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LOW-FIELD NMR METHOD FOR ANALYSIS OF HEAVY OILS

WITHOUT EXTRACTION OF ASPHALTENES

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ABSTRACT
For the analysis of heavy oil samples of the Ashalchinskoye deposit the combined nuclear magnetic resonance (NMR) method to measure the free-induction decay (FID) together with the Carr-Purcell-Meiboom-Gill (CPMG) echo signal’s decay was used. The measurements were carried out on a NMR analyzer Chromatek-Proton 20M, operating at a frequency of 20 MHz. Special control program was created on the NMR analyzer, which automatically tunes and measures full FID curve, then switches to measuring the echo amplitudes decay by the CPMG pulse sequence, and the study is completed by co-processing together all experimental data. This technique makes it possible to measure the amplitudes of the NMR signals and the relaxation times T₂ of the protons of heavy oil components in situ, including asphaltenes, without introducing any perturbations into the analyzed system. Under the influence of paramagnetic centers included to the composition of asphaltene, mainly vanadyl complexes on EPR data, the amplitude-relaxation characteristics of protons in the samples are divided into 6 groups related to solid asphaltenes (in crystalline and amorphous states), resins (high and low density), aromatic and saturated compounds. The amplitudes of NMR signals characterize the content of these fractions in the sample, and the relaxation times are determined by the mobility of molecules and the dynamics of their exchange between fractions. The proposed NMR method is promising for on-line monitoring the technological processes of heavy oil mining, transportation and processing under real conditions on temperature, pressure and the presence of dissolved gases, provided that the design of NMR sensor is adapted to industrial applications.

Keywords SARA, LF-NMR, Vanadyl, Relaxation, Process Monitoring.

INTRODUCTION
Usually, group composition of heavy oils is being investigated by means of the standard SARA (saturates-aromatics-resins-asphaltene) chromatographic test [1]. This method begins with asphaltene precipitation by solvents (pentane, hexane, etc.) followed by chromatographic analysis of maltenes. It is expensive and unsafe, requires a lot of time and considerable effort from qualified personnel. But the main problem is that the SARA method cannot be used to study raw crude oils in situ, since the analyzed sample is divided into fractions and information on the interaction of constituents in the original system is irreversibly lost. Nuclear magnetic resonance (NMR), one of the most outstanding non-invasive methods of analysis, was tested to determine the SARA...
composition of crude oils without extraction of components over 15 years ago [1,2]. The content of fractions in oil was judged by the NMR amplitudes of the signals of proton groups differing by the relaxation times $T_2$. It was shown that the entire range of relaxation times from tens microseconds to some seconds can be divided into intervals (or frames). For heavy oil and bitumen samples, for example, the frames can be analyzed as follows: “The shortest relaxation frame represents the asphaltenes, followed by the second shortest relaxation frame, which represents the resins, followed by the longer relaxation frame which represents the saturated compounds. The longest frame represents the aromatics” [1].

Authors of this study used equipment operating at a relatively low frequency of 1 MHz, which did not allow to measure short microsecond relaxation times corresponding to components with a high viscosity, such as asphaltenes. To increase the mobility of natural oil molecules and, thus, to shift the relaxation times to the measured range (to the slower side), the authors added an equal amount of solvent to the crude oil. Hexane, tetrahydrofuran, trichloroethylene, toluene, kerosene and n-pentadecane were used as the solvent. Comparison of the NMR results with conventional SARA results in the same crude oil samples had gave good agreement. However, the addition of any solvents seriously changes the state of the oil, for example, asphaltenes can precipitate and to change the oil structure and the relationship between the other components of this highly organized system. On the other side, this may be not affecting the result of their content determination by precipitation method. Probably, therefore LF-NMR was successfully used to study the precipitation of asphaltenes in several works [3-5]. Nevertheless, it is obvious that the NMR method with the addition of solvents cannot refer to the methods of analysis of oil “in situ”.

At higher proton resonance frequencies ($10 < f_0 < 40$ MHz) in the low magnetic field (LF) range, the asphaltene signal is clearly observed both in the solid state [6] and into the crude oil [7]. Combining an FID and CPMG pulse train provides information on solid and liquid phases in heterogeneous samples, as was done in the study of lipid-based food products [8]. In our studies, a similar technique was used for the group analysis of heavy oils without preliminary extraction of asphaltenes and other constituents. The purpose of this paper is to present the results, partially published in Russian [7, 9, 10], supplementing them with new data.

EXPERIMENT AND DISCUSSION

The objects of the study were heavy oils from the Ashalchinskoe deposit of Tatarstan (Russia). The average composition of these oils: light hydrocarbons - 57.5%, resins - 35.6%, asphaltenes - 6.8%. The initial content of asphaltenes in the samples was determined by precipitation with hexane according to a standard procedure. To obtain samples with a lower content of asphaltenes, the deasphalted oil (maltene) after evaporation of the solvent was added to the crude oil. Oil samples were placed into ampoules with a diameter of 4 mm (EPR) and 10 mm (NMR), and sealed with a special stopper. The spectrometer CMS-8400 (ADANI, Belarus) X-band (with a frequency of 9.4 GHz) was used to record the EPR spectra. EPR signals of vanadyl-porphyrin complex in asphaltenes and free radicals were detected in all prepared samples (Fig.1). Paramagnetic vanadium and stable radicals are localized in a core of associative combinations of petroleum systems, and this provides these centers with stability and protection against homolytic processes, and allows quantitative use for the rapid
determination of the genetic characteristics of oils [11]. As is known, these centers are localized in the asphaltene fraction, which was experimentally proved in fractional separation experiments with high-speed oil centrifugation [12].

Fig. 1. Spectrum of ESR (a) vanadyl-porphyrin VO\textsuperscript{2+}·P \( (S=1/2, I=7/2(\text{V}) \) and free radical R \((S = 1/2)\) in Ashchalinskoe crude oil; below, a hyperfine splitting structure with the direction of the magnetic field along \( (\parallel) \) and perpendicular to\( (\perp) \) the axis of the direction \( V = O \) is schematically shown; (b) - scan intervals for measuring the lines intensity of VO\textsuperscript{2+} and R; (c) the intensity I of the vanadyl line (VO\textsuperscript{2+}) on the content of asphaltene in the samples (%).

NMR measurements were performed on a Chromatek-Proton 20M [13] analyzer operating at a frequency of 20 MHz as described above. All wishes regarding the subtraction of the background signal, the maximum volume of samples, the correction of the magnet field inhomogeneity and the phasing of pulses, which was recommended in [8] to improve the accuracy of the analysis, were executed. Significantly, that the field correction was performed without the use of additional ampoule with water or triolein.

Fig. 2. Experimental decays of the transverse magnetization (FID and CPMG) of an oil sample containing 5.4\% of asphaltenes and the fitting results of these data based on Equations 1 and 2 after taking into account the inhomogeneity of the magnetic field. Noisy lines from the top characterize the quality of the approximation, fivefold enhanced difference between the measurement results and the fitting curves are presented [9].

The local inhomogeneity of the magnetic field in the probe head was estimated by the FID shape of liquid maltenes located in the own sample exactly in probed space where
it is necessary to consider the inhomogeneity of the field. This extends the FID approximation zone for fitting experimental data from 100 μs [8] to 2 ms or more, depending on the quality of the magnet [7, 9].

Relaxation decay of maltenes is considered simultaneously during of mathematical processing of FID by including the results of T₂ measurement by CPMG program. Additionally, to improve the signal-to-noise ratio when the CPMG program is switched on, the bandwidth of the NMR amplifier has been narrowed from 1.0 MHz to 100 kHz, since the width of the echo signal spectrum is an order of magnitude smaller than of the FID spectrum. All these measures significantly increased the accuracy of measuring the amplitudes of NMR signals, which made it possible to determine up to 6 components of the total relaxation curve if their relaxation times differ by at least three times (Fig. 2).

FID of solid asphaltenes both in the dry state [7] and in crude oil [8, 10] is described by the equation (1):

\[ I(t) = A_{S_c} \ast \exp((-t/T_{2S_c})^2) \sin(bt)/((bt)) + A_{S_{am}} \ast \exp((-t/T_{2S_{am}})), \]  

(1)

where \( A_{S_c} \) - the amplitude of the crystalline, \( A_{S_{am}} \) - of the amorphous part of the asphaltenes, \( T_{2S_c} \) and \( T_{2S_{am}} \) - the corresponding transverse relaxation times of the protons of these fractions. The sum \( (A_{S_c} + A_{S_{am}}) = A_{S_{(solid)}} \) is equal to the amount of solid asphaltenes (in %) determined by precipitation.

The CPMG echo’s decay is best described by the sum of four exponentials (eq. 2):

\[ A(t) = \sum_{k=a,b,c,d} A_k \exp(-t/T_{2k}), \]  

(2)

where \( A_k \): \( A_a, A_b, A_c \) и \( A_d \) – the amplitudes of the signals of saturated (a), aromatic (b) compounds, low (c) and high (d) density resins (HDR and LDR), and \( T_{2k} \): \( T_{2a}, T_{2b}, T_{2c} \) и \( T_{2d} \) – the proton relaxation times of these components. Equality of the amplitudes and relaxation times of the intermediate component d (HDR, Fig.2.FID), that can be determined simultaneously and independently on base the FID data \( (A_d, T_d) \) and CPMG \( (A_d, T_d) \) can serve as a criterion for the total fitting accuracy.

**Table.** Results of NMR analysis at 22°C the heavy oil of Ashalchinskoe deposit [9]. Here \( C_{asph} \) is the content of asphaltenes in the samples based on precipitation by hexane, the remaining designations refer to the NMR parameters and are given in the text. Samples No.1 and No.2 are crude oil from different wells, No.3 and No.4, 5, respectively, were obtained by diluting samples No.1 and No.2 with their own maltenes.

<table>
<thead>
<tr>
<th>№</th>
<th>( C_{asph} )</th>
<th>( A_S )</th>
<th>( T_{2S_c} )</th>
<th>( A_{S_{am}} )</th>
<th>( T_{2_{am}} )</th>
<th>( A_d )</th>
<th>( T_{2d} )</th>
<th>( A_c )</th>
<th>( T_{2c} )</th>
<th>( A_b )</th>
<th>( T_{2b} )</th>
<th>( A_a )</th>
<th>( T_{2a} )</th>
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<tbody>
<tr>
<td>1</td>
<td>7.7</td>
<td>7.2</td>
<td>20</td>
<td>3.6</td>
<td>49.7</td>
<td>14.2</td>
<td>0.37</td>
<td>27.7</td>
<td>1.7</td>
<td>32.1</td>
<td>5.2</td>
<td>19.2</td>
<td>12.3</td>
</tr>
<tr>
<td>2</td>
<td>5.8</td>
<td>6.0</td>
<td>19</td>
<td>3.0</td>
<td>49.6</td>
<td>11.4</td>
<td>0.41</td>
<td>24.7</td>
<td>2.1</td>
<td>30.5</td>
<td>7.3</td>
<td>26.8</td>
<td>20.3</td>
</tr>
<tr>
<td>3</td>
<td>3.8</td>
<td>3.7</td>
<td>17</td>
<td>2.0</td>
<td>58.2</td>
<td>11.5</td>
<td>0.62</td>
<td>20.9</td>
<td>2.7</td>
<td>32.5</td>
<td>9.8</td>
<td>31.3</td>
<td>30.2</td>
</tr>
<tr>
<td>4</td>
<td>2.7</td>
<td>2.4</td>
<td>18</td>
<td>1.2</td>
<td>50.1</td>
<td>13.3</td>
<td>0.85</td>
<td>25.2</td>
<td>4.2</td>
<td>33.4</td>
<td>15.4</td>
<td>25.1</td>
<td>44.4</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>0.7</td>
<td>16</td>
<td>0.1</td>
<td>44.6</td>
<td>13.6</td>
<td>1.74</td>
<td>25.1</td>
<td>8</td>
<td>33.2</td>
<td>29.8</td>
<td>25.5</td>
<td>81.7</td>
</tr>
</tbody>
</table>
It was established (Table) that the total amplitude of the solid phase component of $A_S$ increases in proportion to the content of asphaltenes in samples with a high correlation coefficient ($r^2 = 0.98$, Fig.3a), what have the direct practical importance, for example, for rapid measurement of asphaltene contents. Moreover, the complex shape of this signal (eq.1) and the differences in the measured relaxation times allows us to bind the Gaussian part of the FID to a rigid, near-crystalline part of the asphaltenes, that apparently composing the asphaltene core, and the Exponential component of eq.1 - to a less dense amorphous and porous part of asphaltene, which surrounds a harder core. This assumption agrees with the well-known notions of the structure of asphaltene nanoaggregates and clusters [4, 5].

![Fig. 3. a) Correlation between the amplitude of the solid-phase component and the amount of asphaltenes; b) Dependences of the proton spin-spin relaxation rates of oil fractions on the content of asphaltenes.](image)

Note that the relaxation times of the protons of crystalline and amorphous asphaltene are short and remain practically unchanged in samples with different asphaltene contents (Table). This is due to the rigid lattice of solid asphaltenes and the rapid averaging of the nuclear magnetization of the protons due to direct spin-spin interaction. In the amorphous part of the asphaltene aggregates, the lattice is less ordered and, in addition, mobile resin molecules penetrate it, so that $T_{2_{sam}}$ is noticeably larger than $T_{2_{sc}}$ of the crystalline core protons (~ 2.5 times), but also low changed. On the contrary, the proton relaxation times of HD and LD resins, aromatic and saturated compounds decrease rapidly in inverse proportion to the content of asphaltenes in the samples, so that the corresponding relaxation rates ($1/T_2$) increase almost linearly with increasing amounts of asphaltenes (Fig.3b). The relaxation rate increases most strongly in heavy resins, in the lowest degree - in saturated compounds. The authors of [4] have also established that the different maltene components are affected differently by the presence of asphaltenes. The increase in the relaxation rate is larger for the longer and less mobile hydrocarbon chains, which relax faster than the short chains. It follows, that in the process of thermal motion, the “lifetime” of resin molecules near the surface of asphaltenes is greater than that of aromatic and, of course, saturated compounds.

On the data like those given in Table, a NMR-SARA histogram is constructed in the coordinates $\lg T_2$-$A_i$, which clearly represent the group composition of the oil studied with the characteristic of the fractions relaxation times $T_2$ [9].

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The greatest interest for oil engineers is the question of how external conditions (temperature, pressure, presence of gases) affect the dynamic equilibrium in crude oil and, if possible, in live oil. On Fig.4 are shown the experimental results of the temperature effect on the ratio of fractions in heavy oil under heating and cooling in sealed ampoules in situ. Before the measurements, the samples were kept in a thermostat at a specified temperature for at least two hours. When the ampoules are placed in thermostats at 30°C, 40°C, 50°C and 60°C, the amplitude of $A_S$ reflecting the content of all asphaltene decreases, the amplitude of benzene resins $A_c$ increases, while the alcohol benzene resins $A_d$, aromatic $A_b$ and saturated $A_a$ components practically do not change. When the samples are cooled to 12°C, 10°C, 4°C and $-15°C$, on the contrary, the amplitude of $A_S$ increases, as can be seen, due to the decrease in the components of $A_c$ and $A_d$ resins, and the content of light fractions $A_a$ and $A_b$ practically does not change. Thus, the question of what is the source of the building material during the asphaltene aggregation is unequivocally solved.

Fig.4. The temperature dependences of SARA fractions of heavy oil upon cooling from room temperature to $-15°C$ and heating to $+60°C$ in situ: a) the NMR-SARA components amplitude [11]; b) the relaxation rate $1/T_2$ of protons [unpublished data].

These data directly confirm the known assumptions about the participation of resins in the formation of asphaltene structures and essentially refine them qualitatively and quantitatively. It is possible that the paramagnetic properties of asphaltenes not only serve as paramagnetic doping for NMR probing of samples, but participate in the organization and management of subtle interaction of components in such a complex system as living oil. Unger's school proposed the concept of the spin nature of Oil Dispersed Systems (ODS) and a model was created [11, p.26] that better describes many experimental data. Apparently, the paramagnetism of asphaltene plays a fundamentally important role in the organization and fine-tuning of interactions in complex oil dispersed systems.

CONCLUSION

In the oil industry, reliable methods of non-invasive observation of transformations occurring in natural oil are always necessary, without disturbing the very fine balance between many solid, liquid and gaseous components. In the studies presented, it was
shown that the measurement of the NMR relaxation spectrum of petroleum protons in the range from microseconds to seconds allows quantifying the substances making up the SARA composition of heavy oil, including asphaltenes, in situ. Measurements of many samples can be carried out over a wide temperature range for a short time.

For comparison, the determination only of asphaltenes at temperatures of 25°C, 40°C, 50°C, and 60°C was carried out by gravimetric method [14], H-heptane was used as the precipitant. To obtain the result, it was necessary to create conditions for maintaining the temperature for a long time in the laboratory, where more than one and a half dozen operations are carried out. They include precise dosing and weighing of reagents, very long continuous mixing for complete extraction, centrifugation, washing for complete discoloration of the solvent, etc., that eventually takes more than a one day to measure at each temperature.

The NMR method is free from most of the above difficulties, the preparation of samples is reduced to the sampling of ampoules without the need for accurate weighing, the content of the components is determined with respect to the total amplitude of the signal, which is the sum of the amplitudes of all the protons in the sample volume.

Based on the results obtained, it is asserted that the NMR data more accurately reflect the true composition and nature of the interaction of components in the analyzed samples than the standard methods of chemical analysis, since the using of solvents completely violates the physics-chemical and information structure of the original oil.

The combined FID+CPMG LF-NMR method is promising for on-line application to control the technological processes of oil production, transportation and processing under real conditions of temperature, pressure and the presence of dissolved gases, if the sample in an unchanged state can be supplied to the probehead of the NMR analyzer or the NMR sensor is mounted on the process pipeline.

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REFERENCES


[7] Sakharov B.V., Khasanova N.M., Volkov V.Ya., Joint measurement and combined processing of FID and echo signals in the CPMG series for the evaluation of the component composition of heavy oils [Sovmestnoye izmereniye i kombinirovannaya obrabotka signalov SI i ekha v serii KPMG dlya otsenki komponentnogo sostava tyazholykh neftei], «Novyee dostizheniya YAMR v strukturnykh issledovaniyah». Sbornik tezisov VI Vserossiyskoy konferentsii, Kazan, 6-9 April 2015, Russia, pp. 67-68, 2015.


