Solid-like Component in the Spin-Spin NMR-Relaxation of Heavy Oils

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The study of row heavy oil samples from Tatarstan and Vietnam oil wells was done by solid-echo nuclear magnetic resonance (NMR) technique on the hydrogen nuclei. For the first time in the oil study, the component with short spin-spin relaxation time (T_{2s} = 9.8÷31.2 μs) and free induction decay (FID) shape similar to a solid one was detected for all oil samples. Density ρ, "zero" viscosity η_0, asphaltene content and solid part P_S of ^{1}H NMR signal were measured for whole row oil samples. The correlation between the part P_S of ^{1}H NMR signal and oil density ρ was found for samples of Tatarstan oil, by the other hand, data for samples of Vietnam oil did not show the correlation. No correlation dependences of the part P_S of ^{1}H NMR signal and "zero" viscosity η_0 from asphaltene amount for whole row of oil samples were confirmed, that indicates other crystalline supramolecular structures (more probably, crystalline paraffin) existence in the oil. As a main result, the correlation between oil viscosity and the amount of the solid-like structures in it was found. The significant differences of the solid-echo signal shapes and spin-spin relaxation times of the solid-like structures were obtained for the different oil samples, that demands additional studies.

PACS: 76.60; 82.56

Keywords: Nuclear magnetic resonance, solid-echo, heavy oils, asphaltenes

1. Introduction

Recently due to the depletion of light oils reserve the attention to the exploring of heavy hydrocarbon raw materials such as heavy oil and bitumen begins to be rising. However, the volume of their use still remains so low all over the world. There are few reasons for this: rather high costs for the production and transportation, imperfections of hardware and technological difficulties. All these problems are caused mainly by the high viscosity of heavy hydrocarbon raw materials. It's considered to be the case, that content of high-molecular asphaltenes [1] and paraffin change the oil viscosity significantly. At the same time, molecules of asphaltenes have the ability to be aggregated with each other to form supramolecular structures [2] with characteristics similar to that of crystalline state. Also it is well known, that paraffin molecules are able to form steady supramolecular crystalline structures in the oil.

Since ^{1}H NMR signals in solids and liquids are quite different (FID shape, spin-spin relaxation times T_2) it is possible for the complex system to determine part P_S of ^{1}H NMR signal related to oil solids.

It is reasonable to assume, that correlation between content of solid fraction in the oil and oil viscosity should exist. The purpose of the present work is the verifying of this assumption.

2. Samples and experimental methods

The investigations of density ρ, "zero" viscosity η_0, content of asphaltenes and solid part content P_S of ^{1}H NMR signal were performed for row heavy oil samples from Tatarstan and Vietnam. The oil viscosity was measured by capillary viscosimeter at temperatures below 303 K. The value of "zero" viscosity η_0 was determined as the extrapolated value dynamic viscosity at the zero value of displacement velocity. The content of asphaltenes in the oil was determined by use asphaltenes precipitation from oil solution in heptane. In the last case thirty parts of heptane correspond to one part of oil.

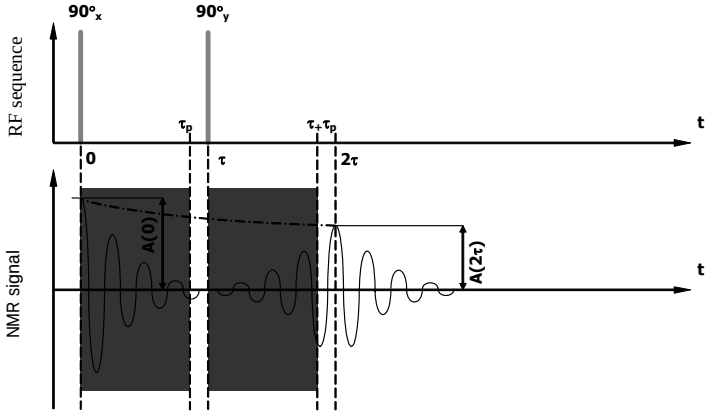

Fig.1. Two-pulse sequence solid-echo

The solid part P_S of ^{1}H NMR signal in the oil was measured by pulse NMR-relaxometer with resonance frequency 19.08 MHz and dead time τ_p = 13μs for the receiving channel. It was found that for all studied oil samples the component with short relaxation time ("short component") exists with the FID shape similar for that of solid. The relaxation time of the short component is about 10 μs and could not be registered by classical liquid-state NMR approaches and by logging. In order to study this component and to determine P_S for different oils we used solid-echo two-pulse sequence [3] (see Fig.1.).

3. Results

In the Table 1 T_2 values and the solid part content P_S are shown for Tatarstan and Vietnamese oils. As one can see from the table, solid component was found in all oils. Relaxation times vary in the range from 9.8 to 31.2 μs. This is a sufficient difference that could mean the different origin of the solid component in the different oils.

Table 1. *Density ρ, "zero" viscosity η_0 , relative solid part content P_S and corresponding transverse relaxation times of the investigated oil samples*

№ well	*ρ, kg/m^3 (T=293 K)*	*η_0, Pa·s (T=303K)*	*P_S, %*	*T_{2s}, μs*
Well 3509 (Tatarstan oil)	904.9	0.105	0.6±0.4	23.9±3
Well 3205 (Tatarstan oil)	923.11	0.108	0.95±0.3	30.2±4
Well 435 (Tatarstan oil)	931.71	0.103	1.4±0.5	13.6±2
Well 3196 (Tatarstan oil)	921.89	0.135	1.65±0.3	12.1±2
Well 3473 (Tatarstan oil)	926.03	0.359	1.9±0.3	17.1±3
Well 3195 (Tatarstan oil)	919.87	0.149	2.1±0.2	25.9±4
Well 4612 (Tatarstan oil)	937.59	0.278	2.4±0.5	13.2±3
Well 3609 (Tatarstan oil)	928.42	0.188	3.4±0.3	31.2±5
Well 4290 (Tatarstan oil)	939.55	0.343	3.9±0.5	14.6±4
Well 69 (Tatarstan oil)	966.44	1.39	5.3±0.5	19.8±4
"White tiger", well 136 (Vietnamese oil)	898.64	>3	6.6±0.8	12.1±3
"Safonov oil" (Vietnamese oil)	923.8	>>10	45.9±5	9.8±2

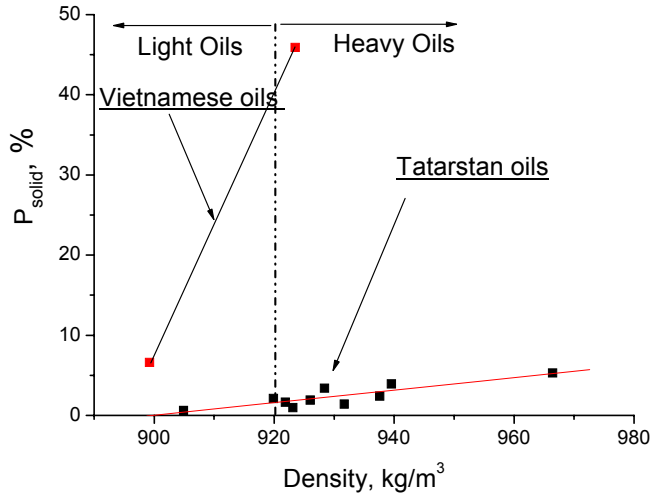

Fig. 2. Correlation between density ρ and P_S

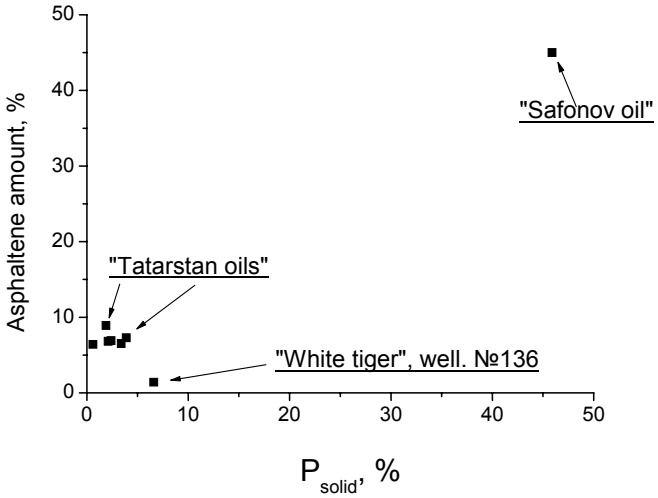

Fig.3. Correlation between asphaltene amount and P_S

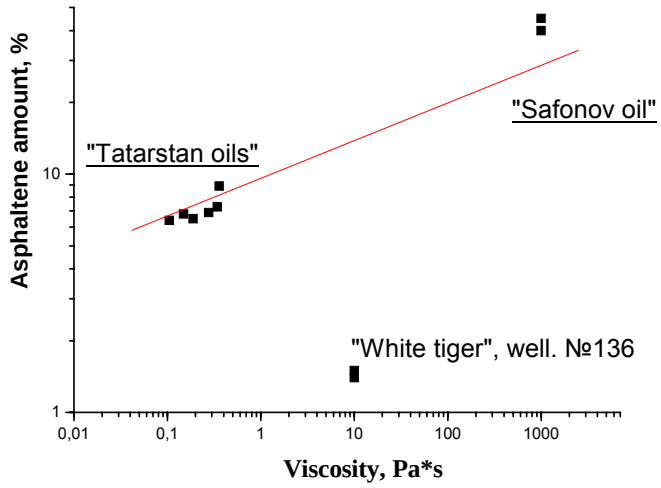

Fig.4. Correlation between asphaltene amount and viscosity

The part P_S of ^{1}H NMR signal characterizes the amount of crystalline formations in the oil, which mainly contains hydrocarbon compounds. But it is well known, that most of crystals have more compact packing of molecules in compare with liquid, and as a sequence, more high density. Then it is reasonable to assume that correlation between the part P_S of ^{1}H NMR signal and oil density ρ should exist. The data on the Fig.2 confirms such correlation for all samples of Tatarstan heavy oil.

One could also assume the existence of correlation between P_s and both viscosity and the amount of asphaltenes (the fraction with the highest density) in the oil. It follows from Figure 3 that there is no correlation between asphaltene content and P_S. (We should note here that asphaltene amount was determined as heptane- unsoluble fraction for all samples). Figure 4 shows also the absence of any correlation between asphaltene amount and viscosity. Hence, we can assert, that asphaltenes are not single molecules, and they are able to form crystalline supramolecular structures. Although, the presence of the later in the oil has an essential impact on the oil viscosity, other solid-state formations have also a strong influence on the oil viscosity. In particular, oils with a high content of paraffin possess a high viscosity under room temperature. As example, Vietnamese oil (well 136), which containing a large amount of crystalline paraffin (up to 6-7%) can be mentioned here. For this oil, the part P_S of ^{1}H NMR signal occurs mainly due to crystalline paraffin but not asphaltenes. It was confirmed by NMR investigations of deasphaltened oils.

At the same time it was found that part P_S correlates quite strong with “zero” viscosity of oil (Fig. 5). This correlation enables to conclude that viscosity of heavy oil, which represents a colloidal system, is mainly determined by the content of solid-state formations independently on their nature – asphaltenes or paraffins.

4. Summary

Thus, we have found the correlation between oil viscosity and the amount of the solid-like structures in it. At the same time, the absence of the correlation between P_s and asphaltene amount leads to the assumption that solid component of NMR signals is determined by the presence of other solid components, more likely paraffin.

The shapes of solid echo signal and spin-spin relaxation times were different for different oils, but we are not ready yet to discuss these differences now because of very complicated shape of NMR signal as well as the smallness of these differences. The additional studies are necessary to clarify the reasons for these differences. Nevertheless we can conclude now that even a small amount of solid component in the oil leads to valuable changes in the viscosity.

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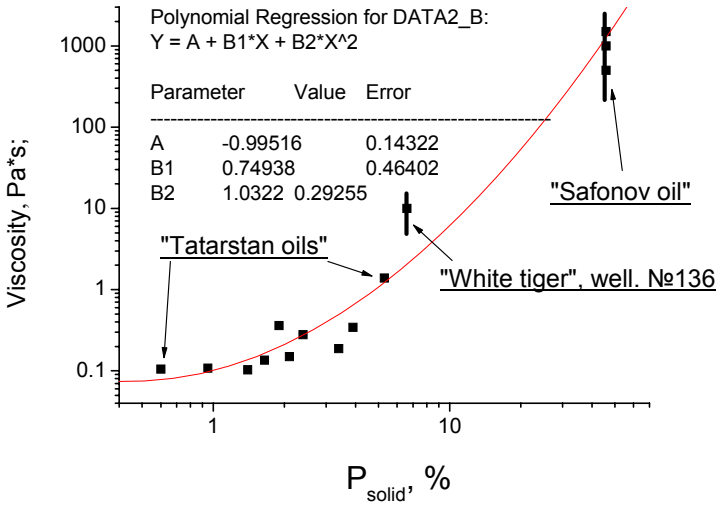

Fig.5. Correlation between the "zero" viscosity η_0 and solid part content P_S for different oils

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