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Qualitative and quantitative analysis of oil samples extracted from some Bashkortostan and Tatarstan oilfields based on NMR spectroscopy data

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ABSTRACT

Measurements of crude oil samples by nuclear magnetic resonance spectroscopy were carried out. The quantitative fractions of aromatic molecules and functional groups constituting oil hydrocarbons in several samples were determined and their slight variation from sample to sample was shown. Information on content of general functional groups (tertiary and primary carbon atoms, aromatic cores) and possible presence of olefins or water impurity can be obtained. Basic ^{1}H measurements are rather fast and require several minutes. Experiments on modern high-field spectrometers provide better resolution of overlapping regions in ^{13}C NMR spectra and thus would be more convenient to get detailed information on the amount of different alkyl substituents. Slight but obvious differences were observed between the spectra of the samples taken from different levels of the same oil well.

1. Introduction

Knowledge of the chemical composition and physicochemical properties of crude oils, along with features of the geological and geochemical conditions, is of primary importance for solving problems of the origin of crude oils and for petroleum refining, since it enables variations in the commercial and technical characteristics of crude oils to be predicted and the expediency of combining crude oils from different fields during refining to be assessed (Kvalheim et al., 1985).

Petroleum as a natural object contains hundreds of substances mainly belonging to the three homologous series of hydrocarbons (alkanes, cycloalkanes, and aromatic hydrocarbons), as well as heteroatomic compounds (particularly, asphaltene-resinous substances) containing non-metals (sulfur, oxygen, nitrogen) and trace elements (V, Ni, Fe, Zn, etc.) (Speight, 2014; Pokonova et al., 1984; Van Ness and Van Westen, 1951). Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties and ultimately its behavior during refining. Structural recognition of the oil constituents is the prerequisite of different techniques used for heavy oil upgrading. In contrast to other physical-chemical methods (De Peinder et al., 2008; Satya et al., 2007; Jehlička et al., 2003; Sjoblom et al., 1998), nuclear magnetic resonance (NMR) spectroscopy allows obtaining both qualitative (type of molecules) and quantitative (content of compounds) information on a mixture of organic compounds. The history of ^{1}H and ^{13}C NMR spectroscopy shows that application of these techniques for compositional characterization of petroleum fractions was a breakthrough and was considered a novel development in this area (McLean and Kilpatrick, 1997; Trejo et al., 2004).

There are many methods for investigation of oil composition including gas chromatography and quantitative fluorescence techniques (Xixian et al., 2000; Fuhua et al., 2001a, 2001b; Xiexian et al., 2003; Xingli et al., 2007). Although these methods can resolve some problems, they can only qualitatively describe the fluorescence characteristics based on the variable chromatography curves (Zhizhan et al., 2015).

NMR has the advantage to provide directly molecular details determining physical-chemical properties of a sample at a macroscopic level (Lintelmann, 1995). In fact, an NMR spectrum contains information in terms of the molecular functional groups and, if recorded with the proper resolution, may allow characterizing a sample at the molecular level (Allen et al., 1985; Behera et al., 2008). Modern NMR spectroscopy technique is based not only on increased sensitivity and resolution, but also applies two-dimensional methods, which provide additional information on the composition of oil samples from NMR spectra. Taking into account the importance of oil to the economy, there is a very important and urgent task for adaptation of modern 1D NMR (^{1}H, ^{13}C) and 2D NMR (COSY, HSQC experiments) spectroscopy to determination of oil composition.

^{1}H NMR spectroscopy is a relatively fast method, which does not

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require complex sample preparation. Accessible spectral range of proton resonances is not wide, and hence little information can be obtained from direct comparison of ^{1}H spectra. ^{1}H NMR spectra of crude oils contain a great number of signals reflecting their chemical complexity (Gupta et al., 1986; Kushnarev et al., 1989; Hasan et al., 1983). Therefore, to exploit the full information content of the NMR data acquired on complex systems, different multivariate data analysis methods were developed (Alam and Alam, 2004). Statistical analysis may be successfully used to predict important properties of oil (API gravity, carbon residue, wax appearance temperature, and basic organic nitrogen) based on a large set of studied samples (Duarte et al., 2016). Use of ^{1}H NMR spectroscopy on neat crude oil samples combined with partial least squares (PLS) modeling has high potential to predict crude oil properties (Masili et al., 2012). If ^{13}C data is added, much more information on chemical composition can be extracted; however, this requires more experimental time. NMR data can be combined with other experiments (mass-spectrometry, elemental analysis, etc.); an example of such a study using Monte Carlo simulation to reconstruct molecular composition of gasoils and heavy fractions is presented in Hudebine and Verstraete (2004); Verstraete et al. (2010). Organic compounds contained in rocks can also be studied in solid phase by NMR using the magic-angle spinning method; as an example, studies of kerogen can be mentioned (Bushnev et al., 2010; Bushnev and Burdelnaya, 2012).

The aim of this study was to determine the qualitative and quantitative composition of a number of oil fields from the Republics of Bashkortostan and Tatarstan by modern methods of NMR spectroscopy. Oil samples from the following fields: Kontuzlinsk (I), Hatyrovsk (II), Akansk (III), Selengush (IV) were studied. Also a comparative analysis of oil samples from top (V) and lower (VI) parts of Bashkirian oil well (Akansk field) was done.

2. Materials and methods

^{1}H (500.1 MHz) and ^{13}C (125.8 MHz) NMR experiments on oil samples (I – VI) were performed on a Bruker Avance II 500 NMR spectrometer. Oil samples were diluted with carbon tetrachloride or deuterated benzene to reduce viscosity and to facilitate shimming (in the case of C_6D_6); relaxation measurements were made without dilution. The volume fraction of oil in the mixture with a diluent was 65–80%. ^{1}H NMR spectra were recorded using 30° pulses; acquisition time was 4.09 s and the additional relaxation delay between scans was 1 s; spectrum width was 16.0 ppm; 100 scans were accumulated. ^{13}C NMR spectra were recorded using 30° pulses with broadband proton decoupling; delays between pulses were 40 s (and acquisition time was 1.44 s); spectrum width was set to 180.7 or 200.8 ppm; number of scans was 250 or 1000. Exponential digital filter with the LB parameter of 3 Hz was applied prior to Fourier transformation. Measurements were made at the temperature of 25 °C.

^{1}H, APT ^{13}C and ^{1}H,^{13}C-HSQC NMR spectra were recorded on a Bruker Avance III HD 700 NMR spectrometer equipped with a cryoprobe. Field lock and shimming were achieved using the deuterium signal from D_2O in glass capillary placed into the 5 mm NMR tube together with the investigated oil sample.

3. Results and discussion

The group analysis method can be used to determine the oil composition, wherein the composition is expressed as relative quantities of different types of molecules, such as *aromatic molecules*, *olefins*, *alkanes*, and *cycloalkanes* and their numerous isomeric analogues. The substance is considered *aromatic*, if its molecule has an aromatic ring; an *olefin*, if a double bond is present. Molecule is called *cycloalkane* if it has 5- or 6-membered saturated rings; *alkanes* represent saturated hydrocarbon chains. Oil fractions can be described as the average ratio of structural groups (structural-group analysis). It means that some “average” molecule of mixture is defined by a certain set of numbers.

Some byproducts of oil refining are difficult to study due to their high viscosity at the room temperature and their stickiness to all kinds of containers. This makes the analysis of such objects a rather cumbersome and costly procedure. Some of these analyses have to be performed for days and weeks (Speight and Özüm, 2001). Faster and less expensive approaches to analysis in this case are spectroscopic methods. Thus optimization of NMR is of great interest to investigate refinery products at significantly lower prices and in much shorter times (Molina et al., 2010).

According to the definition given in the literature for the chemical shift parameter as a quantitative measurement used in NMR spectrometry, the integration can be performed using the specified regions in ^{1}H and ^{13}C NMR spectra. Different integration domains for ^{1}H NMR spectra are discussed in the Calemma et al. (1995). Application of ^{1}H NMR spectroscopy to the analysis of oil fractions is limited by a small range of chemical shift values for all classes of organic compounds (15 ppm), so compounds with a similar structure in complex mixtures give an average, strongly broadened signal. Also, the spin-spin interaction between protons leads to further complication of spectra, thus ^{1}H NMR spectroscopy is used to solve a number of particular problems of structural analysis. ^{1}H NMR spectrum allows defining the degree of substance's aromaticity in mixture. Also a comparison of proportions of aromatic atoms of hydrogen and carbon (from ^{13}C NMR spectrum) determines the degree of substitution of the aromatic oil fraction.

^{13}C NMR spectroscopy is much more informative due to the wide range of chemical shifts (200 ppm) of ^{13}C nuclei (Breitmaier and Woelter, 1986; Friebolin, 1991). Moreover, broadband decoupling between ^{1}H and ^{13}C nuclei facilitates interpretation of ^{13}C NMR spectra. This method can be applied for analysis of mixtures containing molecules of known type; the paper (Makhiyanov and Safin, 2006) gives an example applied for polymers, and (Tomi et al., 1995) describes study of essential oils. Crude oil contains vast number of compounds; however, spectral width of ^{13}C spectra still allows classifying them into several classes even if individual components cannot be identified. Both ^{1}H and ^{13}C NMR spectra of oil samples in solution already have been described in literature (Kalabin et al., 2000); corresponding detailed information is presented in Tables 1 and 2.

^{1}H and ^{13}C NMR spectra of the oil sample from upper part of Bashkirian horizon (V), mixed with CCl_4, are shown in Figs. 1 and 2. ^{1}H NMR spectra, as it was expected, provide little information because resonance lines of similar-structure organic fragments merge in broad signals and become difficult to distinguish. However, numerical data are suitable for comparing oil samples with each other.

^{13}C NMR spectra contain numerous distinguishable signals, which can be assigned to different typical regions and thus give information on the fractions of aromatic, primary (CH_3), secondary (CH_2), and other types of carbon atoms. The combination of ^{1}H and ^{13}C NMR spectra allows estimating the average length and branching of aliphatic chains.

Table 1
Distribution of ^{1}H NMR chemical shifts of functional groups defining the composition of oil samples (Kalabin et al., 2000).

^{1}H NMR chemical shifts range, ppm	Organic functional group
0.5–1.0	γ-CH_3-groups and some CH- and CH_2- groups in naphthenic fragments
1.0–1.7	β-CH_2- and some β-CH- groups in aromatic compounds
1.7–1.9	β-CH-, CH_2- groups in hydroaromatic compounds
1.9–2.1	Methyl groups (CH_3) in α-olefins
2.1–2.4	Methyl groups (CH_3) in α-position to aromatic carbons
2.4–3.5	CH- and CH_2- groups in α-position to aromatic carbons
3.5–4.5	Bridging CH_2- group (diphenylmethane)
4.5–6.0	Protons of olefin groups
6.0–7.2	Protons of single-cycle arenes
7.2–8.3	Di-, three- and tetra-aromatic protons
8.3–8.9	Some three- and tetra-aromatic protons
8.9–9.3	Protons of some four-cycle arenes