Phase state of an organic matter for NMR relaxation in low fields of rocks of the Bazhenov suite (Western Siberia)

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Abstract. The work of many researchers is devoted to studying the problem of the features of the formation of the Bazhenov suite and organic matter. Various methods are used to study the type and state of organic matter, despite this, the problem associated with the phase state and type of organic matter in these deposits, the methods for studying those remains relevant. One of these methods is the NMR relaxation method in low fields. For the analysis of heavy oils, the method of simultaneous measurement of the free induction decay (FID) together with the decay of the echo signal in the Carr-Purcell-Meiboom-Gill (CPMG) pulse program was used. We studied the decay form of relaxation curves and their approximation by a mathematical model adequate for solid, liquid, and gaseous states of matter, which contains information on the geochemical and petrophysical properties of organic matter, as part of a single reservoir, including both the mineral part and the fluid part.

1. Introduction

The problem of studying unconventional hydrocarbon reservoirs is urgent (the Domanik rocks of the Republic of Tatarstan, the Bazhenov suite of Western Siberia, the formation of which took place during the Volga and early Berrian centuries in the deep-sea epicontinental West Siberian Sea). A complex characteristic of hydrogen-containing components in shale and other rocks of unconventional objects is associated with the properties of kerogen itself: to simultaneously be a hydrocarbon sorbent, a hydrocarbon keeper and a new hydrocarbon generator. Thus, first in laboratory studies, the creation of new analytical methods for studying these states of hydrocarbons, methods for their interpretation and their application in the development, extraction and processing of hydrocarbons is required. Laboratory studies of the kerogen substance are widely developed: pyrolysis of kerogen of the Bazhenov shale: kinetics and influence of inherent pyrite [1]; laboratory investigations of hydrous pyrolysis as ternary enhanced oil recovery method for the Bazhenov formation [2]; organic structural properties of kerogen as predictors of source rock type and hydrocarbon potential [3]. Research directly in the breed is important, such as, temperature dynamics of organic matter of the Bazhenov suite from electron paramagnetic resonance [4]. Laboratory studies of the behavior of organic matter of the Bazhenov deposits during thermal effects [5].
Along with traditional methods, an exponential increase in the work is observed using the NMR relaxation method in low fields (NMR LF) for the petrophysical analysis of shale rock of wells based on the construction of two-dimensional T1-T2 maps and the Rock-Eval geochemical method [6, 7]. New approximations in the construction of T1-T2 maps were achieved by improving the hardware characteristics for evaluating the solid-phase components of organic matter (kerogen, asphaltenes, OH groups in clay minerals). The Rock-Eval (Basic/Bulk-Rock) methodology adapted to the properties of shale rocks was also improved. Thus, to some extent, it was possible to combine the petrophysical and geochemical characteristics of organic matter in shales [6, 7]. Oil and its products are heterogeneous systems; therefore, all sorts of additional adjustments will always be needed along with the direct self-consistent FID + CPMG method proposed for the numerical analysis of the components of heavy oil and bitumen [8].

The aim of our work is to obtain a quantitative characteristic of the phase state of organic matter in the rocks of the Bazhenov suite (BS later) using the new method of self-consistent FID + CPMG NMR LF relaxation [8]. The initial amplitude of the NMR signal is directly proportional to the number of protons, and it can be correlated with the volume or mass of the substance in the measurement region, which makes the NMR method a direct method for determining porosity [9].

The relaxation times and proton amplitudes of the components of all groups of organic molecules are determined from the attenuation rate of the amplitudes in different parts of the relaxation curve, which makes the NMR method a direct analytical method for determining the geochemistry of organic matter in the analyzed samples [10]. We have not identified such an approach to the analysis of the properties of the organic matter of rocks of the Bazhenov suite in the published literature on the study of oil-bearing rocks in both conventional and shale deposits. The creation of reliable methods for the non-invasive study of shale rocks as whole, organic and mineral parts of matter, as well as liquids in the pore space is in demand, both from experimental and theoretical points of view.

2. The object of study and its characteristics

The object of study of the Bazhenov suite [4, 5] (Fig. 1). In the section of the Bazhenov suite, the “normal” type of rock was represented in our study by typical samples №9, №1. To study organic matter, different parts of the samples were preliminarily selected according to their macro characteristics and color: the dark area (further “AN-black”) and the light area (further “AN-white”). Samples of the overlying the Achimov suite of quartz-feldspar sandstones are represented by samples №3 and №4.

Figure 1. Structural and textural features of the studied rocks: a) “normal” section of the Bazhenov suite; b) “anomalous” section; c) rocks of the Achimov suite.

The rocks of the “normal” section are composed of black, dense mudstones, the “anomalous” section is represented by interbedded sandstones with mudstone. The material composition of the rocks of the Bazhenov suite differs from the rocks of the “anomalous” type and the Achimov deposits [4, 5].
Particular attention was paid to the study of the distribution of organic matter in the rocks of the Bazhenov deposits. The heterogeneity of the distribution and forms of organic matter is characteristic: from scattered, disseminated forms to contents in the form of large clusters, lenticular secretions with the remains of detritus fragments. According to the results of SEM studies, it was found that the rocks of the Bazhenov formation have microporosity. Pores in different parts of the rock differ in size and shape. In samples of deeper depth intervals, felt forms of illite are developed that perform a void space, but the pores remain permeable. In large pores - grains of secondary quartz. In association with clay minerals, pyramid phramboids (of various shapes and sizes) are present in the void space, and they are finely dispersed throughout the rock volume [4, 5].

NMR LF measurements were made on a Proton 20M NMR analyzer, manufactured by CJSC SKB chromatec, Russia (http://www.chromatec.ru). The resonance frequency for protons is 20 MHz. Rock samples were crushed and then were placed in ampules with a diameter of 10 mm. Dead time is no more than 10 microseconds. The duration of the 90°th pulse was 2.4 μs, the 180°th pulse was 4.7 μs [8]. The results were processed using a specially designed multi stage fitting program based on the Solver Excel software package. This makes it possible to observe all the components of heavy oil from light fractions to resins and asphaltenes without resorting to heating.

When calibrating the NMR signal per mg of water, the magnitude of the total amplitude of the FID signal determines the relative proton content or proton index RHI, mgN/g in organic matter [11] and characterizes the amount of hydrogen in organic matter relative to the content of protons of H2O water molecules with mass mw: RHI = (A0(w)/m_w)*(m_w/A0(w)), where A0(w) is the amplitude of the rock signal, whose mass is m_b, is compared with the amplitude A0(w) of the water signal and mass m_w [12]. The signal is proportional to hydrogen density, an indicator of porosity and a kind of bridge combining the geochemical and petrophysical properties of shale rock. Since the survey and the mathematical model are consistent with the phase state of asphaltene, paraffin, OH, interpackage water in clay minerals, the proposed method becomes an effective tool regardless of the heterogeneous state of organic matter and water molecules.

3. Experimental part

The experimental curves of the relaxation attenuation of the NMR amplitudes of the FID of protons are presented on the same graph in the samples of “normal” (Fig. 2a) and “anomalous” sections of rocks of the Bazhenov suite are shown in figures (Fig. 2b). The shape of the signals in the range from the beginning to 50 mks clearly shows a change in the number of solid-phase - rapidly decaying parts and liquid-phase parts in the relaxation attenuation of the signals. The decay form of relaxation of protons of organic matter in the “normal” type of rocks of the Bazhenov suite of samples №1 and №9, №AH-black is almost identical. This suggests the syngenetic properties of organic matter.

In samples of the “anomalous” type, a similarity of organic matter is observed in the Achimov deposit (samples №3, №4), which, apparently, is accompanied by the identity of the mineral composition of the rock. The decay form of the “anomalous” part of the AH-white rock differs in the solid-phase and liquid-phase parts of relaxation. Thus, it can be assumed, that the decline in the FID is an integral part of testing shale rock (organic matter) and already at this stage of the analysis is its “signature”.

The approximation of the experimental relaxation curves of the FID is presented in the table 1. The results of the FID relaxation curves analysis (Fig. 2) of solid and liquid phases of organic matter of the Bazhenov suite and the Achimov suite nature and after oil extraction were fitting in table 1.
a) “normal” section of the Bazhenov suite

b) “anomalous” section of the Bazhenov suite and the Achimov suite

**Figure 2.** The amplitudes of the echo signals (mgH/g), as well as the FID points, and the function of the FID fitting OM: a) “normal” section of the Bazhenov suite; b) “anomalous” section of the Bazhenov suite and the Achimov suite. Inset is the solid-phase part of the signal up to 200μs.

By analogy with the NMR of asphaltenes [1] Aos, the intensity of the rapidly decaying solid-phase component with Gaussian $T_{2sc}$ and exponential $T_{2sam}$ relaxation times is indicated. The exponential component is characterized by the $f_{am}$ coefficient of the amorphous fraction different from the Gaussian “crystalline”, rigidly organized structure. The number of molecules of two liquid-phase components, indicated by Aol and Aolexp, differ in the length of relaxation time - long $T_{2l}$ (ms) and average $T_{2exp}$ (μs).

As a pilot experiment, cold extraction with HC chloroform was performed and the change in the phase state of organic matter in the rock was evaluated (Table 1). The control was carried out by the color of
the extract. In the phase state, organic matter is marked by a decrease in the hydrogen index RHI and Aos - the percentage of solid phase in the light and black parts of the samples of the “anomalous” section. The preservation of a high fraction of the solid-phase component indicates a high portion of the insoluble part of organic matter in the samples. The second change concerns the components of the liquid phase and has a diverse nature. Our results confirm the view that kerogen and asphaltenes contain similar compositional macromolecular structures.

The research results indicate that the deposits of the Bazhenov formation not only contain a large number of ready and hard to recover hydrocarbons, but also have additional generation potential. Hydrocarbons mining is carried out only from the “anomalous” section of the Bazhenov suite due to clinoform complexes of the Achimov formation. The cost-effective extraction of hydrocarbons from a “normal” section requires a more detailed study of the state of organic matter for the application of new technologies for the development and production of hydrocarbons.

Table 1. The results of the FID relaxation curves analysis (Fig. 2) of solid and liquid phases of organic matter of rocks of the Bazhenov suite and the Achimov suite - nature and after oil extraction

| samples        | Solid Phases | Liquid Phases - malties | RHI   | AOS | AOL | FID index mgH/g |
|----------------|--------------|-------------------------|-------|-----|-----|-----------------|
|                | Aos, %       | T2_mks, mks f_mks, mks | T2_mks, mks | Aolexp%, | T2_mks, mks | Aol, % | T2_mks, mks | |
| "normal" section BS |               |                         |       |     |     |                 |
| #AN-black      | 98.33        | 16.45                   | 0.23  | 24.76 | 1.55 | 117.32          | 0.12 | 20000       | 24.49 | 24.08 | 0.41 | 4.87 |
| #9             | 92.52        | 19.57                   | 0.36  | 16.53 | 7.28 | 80.20           | 0.20 | 112765      | 19.10 | 17.67 | 1.43 | 13.44 |
| #1             | 95.06        | 19.57                   | 0.21  | 27.51 | 4.66 | 100.89          | 0.28 | 70000       | 17.42 | 16.56 | 0.86 | 6.28 |
| AN-white       | 81.05        | 29.05                   | 0.83  | 22.58 | 17.76 | 112.45          | 1.19 | 9601        | 2.30  | 1.87  | 0.44 | 1.54 |
| #4             | 87.11        | 17.49                   | 0.25  | 27.73 | 8.33 | 148.48          | 4.56 | 10664       | 2.29  | 2.00  | 0.30 |
| #3             | 93.21        | 17.29                   | 0.20  | 31.65 | 4.59 | 198.85          | 2.20 | 1244        | 5.37  | 5.01  | 0.36 |
| after extraction “normal” section of the Bazhenov suite | | | | | | | | | | | | |
| #AN-black_ex   | 98.29        | 16.69                   | 0.22  | 24.98 | 1.56 | 162.01          | 0.15 | 27770       | 19.62 | 19.29 | 0.34 |
| #9_ex1         | 95.30        | 19.21                   | 0.18  | 29.74 | 2.44 | 134.54          | 2.26 | 55000       | 14.95 | 14.24 | 0.70 |
| #9_ex2         | 95.28        | 19.59                   | 0.13  | 52.68 | 0.93 | 148.37          | 3.79 | 11482       | 5.94  | 5.66  | 0.28 |
| #1_ex          | 90.65        | 17.82                   | 0.15  | 35.37 | 4.61 | 395.66          | 4.75 | 90000       | 11.14 | 10.10 | 1.04 |
| after extraction “anomalous” section BS | | | | | | | | | | | | |
| AN-white_ex    | 68.65        | 29.92                   | 0.16  | 52.38 | 28.10 | 88.56           | 3.25 | 8500        | 0.77  | 0.53  | 0.24 |

4. Discussion and conclusions

1. Samples of the Achimov deposits: fine-grained quartz-feldspar sandstones contain about 2.3% of organic matter. In the composition of the organic matter 78% falls on the solid phase, which is associated with both the organic matter itself and clay cement in the void space. During the extraction of samples, with a decrease in the fraction of the solid phase to 50%, the relaxation time of the crystalline part is retained, while the fraction of the amorphous part decreases from 0.87 to 0.34 with an increase in its mobility from 24 to 40 μs. The hydrocarbons are being dissolved in the composition of the organic matter and in the clay cement of the Achimov suite (an easily extractable part of the organic matter).
2. Samples of the Bazhenov suite: 24.4% organic matter in its composition, of which 96% are of the solid phase, and the proportion of the amorphous part is 0.26. The liquid phase is a very small fraction, only about 4%, consists of sedentary kerogen molecules (during extraction, the temporary components of the solid phase practically do not change).

3. The use of the self-consistent FID + CPMG method of NMR LF relaxation allows one to analyze the phase state and obtain quantitative characteristics of organic matter in the rocks of the Bazhenov formation.

Acknowledgements

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

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