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NMR-Spectroscopy Determination of Fragmentary Composition of Bitumen and its Components

B.B. Teltayev[1*] and T.M. Seilkhanov[2]

[1]Kazakhstan Highway Research Institute, 050061, Nurpeissov Str. 2A, Almaty, Kazakhstan
[2]Kokshetau State University after Sh. Ualikhanov, 020000, Abai Str. 76, Kokshetau, Kazakhstan

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Abstract

This paper represents and discusses the results of quantitative determination for fragmentary composition of road bitumen of grade BND 100/130 and its components (asphaltenes, resins and oils) by NMR spectroscopy method. Group chemical composition of the bitumen has been determined by adsorption chromatography method. It has been identified that the bitumen and its components consist only of aromatic and aliphatic protons, which account for 2.4–10.2% and 9.8–97.6% respectively. Availability of olefinic elements in them has not been identified. The most part (79–81%) of nuclei of carbon atoms relates to quaternary carbon atoms of saturated compounds. Primary carbon atoms at methylene group (CH_2) are contained in the least quantity: bitumen – 1.32%; asphaltenes – 0.6%; resins – 3.24% and oils – 2.11%. Primary carbon atoms, linked with CH-group or aromatic nucleus, occupy an intermediate position and are contained in the quantity of 17–20%.

1. Introduction

Bitumens are one of the important materials in the world, which are used for preparation of asphalt concretes. Bitumens are obtained by different ways from oil, extracted from different sources. Therefore physical, chemical, rheological and other properties of bitumen, differing from each other by source of oil and way of obtaining, vary greatly [1]. Specialists understand that great difference in properties of bitumen depend on their chemical structure. However, in spite of the fact that bitumens are used and investigated for a long time, at present the reliable methods for determination of their chemical composition are not available. Only their approximate chemical composition is known: carbon – 80-85%, hydrogen – 8-11.5%, oxygen – 0.2-4%, sulfur – 0.5-7%, nitrogen – 0.2-0.5% by weight [2].

Among numerous physical methods of chemical analysis spectroscopy of nuclear magnetic resonance (NMR-spectroscopy) becomes widely used in the analysis of oil and petrochemicals [3–7]. Also the works have been published, where the results are represented for the use of NMR-spectroscopy to the analysis of chemical composition and physical characteristics of road and industrial bitumens [8–10].

Fundamental base for quantitative NMR-spectroscopy is proportionality of signal intensity in NMR specter to the quantity of magnetic-sensible nuclei, responsible for frequency of specific resonance [11]. Information about complicated organic systems by NMR method can be obtained in the form of isotope, element, fragmentary and component composition. At NMR-spectroscopy the data are taken into account regarding position, intensity and multiplicity of signals in specter (component composition) and integral intensities of specific sections of specter (fragmentary or structural and group analysis) [3]. Quantitative determination of ratio for components in the mixture can be made by calculation of integral intensities of atom or group of atoms, characteristic for one or another component. The advantage of NMR-spectroscopy, compared with methods of chromatography, mass-spectrometry, optical spectroscopy, is the possibility of obtaining of quantitative information without application of standard samples and reference substances or mixes.

*Corresponding author. E-mail: bagdatbt@yahoo.com

This paper represents and discusses the results of quantitative determination for fragmentary composition of road bitumen of grade BND 100/130 and its components (asphaltenes, resins and oils) by NMR-spectroscopy method.

2. Material and methods

2.1. Bitumen

Road bitumen of grade BND 100/130 has been selected for the research, produced at Pavlodar petrochemical plant from crude oil of Western Siberia (Russia) by method of direct oxidation. Its characteristics satisfy the requirements of the standard of Kazakhstan ST RK 1373-2013 [12]. The main standard characteristics of the bitumen have been determined in the laboratory of Kazakhstan Highway Research Institute and represented in the Table 1.

2.2. Group chemical composition of bitumen

Group chemical composition of the bitumen has been determined by adsorption chromatography method [13]. According to this method the asphaltenes are determined by double deposition of bituminous mortar (5 g) and n-heptane (200 g). The remainder of the hydrocarbon mixture, consisting of resins and oils, is placed into glass chromatograph column, filled with the coarse-grained silica gel. For desorption the dissolvents are supplied into chromatograph column sequentially, consisting of *n*-heptane and benzene in the ratios by weight: 90/10; 85/15; 80/20; 75/25; 70/30. The refraction coefficient is determined for each fraction, obtained by adsorption division. It is accepted that lighter fractions, for which refraction coefficient can be determined, relate to oils. Resins represent by themselves the fractions of high color, having solid consistency, for which it is impossible to determine the refraction coefficient.

2.3. NMR-spectroscopy

^{1}H and ^{13}C NMR-spectroscopy allows determining of atom quantity for hydrogen and carbon, their distribution in functional groups in complicated organic systems.

In this paper the specters of NMR nuclei for hydrogen ^{1}H and carbon ^{13}C, dispersed in deuterated chloroform, have been recorded in the spectrometer JNM-ECA Jeol 400 (Japan) at the temperature of 25 °C. Working frequencies for nuclei ^{1}H and ^{13}C have been accepted equal to 399.78 MHz and 100.53 MHz respectively. Chemical shifts δ have been measured in relation to the signals of residual protons or atoms of carbon of deuterated chloroform.

As it is known, NMR spectra represent by themselves the graphic image of signal intensity from chemical shift of nuclei elements (in this work ^{1}H and ^{13}C). By now dependences have been determined between piecewise integral intensities of NMR-signals and various functional groups of chemical elements [3–7, 10]. These dependences allow determination of availability and relative quantity of various functional groups by integrating of NMR spectra in characteristic intervals.

According to the methods, recommended in the works [3, 6], the intervals of chemical shifts of proton and carbon specters with their corresponding interpretations are shown in the Tables 2 and 3.

Table 1
Main standard characteristics of the bitumen

Indicator	Measurement unit	Requirements of ST RK 1373-2013	Values
Penetration depth of the needle, 25 °C, 100 g, 5 s	0.1 mm	101-130	110
Penetration Index	-	-1.0...+1.0	0.82
Ductility at the temperature of: 25 °C 0 °C	 ≥90 ≥4.0		 135 6.6
Softening point	°C	≥ 43	44
Fraas brittle point	°C	≤ -22	-30.2
Dynamic viscosity at 60 °C	Pa·s	≥120	121
Kinematic viscosity at 135 °C	mm^2/s	≥180	329

Table 2
Intervals of variation and interpretation of chemical shifts of ^{1}H nuclei

δ(^{1}H), pm	Atom description	Functional group
0.5-1.0	H_γ	CH_3-groups of saturated compounds. CH_3-groups in γ- and further positions to aromatic ring
1.0-2.0	H_β	CH_2- and CH-groups of saturated compounds. Atoms of hydrogen of β-methyl, β- and further methylene and methine groups at aromatic ring
2.0-4.0	H_α	Atoms of hydrogen in α-position to aromatic and carbonyl carbons, heteroatoms
4.5-6.3	H_{ol}	Atoms of hydrogen of olefinic groups
6.3-9.0	H_{ar}	Atoms of hydrogen of aromatic nuclei, phenol hydroxyls

Table 3
Intervals of variation and interpretation of chemical shifts of ^{13}C nuclei

δ(^{13}C), ppm	Atom description	Functional group
7-17	C_{pm}	Primary carbon atoms at methylene group
17-25	C_{pa}	Primary carbon atoms, linked with CH-group or aromatic nucleus
17-50	C_{sq}	Secondary and quaternary atoms of C of saturated compounds
25-65	C_{al}	Aliphatic CH-groups
25-50	C_q	Quaternary carbon atoms of saturated compounds
108-118	C_{ol}	Olefinic fragments
110-135	C_t	Tertiary atoms of C of aromatic systems
130-137	C_m	Methyl-substituted aromatic atoms of carbon
137-148	C_a	Alkyl- and naphthyl-substituted atoms of carbon of aromatic nuclei
148-170	C_{ar}	Carbon atoms in aromatic compounds, substituted by phenol or ether group
170-200	C_c	Carbon atoms in carbonyl group

By integrating of specters in each of the mentioned intervals for variation of chemical shifts one can calculate quantity of atoms for hydrogen ^{1}H and carbon ^{13}C, related to the relevant functional groups. Summary integral intensity of ^{1}H signals is calculated under formula:

$$\bar{H}_{sum} = H_{ar} + H_\alpha + H_\beta + H\gamma, \tag{1}$$

where H_{ar}, H_α, H_β, H_γ are integral intensities of aromatic protons H_{ar} and protons in α-, β- and γ-positions in aromatic ring.

Percentage of aromatic and aliphatic protons are determined respectively under the formulas:

$$\bar{H}_{ar} = \frac{H_{ar}}{\bar{H}_{sum}} \cdot 100\,\%, \tag{2}$$

$$\bar{H}_{al} = \frac{H_\alpha + H_\beta + H_\gamma}{\bar{H}_{sum}} \cdot 100\,\%. \tag{3}$$

Percentage of protons in α-, β- and γ-positions to aromatic ring is obtained respectively under the formulas:

$$\bar{H}_\alpha = \frac{H_\alpha}{\bar{H}_{sum}} \cdot 100\%, \quad \bar{H}_\beta = \frac{H_\beta}{\bar{H}_{sum}} \cdot 100\%, \quad \bar{H}_\gamma = \frac{H_\gamma}{\bar{H}_{sum}} \cdot 100\%. \tag{4}$$

3. Results and discussion

By the method of adsorption chromatography has been determined that the considered bitumen of grade BND 100/130 contains asphaltenes – 15.1%, resins – 29.9% and oils 55%.

NMR specters of bitumen and its components (asphaltenes, resins and oils) have been obtained according to the results of measurement for chemical shifts of ^{1}H and ^{13}C. As an example, Figs. 1 and 2 show ^{1}H and ^{13}C NMR specters for the bitumen. As it is seen, in the NMR specter of ^{1}H intensive signals corresponding to chemical shifts equal to 1.27, 0.90 and 0.88 ppm have been obtained. And there are more intensive signals on NMR specters of ^{13}C and they correspond to chemical shift from 11.6 to 37.64 ppm. The most intensive of them, equal approximately to 0.7, corresponds to chemical shift 29.87 ppm.

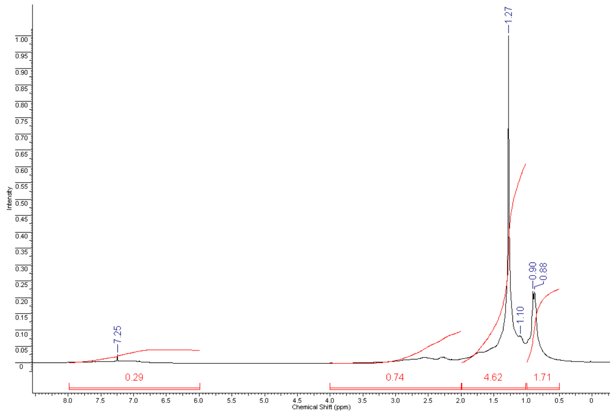

Fig. 1. ^{1}H NMR specter of bitumen of grade BND 100/130.

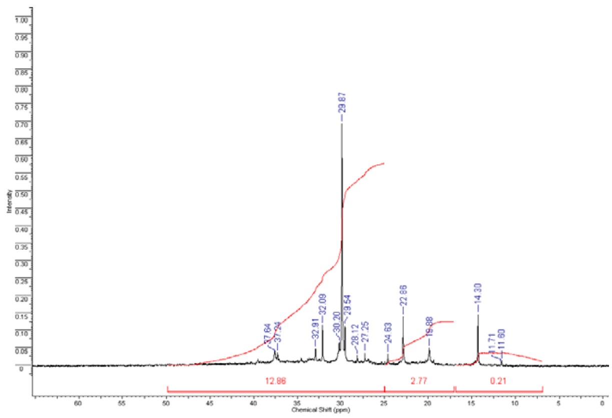

Fig. 2. ^{13}C NMR specter of bitumen of grade BND 100/130.

It should be emphasized that there are not any olefinic elements of hydrocarbons in the investigated bitumen and its components. Similar results for road bitumens of grades 70/100 and 160/220 and industrial bitumen of grade 160/220 have been obtained by Rossi C.O. and others [10]. Chemical shift, equal to 128.47 and falling in the interval of shifts from 110 to 135 ppm, which shows availability of tertiary atoms of carbon in aromatic systems, has been recorded only in resins.

Summary integral intensities of signals in NMR specters of ^{1}H and ^{13}C of bitumen and its components, determined by integrating in characteristic intervals, are represented in Tables 4 and 5. Percentage of ^{1}H and ^{13}C in functional groups, determined on the basis of data of the Tables 4 and 5, is given in Tables 6 and 7.

The analysis of the obtained results shows that content of aromatic protons in bitumen, asphaltene, resins and oils is 3.94%, 10.17%, 5.12% and 2.38%, i.e. it decreases with condensation degree decrease. The most part of protons related to CH- and CH_2-groups of saturated hydrocarbons and aromatic ring in β- and further positions and increases with condensation degree decrease: bitumen – 62.77%; asphaltenes – 47.3%; resins – 57.89% and oils – 67.11%. Methyl protons (CH_3) in bitumen and its components are contained in saturated hydrocarbons and occupy γ- and further positions in aromatic ring. Their content is practically

Table 4
Summary integral intensity of signals of ^{1}H NMR

Interval of chemical shift δ(^{1}H), ppm	Bitumen	Structural components of bitumen		
		Asphaltenes	Resins	Oils
0.5-1.0	1.71	1.70	1.65	1.78
1.0-2.0	4.62	3.07	3.96	5.08
2.0-4.0	0.74	1.06	0.88	0.53
6.0-8.0	0.29	0.66	0.35	0.18
Summary interval 0.5-8.0	7.36	6.49	6.84	7.57

Table 5
Summary integral intensity of signals of ^{13}C NMR

Interval of chemical shift δ(^{13}C), ppm	Bitumen	Structural components of bitumen		
		Asphaltenes	Resins	Oils
7-17	0.21	0.04	0.57	0.39
17-25	2.77	1.35	3.06	3.10
25-50	12.86	5.27	12.36	14.99
110-135	-	-	1.62	-
Summary interval 7-135	15.84	6.66	17.61	18.48

Table 6

Fragmentary composition (% according to the quantity of ^{1}H NMR)

Type of atoms	Bitumen	Structural components of bitumen		
		Asphaltenes	Resins	Oils
H_{α}	10.06	16.33	12.87	7.00
H_{β}	62.77	47.30	57.89	67.11
H_{γ}	23.23	26.20	24.12	23.51
$H_{a\ell}$	96.6	89.93	94.88	97.62
H_{ar}	3.94	10.17	5.12	2.38

Table 7

Fragmentary composition (according to the quantity of ^{13}C NMR)

Type of atoms	Bitumen	Structural components of bitumen		
		Asphaltenes	Resins	Oils
C_{pm}	1.32	0.60	3.24	2.11
C_{pa}	17.49	20.27	17.37	16.78
C_{q}	81.19	79.13	70.19	81.11
C_{t}	-	-	9.20	-

similar and accounts for 23.23–26.20%. Content of protons in α-position to aromatic and carbonyl carbons and heteroatoms decreases from 16.33% (asphaltene) to 7.0% (oils) with condensation degree decrease.

Thus, aromatic and aliphatic protons in bitumen and its components account for 2.4–10.2% and 89.8–97.6% respectively.

It is seen from Table 7 that in bitumen and its components the most part (79–81%) of nuclei of carbon atoms relates to quaternary carbon atoms of saturated compounds. Primary carbon atoms at methylene group (CH_2) are contained in the least quantity: bitumen – 1.32%; asphaltenes – 0.6%; resins – 3.24% and oils – 2.11%. Primary carbon atoms of CH-group or aromatic nucleus occupy an intermediate position and are contained in the quantity of 17–20%.

4. Conclusions

NMR-spectroscopy determination and analysis of fragmentary composition of bitumen and its components, performed in this work, allowed drawing the following conclusions:

1. Bitumen and its components consist only of aromatic and aliphatic protons, which account for 2.4–10.2% and 9.8–97.6% respectively. Availability of olefinic elements in them has not been identified.

2. In bitumen and its components the most part (79–81%) of nuclei of carbon atoms relates to quaternary carbon atoms of saturated compounds. Primary carbon atoms at methylene group atoms (CH_2) are contained in the least quantity: bitumen – 1.32%; asphaltenes – 0.6%; resins – 3.24% and oils – 2.11%. Primary carbon atoms, linked with CH-group or aromatic nucleus occupy an intermediate position and are contained in the quantity of 17–20%.

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