition, the $R_2$ relaxivity of CH$_3$ is 2-5 times greater than that of CH$_2$. The data
show that the high $\frac{1}{T_2}$ and $R_2$ relaxivity are caused by several relaxation mechanisms. Data
suggest that 400 MHz NMR data can discriminate petroleum fluids from other fluids in oil
fields. Data also imply that high $R_2$ relaxivities may be obtained by low field NMR if CDCl$_3$
was used as solvent. These may open a new window for NMR logging.

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