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Petrochemicals**UV - AND  $^1\text{H}$  NMR SPECTROSCOPIC STUDIES OF AROMATIC HYDROCARBONS OF PETROLEUM DEPOSITS SURAKHANI****Corresponding Member of NAS of Azerbaijan F.I.Samadova, R.A.Jafarova, U.J.Yolchuyeva, B.M.Aliyev, S.F.Ahmadbayova, S.Y.Rashidova, N.A.Rzayeva**

*The first time with the help of modern high-sensitivity UV - and  $^1\text{H}$  NMR spectroscopy the structural-group composition of aromatic petroleum hydrocarbon fields of Surakhani (well №1311) with a boiling point  $<600^\circ\text{C}$  and its fractions have been studied. It is shown that the composition of the oil and its fractions include mono-, bi-, tri-, tetra- cyclic aromatic hydrocarbons as well as their alkyl-substituted. Their amount has been determined. By  $^1\text{H}$  NMR spectroscopy in the studying sites have been found the total content of polycyclic aromatic hydrocarbons and their aromaticity.*

**Keywords:** oil fields of Surakhani, UV spectroscopy,  $^1\text{H}$  NMR spectroscopy, calorimetry, polycyclic aromatic hydrocarbons, alkyl substituted aromatic hydrocarbons

Due to the intensive development of Azerbaijan's oil industry from an economic and environmental point of view it requires the study of composition and properties of oils of new oil fields.

It is known that the oil is a complex mixture of aromatic, paraffinic, naphthenic, olefinic hydrocarbons [1]. The study of the chemical structure of petroleum hydrocarbons can serve as one way of caring attitude towards them, because they store information about the composition and the structure of the original biological molecules.

Aromatic hydrocarbons (AH) are one of the most common classes of organic compounds of oil. The main part of the oil arenes are compounds containing no more than three benzene rings. Monocyclic aromatic petroleum hydrocarbons are represented alkylbenzenes and their naphthene analogues bicyclic - derivatives of naphthalene and biphenyl, diphenyl alkanes and their analogues naphthene, aromatic tricyclo - derivatives of phenanthrene and anthracene, and may also contain naphthenes to 4-5 cycles per molecule. Tetracyclic AH compounds are represented rows of chrysene, pyrene, 2,3 and 3,4-benzo phenanthrenes, fluoranthene and triphenylene. The proportion of hydrocarbons with five and a large number of condensed rings is very small. Aromatic hydrocarbons comprising 5-8 condensed benzene rings are, substantially unsubstituted [2]. The oil composition may include gaseous ( $\text{C}_1\text{--C}_4$ ), liquid ( $\text{C}_5\text{--C}_{15}$ ) and par-

ticulate ( $\text{C}_{16}\text{--C}_{60}$ ) paraffins. Condensed polycyclic compounds contained in the high boiling petroleum fractions [3].

The composition and properties of Azerbaijani oils described in detail in [4,5]. Oil from the field Surakhani for its unique properties (low density and molecular weight, high biological activity and so on) is of great interest. This oil has long been used in folk medicine to treat a number of diseases [6-8]. The study of its structural-group composition and spectral properties are very promising and may contribute to a more rational using of the oil and extracted from its components.

**The object and the experimental method**

The object of investigation for the first time the oil fields of Surakhani (well №1311) was used. This oil is a dark brown liquid with a boiling end  $<600^\circ\text{C}$  and is characterized by the following properties: density,  $\rho_{420} - 841,7 \text{ kg/m}^3$ , viscosity,  $400^\circ\text{C} - 6.33 \text{ mm}^2/\text{s}$ , an acid number of - 2.55. According to chromatographic analysis (instrument: Agilent Technologies 6890N), this oil consists of (% by moles): paraffin (67, 40), iso-paraffin (9.356), olefin (2,522), naphthenic (5.709), aromatic (15,01) hydrocarbons. Alkylaromatic hydrocarbons take up the prominent place among the AH. Furthermore, unsaturated hydrocarbons (4-methylhexyl-1, 3,4-dimethylpent-2, etc.), and hydrocarbons with a hybrid structure (4-methylindane, 2,3-digidroindan) have been identified.

Table

**The material balance and characteristics of hydrocarbon emissions  
from oil fields of Surakhani (well №1311)**

| Hydrocarbons       | Yield, % weight. | Refractive index, $n_d^{20}$ | Density at 200C, kg / m <sup>3</sup> |
|--------------------|------------------|------------------------------|--------------------------------------|
| Paraffinic naphtha | 75,42            | 1,4550                       | 825,0                                |
| Aromatic           |                  |                              |                                      |
| I gr.AH            | 5,87             | 1,5108                       | 836,8                                |
| II gr.AH           | 3,68             | 1,5357                       | 869,5                                |
| III gr.AH          | 6,23             | 1,5768                       | 902,6                                |
| IV gr.AH           | 4,70             | 1,5990                       | 984,8                                |
| Resin              | 4,10             | -                            | 1003,1                               |

The ratio of individual components in the oil vary widely. Thus, the content of paraffinic hydrocarbons naften- (PHN) is almost six times higher than aromatic, and aromatic content of about 2.6 times greater than the naphthenic. Unlike Naphthalan oil [9,10] we have studied the oil mainly composed of paraffin hydrocarbons having a number of carbon atoms in the molecule, C<sub>6</sub> and C<sub>9</sub>-C<sub>13</sub>. The iso-paraffin hydrocarbons interval carbon atoms equals C<sub>6</sub>-C<sub>13</sub>. In the Surakhani oil has also been detected mono-, bi- and tricyclic naphthenes, which have isomers of 15 (number of carbon atoms of the C<sub>6</sub>-C<sub>11</sub>). In general, the identified up to 6 condensed naphthene rings, each of which has several isomers. With respect to the other components of the olefinic hydrocarbon content it is very small, the number of carbon atoms is C<sub>6</sub>-C<sub>8</sub> and C<sub>12</sub>.

For the study of polycyclic aromatic hydrocarbons (PAHs) from the oil fieldsof Surakhani first time we used a highly sensitive UV - spectroscopy and NMR <sup>1</sup>H. Because the oil is a mixture of various hydrocarbons to study the composition and structure of the oil from the well №1311 it was separated into different hydrocarbon groups according to GOST 11858-85. The table below shows the material balance and characteristics of the selected samples.

For the purpose of identification and structural-group composition of aromatic hydrocar-

bons in the oil Surakhani (well №1311) and its fractions was conducted sample analysis on UV spectrophotometer model (JENWAY) 6850 UV / visible portion of the spectrum (190-1100nm). The excitation source is a deuterium lamp and an incandescent lamp. Investigations have been carried out at room temperature. Isooctane was used as the solvent. The amount calculated by the method of PAHs [11,12]. NMR spectra of hydrocarbons were recorded on a pulsed Fourier spectrometer by the firm of "Bruker" at an operating frequency of 300.18 MHz in deuterated benzene solution at room temperature. The relative abundance of various structural groups of protons were determined by integrating the respective bands of resonant absorption.

#### Results and Discussion

One of the main components of the oil are PAHs [13]. Their electronic band are connected with one type of transition ( $\pi \rightarrow \pi^*$ ). The establishment of the structure the molecule is reduced to identify the relationship between the size and shape of the system and the parameters of  $\pi$ - electron transitions (wavelength, intensity, polarization, vibrational structure) [14].

By UV spectroscopy the structural-group composition of aromatic oil Surakhani (well №1311) and its fractions has been studied. There has been detected the absorption bands charac-

teristic of benzene (206 nm), naphthalene (226 nm) and anthracene (275nm) hydrocarbons and also their alkyl substituted in an amount of 20 wt.%, which correspond to data obtained by IR and NMR spectroscopy (20.48 wt.%). The presence of trace amounts of tetrasubstituted PAH in the composition of current oil is not excluded.

The study of electronic absorption spectra shows that with increasing concentrations of the solutions fractions of AH absorption spectrum is shifted to longer wavelengths the spectral region (Figure 1). If you compare the electronic spectra of fractions to the spectrum of native oil, it can be seen that the spectra of fractions clearer and has a certain maximum, ie, devoid of individuality broad absorption band of the native oil, in the case of fractions is divided into clearer highs PAH molecules. This is due to electron-phonon interaction PAH molecules. When the distance between the molecules of the electron-phonon interaction becomes weak, which leads to erosion of the spectra [14]. The studies fractions I-IV gr. AH has shown that the electronic absorption spectra with increasing number of the group fractions are displaced to longer wavelengths the spectral region that is associated with a condensed PAHs and their alkyl substituted.

On the other hand, if one compares the electronic absorption spectra of I and IV gr. AH at 250-300 nm, so the amount of absorption changes in the following order:

$$D_{\text{I gr. AH}} (1.7) < D_{\text{II gr. AH}} (2.9) < D_{\text{III gr. AH}} (3.2) < D_{\text{IV gr. AH}} (3.5)$$

From the electronic absorption spectra of II and IV gr. AH, it is seen that the intensity of the absorption maximum at  $\lambda = 206$  nm in the case of II gr. AH almost two times higher than IV gr. AH. In the study of the UV spectra of the resin derived from oil fields of Surakhani is registered intense absorption band in the spectral region of 350-600 nm. This band is connected with the cyclic structure, electron-donor and electron-acceptor substituents.

A study of the electronic absorption spectra shows that in contrast to the I and II gr. AH, the absorption spectra of III and IV gr. AH extend to almost 700 nm, but because of the overlap of the absorption bands in this region of the spectrum failed to conduct a quantitative analysis (Figure 1). This spectral region can be linked to a mono-, bi-, and tricyclic alkyl substituted PAH and higher cyclic aromatic hydrocarbons [14].

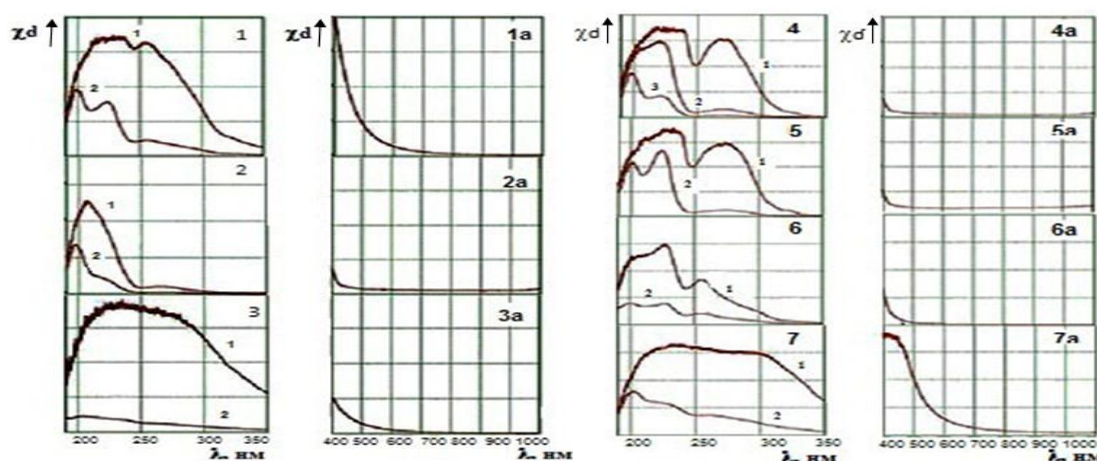


**Fig.1.** Electronic absorption spectra Surakhani oil and its fractions (well №1311) at different concentrations (solvent iso-octane), g / l:

1) Oil:  $c_1=2,13(1)$ ,  $c_2=0,656(2)$ ; 2) Paraffin-naphthenic fraction:  $c_1=6,2(1)$ ,  $c_2=1,77(2)$ ; 3) resin:  $c_1=0,71(1)$ ,  $c_2=0,134(2)$ ; 4) I gr. AH:  $c_1=1,4(1)$ ,  $c_2=0,267(2)$ ,  $c_3=0,082(3)$ ; 5) II gr. AH:  $c_1=0,984(1)$ ,  $c_2=0,188(2)$ ; 6) III gr. AH:  $c_1=0,253(1)$ ,  $c_2=0,0595(2)$ ; 7) IV gr. AH:  $c_1=0,81(1)$ ,  $c_2=0,19(2)$

For the study of aromatic hydrocarbons of well №1311 there has been used the method of NMR  $^1\text{H}$ .  $^1\text{H}$ -NMR spectroscopy data demonstrate that the average molecule selected hydrocarbons have molecular weights in the range 182-435 and contain 13-32 carbon atoms and 26-47 hydrogen atoms. The lowest hydrogen deficiency (Z) possess NPU ( $Z = 0,1$ ), the remaining fraction of aromatic hydrocarbons are Z within 5.3 - 16.6, that indicates the increasing the number and proportion of aromatic cycles in the middle part of the molecule. The atomic ratio of H / C for aromatic fractions is 1.45-1.63, which is typical for these classes of compounds. A relatively high value of H / C = 2.02 for the NPC may be due to the extremely small content in this fraction of the aromatic rings and the large weights of the various groups and the aliphatic units. As part of the principal amount NPU H atoms included in the average molecule, are concentrated in the saturated fragments (H sat.). The remaining (aromatic group and resin) H sat. varies within ~ 84-96%. Virtually all studied fractions are protons in position  $\text{H}_\beta$  within (~ 39 - 57%),  $\text{H}_\gamma$  within (~ 19 -25%) and  $\text{H}_\alpha$  within (~ 11 - 26%). A relatively large proportion of H atoms in  $\text{H}_\gamma$  for a fraction of NPC shows a high degree of branching of the aliphatic chains in these molecules (NAFTA-iso).

For the studied groups of hydrocarbons degree of aromaticity ( $f_a$ ) has been determined a graphical method. The degree of aromaticity in the range of hydrocarbon groups I-IV increases, reaching a maximum at the III-group (~ 0.45). And in hybrid resin molecules the degree of aromaticity (0.21) is not high, which is also confirmed by the low value of  $\text{H}_{ar}$ . Reaching only 4.5% of the total number of atoms H. It should be noted that the share of the naphthenic part of these molecules is very high.

Carried out the study showed that the composition of the high boiling oil fractions from Surakhani field, unlike the low-boiling fractions (<350 ° C) include higher cyclic (> 5 rings) aro-

matic hydrocarbons. It is paraffin-naphthenic origin. The obtaining information about the the composition and structure of the components of the oil fields of Surakhani (well №1311) allow more based approach to addressing their rational use.

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[Ulviyya.yolcujeva@mail.ru](mailto:Ulviyya.yolcujeva@mail.ru)**SURAXANI NEFTİNİN AROMATİK KARBOHİDROGENLƏRİNİN UB- VƏ  
NMR <sup>1</sup>H- SPEKTROSKOPİK TƏDQİQİ****F.İ.Səmədova, R.Ə.Cəfərova, Ü.C.Yolcujeva, B.M.Əliyev, S.F.Əhmədbəyova,  
S.Y.Rəşidova, N.Ə.Rzayeva**

İlk dəfə olaraq yüksəkhəssaslıqlı UB- və NMR<sup>1</sup>H-spektroskopiyanın köməylə < 600°C qaynama temperaturu Suraxanı neftinin və onun fraksiyalarının (quyu №1311) aromatik karbohidrogenlərinin struktur-qrup tərkibi tədqiq edilmişdir. Bu neftin və onun fraksiyalarının tərkibinə mono-, bi-, tri- və tetratsiklik aromatik karbohidrogenlərin, həmçinin, onların alkiləvəzölünmüşlərinin daxil olduğu göstərilmiş və miqdarı təyin edilmişdir. NMR<sup>1</sup>H-spektroskopiyanın köməylə tədqiq edilən obyektlərdə politsiklik aromatik karbohidrogenlərin ümumi miqdarı və onların aromatikliyi təyin edilmişdir.

**Açar sözlər:** Suraxanı nefti, UB- spektroskopiya, NMR<sup>1</sup>H- spektroskopiya, kalorimetriya, politsiklik aromatik karbohidrogenlər, alkil əvəzölünmüş aromatik karbohidrogenlər

**УФ - И ЯМР <sup>1</sup>H- СПЕКТРОСКОПИЧЕСКИЕ ИССЛЕДОВАНИЯ АРОМАТИЧЕСКИХ  
УГЛЕВОДОРОДОВ НЕФТИ МЕСТОРОЖДЕНИЯ СУРАХАНЫ****Ф.И.Самедова, Р.А.Джафарова, У.Дж.Йолчуева,  
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Впервые с помощью современной высокочувствительной УФ - и ЯМР <sup>1</sup>H- спектроскопии исследован структурно-групповой состав ароматических углеводородов нефти месторождения Сураханы (скважина №1311) с температурой кипения <600°C и ее фракций. Показано, что в состав этой нефти и ее фракций входят моно-, би-, три-, тетра- циклические ароматические углеводороды, а также их алкилзамещенные. Определены их количества. По ЯМР <sup>1</sup>H- спектроскопии в исследуемых объектах найдены суммарное содержание полициклических ароматических углеводородов и их ароматичность.

**Ключевые слова:** нефти месторождения Сураханы, УФ- спектроскопия, ЯМР-<sup>1</sup>H спектроскопия, calorиметрия, полициклические ароматические углеводороды, алкилзамещенные ароматические углеводороды