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Application of high resolution NMR (^{1}H and ^{13}C) and FTIR spectroscopy for characterization of light and heavy crude oils

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ABSTRACT

High-resolution nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy experiments were applied to obtain detailed information on the hydrocarbon chemistry of three light and three heavy crude oils. Quantitative fractions of aromatic molecules and functional groups constituting oil hydrocarbons were determined by ^{13}C NMR spectroscopy and comparative analysis of the oil samples with different viscosity, origin and preliminary treatment. SARA composition and some important information about aromaticity, oxidation behavior, branching, aliphaticity and sulfurization of studied oil samples were obtained. Integral characteristics of high-resolution NMR and FTIR spectra have a great potential to study the structure and characterization of light and heavy crude oils, which could substitute present traditional fractionation procedures. Relationships between spectroscopic parameters obtained by high-resolution NMR and FTIR spectroscopy methods and crude oil compositions can be useful for fast prediction of crude oil properties due to different type of treatment, including thermal methods for enhanced oil recovery. Also quantitative proportions of functional groups obtained by NMR and spectral indices obtained by FTIR can be one of the criteria for developing fingerprint approach.

1. Introduction

^{1}H and ^{13}C NMR spectroscopy is well-known recognized technique for establishing structural formulas, spatial and electronic structure of either first synthesized or isolated from natural raw materials individual organic compounds (Usachev et al., 2013a, 2013b, 2017a; Kononova et al., 2017; Rakhmatullin et al., 2015, 2017a; Abdrakhmanov et al., 2017; Khodov et al., 2017). In recent years, there has been a growing interest in using NMR spectroscopy for studying various objects in petroleum chemistry (Gao et al., 2017; Mondal et al., 2017; Alcazar-Vara et al., 2016; Smirnov and Vanyukova, 2014). The NMR method opens wide opportunities in studying the structure of oil disperse systems and determining their physical and chemical characteristics. The NMR method can help to determine aromatic and aliphatic hydrogen and carbon atoms in crude oil samples. Areas under resonance peaks in NMR spectra characterize the amount of ^{1}H or ^{13}C atoms of corresponding chemical types. Integration of the peaks and subsequent manipulations and calculations yield quantitative proton and carbon type analyses (Kushnarev et al., 1989). ^{1}H and ^{13}C NMR can be applied to obtain information on content of general functional groups (tertiary and primary carbon atoms, aromatic cores) and possible presence of olefins or water impurity (Rakhmatullin et al., 2017b). However, it has not been widely used yet for analysis of high-molecular weight oil samples because of their complex structural organization. Number of works on the NMR analysis of crude oils and petroleum products, including oil residues, is limited. This circumstance is largely due to the natural shift of interests towards the study of the properties of heavy oil, for which the possibilities of NMR are limited. In particular, the correlation between viscosity of oil and relaxation times in these objects is no longer observed clearly as for light oils, and the use of pulsed NMR method is becoming increasingly problematic.

High resolution NMR spectroscopy has provided detailed chemical information on the proton and carbon chemistry of petroleum materials for over 60 years (Edwards, 2011). Today high resolution NMR instrumentation used to derive detailed multinuclear hydrocarbon information is based on superconducting magnet technologies (Derome, 1987; Rule and Hitchens, 2006; Kolosova et al., 2016; Usachev et al., 2017b; Galiullina et al., 2017). In the case of oil and petroleum products containing typically hundreds of compounds, mainly hydrocarbons, an important feature of NMR spectroscopy is a strict

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correlation of integral intensities of separate groups of signals in certain chemical shifts ranges in ^{1}H and ^{13}C NMR spectra with the content of the corresponding molecular fragments (Holzgrabe, 2017; Poveda et al., 2014; Da Silva Oliveira et al., 2014). Note that approaches widely used in petrochemical methods of analysis, such as elemental (X-ray fluorescence, absorption and emission optical spectroscopy), fragment and component (IR spectroscopy, mass spectrometry, chromatography) analyses are indirect (unlike NMR) because they require using reference materials for quantitative investigations. It should also be noted that the quantitative ^{13}C NMR spectrum is the only direct method for measuring aromaticity (C_{ar}) – relative percentage of aromatic carbon atoms in hydrocarbons (McBeath et al., 2011; Fergoug and Bouhadda, 2014; Lee and Glavincevski, 1999).

SARA (saturates, aromatics, resins, and asphaltenes) analysis is another important application in crude oil composition studies, because these data are used for predicting the oil recovery using specific technology, the compatibility and stability of blends of crude oils to anticipate problems of sedimentation during storage and transportation (Aske et al., 2002). Some studies have revealed that NMR can be used for predicting SARA composition of crude oils (Molina et al., 2010; Sanchez-Minero et al., 2013). NMR results were used to obtain the concentration of aromatic-hydrogen and aromatic-carbon, from which aromaticity factors were computed and correlated to SARA analysis. This allowed developing correlations for predicting SARA composition of crude oils with a wide range of API gravity (10–33°) (Sanchez-Minero et al., 2013).

FTIR spectroscopy has been an important analytical tool for determining the chemical composition and structures of the components of crude oils and their refined products for more than four decades (Brown et al., 1975). Many of the early investigations emphasized the isolation of various types of hydrocarbons, e.g., paraffins, naphthenes, and olefins, from petroleum. Infrared spectra of all types of hydrocarbons have been measured and catalogued by the National Bureau of Standards, API Project 44 (American Petroleum Institute Project 44). Since petroleum and the products of petroleum are mixtures of many hydrocarbons, much emphasis has been placed on using IR spectra to quantitatively measure the composition of mixtures. In addition to measuring the composition of hydrocarbon mixtures this method has been also used in determining the degree of branching in paraffins, e.g., methods have been suggested to determine the number of CH_3 and CH_2 groups in hydrocarbons (Rericha and Horak, 1967, 1968).

The aim of this study was to determine the qualitative and quantitative composition of six different crude oil samples by means of the high-resolution ^{13}C NMR spectroscopy, FTIR spectroscopy and SARA analysis and to find some general relationship between spectroscopic parameters and crude oil composition. These relationships can be useful for fast prediction of crude oil properties changing upon different type of treatment, including thermal methods for enhanced oil recovery.

2. Materials and methods

Viscosity of the samples used in this study is reported along with the extraction method in Table 1. There are three low viscosity oils (**1**), (**2**) and (**3**), one semi-heavy oil (**4**), and two high viscosity oils (**5**) and (**6**). These samples were provided by Tatneft, Zarubezhneft and RITEK oil companies. Crude oils (**1**), (**3**), (**5**) and (**6**) were extracted by thermal enhanced oil recovery (EOR) methods.

Table 1
Viscosity and extraction method of studied oil samples.

Sample number	Viscosity, mPa*s	Extraction method
1	7.5	high pressure air injection (HPAI)
2	5.95	primary recovery
3	37.2	high pressure air injection (HPAI)
4	106	primary recovery
5	2420	SAGD
6	49700	cyclic steam simulation (CSS)

2.1. NMR spectroscopy

NMR experiments on the studied oil samples (**1**–**6**) were performed on a Bruker Avance II 500 NMR spectrometer. Field lock and shimming were achieved using the deuterium signal from D_2O in a glass capillary placed into the 5 mm NMR tube together with the investigated oil sample. All samples were studied without dilution. ^{1}H NMR spectra were recorded using 30° pulses (zg30 pulse program); acquisition time was 4.7 s; pre-scan delay was 6.5 μs, and the relaxation delay between scans was 2 s; spectrum width was 12.0 ppm (6000 Hz); 400 scans were accumulated. ^{13}C NMR spectra were recorded using 90° pulses with inverse gated broadband proton decoupling (zgig pulse program); relaxation delay between pulses was 9 s (and acquisition time was 3.5 s); spectrum width was set to 220.0 ppm; number of scans was 3200. Exponential digital filter with the lb parameter of 10 Hz was applied to process ^{13}C NMR spectra prior to Fourier transformation. Measurements were made at the temperature of 30 °C. All NMR spectra were integrated after baseline correction, and a mean of at least three integration values were taken for each calculation. The relative standard deviation of the results of manual integration did not exceed 3%. Estimation of molar fractions of primary, secondary, tertiary, aromatic and quaternary carbons was carried out in a way similar to our previous work (Rakhmatullin et al., 2017b).

Information obtained by quantitative integration of aromatic signals in individual spectral ranges is represented by the fraction of the corresponding carbon atoms relative to their total number. Fraction of aromatic carbons C_{ar} can be straightforwardly found from NMR spectra:

$$C_{ar} = \frac{I_{ar}}{\sum_j I_j}, \tag{1}$$

where C_{ar} is the fraction of aromatic carbons, I_{ar} is the total integral intensity of aromatic carbons and I_j is the integral intensity of all functional groups in ^{13}C NMR spectrum of the sample.

It is impossible to obtain unambiguous information on the content of hydrocarbons (alkanes, cyclanes) from ^{13}C NMR spectra, although this information is contained in the fragmentary composition, which can be determined with high accuracy (Kushnarev et al., 1989). If integral intensities of individual groups signals in the ^{13}C NMR spectrum are known, then corresponding molar fractions of tertiary, primary, secondary and quaternary carbons can be calculated by the following formulas (Kalabin et al., 2000):

$$C_t = ((1.04I_t - 0.034I_{sq})/(I_t + I_{sq} + I_p))(1 - C_{ar}), \tag{2}$$

$$C_p = ((1.02I_p - 0.006I_{sq})/(I_t + I_{sq} + I_p))(1 - C_{ar}), \tag{3}$$

$$C_{sq} = ((1.04I_{sq} - 0.04I_t - 0.02I_p)/(I_t + I_{sq} + I_p))(1 - C_{ar}), \tag{4}$$

where C_t is the fraction of tertiary carbons; C_p – fraction of primary carbons; C_{sq} – fraction of secondary and quaternary carbons (due to the complexity of separation of methylene and methine signals, their summary contents is estimated); I_t is the total integral intensity of tertiary (CH) groups; I_{sq} – total integral intensity of secondary (CH_2) and quaternary groups, I_p – total integral Intensity of primary (CH_3) groups in ^{13}C NMR spectrum of the oil sample.

Mean chain length (MCL) was calculated as:

$$MCL = 2*\left(\frac{C_{sq} + C_t}{C_p}\right) + 2. \tag{5}$$

The aromaticity factor (F_{CA}) can be calculated from the equation (Sanchez-Minero et al., 2013):

$$F_{CA} = \frac{C_{ar}}{C_{ar} + C_{al}}, \tag{6}$$