

UDC 665.6:(547.2+547.5+547.7+547.8)

DOI: 10.15372/CSD20190113

Oil Resins and Asphaltenes of Different Chemical Nature

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Abstract

The paper substantiates the research results on the composition and structure of resinous-asphaltenic materials of low resin and heavy highly resinous oils by a set of physicochemical research methods (extraction, liquid adsorption chromatography, elemental analysis, cryoscopy in benzene, IR and ^1H NMR spectroscopy, structural group analysis, the selective chemical breakdown of sulphide, ether, and ester bonds, and also by gas chromatography-mass spectrometry). Similarities and differences of the structural-group composition of resins and resin nitrogenous bases were detected. Compositions of moieties bound *via* ether/ester and sulphide bridges in resin and asphaltene molecules, and also those of compounds adsorbed by occluded asphaltenic species were investigated. As determined, composition and structure peculiarities of resin and asphaltenic molecules were dependent on the chemical nature of the initial oil species.

Key words: asphaltenes, resins, structural moieties, nitrogenous bases, structural-group and individual composition

INTRODUCTION

Resinous-asphaltenic materials in oil account for a large share of produced and processed oil raw materials [1, 2]. In this regard, the information about the composition and structure of oil resins and asphaltenes is important from the standpoint of oil genesis, production, transportation, storage, and processing [3–5]. The framework of resin and asphaltene molecules is comprised of naphthenic, aromatic, and heteroaromatic rings with alkyl side substituents [6, 7]. Heteroatom content in the structure of resinous-asphaltenic materials (RAM), moreover, about 90 % of heteroelements present in the oil is concentrated in resins [8]. A high concentration of hetero- and microelements as a part of RAM significantly complicates the progression of catalytic processes of recycling oil raw materials, has a negative effect on the quality of commodity oil products, environment, and human health [9]. Accordingly, research, the outcomes of which allow the assessment of the functional condition of het-

eroatoms (S, N, O) in resins and asphaltenes, become relevant.

The paper lists the results of the comparative analysis of the composition and structure of asphaltene and resinous components of light and heavy oils. There were generalized the data according to the composition of: 1) structural moieties bound *via* ether/ester and sulphide bridges in RAM molecules; 2) compounds adsorbed/occluded by asphaltenic molecules; 3) nitrogenous bases (NB) in resins. The common approach towards the structural research on resins and asphaltenes has enabled to reveal peculiarities of the composition of molecules in oil components of oils in varying chemical nature and determine their similarities and differences. The results of the performed analysis are of important fundamental and applicational significance due to a steady increase in explored and recoverable reserves of heavy oils that are characterised by a high content of high-molecular-weight heteroorganic compounds in the total balance.

EXPERIMENTAL

Resinous-asphaltenic materials in light oil from the Krapivinskoye field (I) (West Siberian oil and gas basin, Russia) and heavy oil of Usinskoye field (II) (the Timan-Pechora oil-gas basin, Russia) were research objects. The constituents are significantly different in density, the content of RAM and heteroatoms (Table 1).

In order to isolate asphaltenes and resins, the standard technique was used [10]. Asphaltenes were differentiated onto high- (HMA) and low-molecular-weight (LMA) components and compounds adsorbed/occluded by their molecules, *i.e.* maltenes [12]. Fractions of low-polar and polar compounds eluted by mixtures of *n*-hexane and benzene, and also by methanol and chloroform (1 : 1 and 1 : 4 by volume, respectively) were isolated from maltenes by column liquid adsorption chromatography using ASK silica gel.

The partitioning of NB was carried out from a hexane solution of resins according to a scheme involving deposition steps of high-molecular-weight bases with hydrogen chloride (K-1), the additional deposition of hydrocarbon-soluble high-molecular-weight nitrogenous base chlorides with diethylamine (K-2), and extraction of low-molecular-weight NB with sulphuric acid solution (K-3) [13].

Samples of resins, asphaltenes, high- and low-molecular-weight NB were exposed to structural-group analysis *via* the technique premised on the combined use of elemental composition data, (Vario EL Cube C-, H-, N-, S-analyser), average molecular weights (MW) (by cryoscopy in benzene), and ¹H NMR data (Bruker AVANCE AV 300 spectrometer at 300 MHz in CDCl₃ solutions). In the course of calculations, there were determined the following parameters: m_a – quantity of structural units in the average molecule; K_o^* , K_a^* , and K_n^* – total number of cycles, number of aromatic and

naphthenic rings in the structural unit, respectively; C^* and C_p^* – total number and number of carbon atoms in the paraffin fragments of the structural unit, correspondingly, and C_γ – amount of carbon atoms in the terminal methyl groups not bound to the aromatic ring.

The breakage of sulphidic and ether/ester bonds in molecules of resins and asphaltenes was carried out using nickel boride and boron tribromide, respectively. Conditions for selective reactions are described in [12].

The analysis of liquid products of liquid products of chemical decomposition of RAM, slightly polar fractions of maltenes and low-molecular-weight NB was performed by gas chromatography-mass spectrometry (GC-MS) using Thermo Scientific DFS system. Conditions for producing spectra, their processing and approaches to the determination of compounds are given in [12].

RESULTS AND DISCUSSION

Asphaltenes

The content of asphaltenes in oil II is by 4.3 times higher than that in oil I (see Table 1). They are characterised by higher values of average MW (1405 against 940 Da) and sizes of the average species due to a greater number of structural units in their composition ($m_a = 3.0$ against 2.2) compared to asphaltenes in oil I. In this case, the structural units of asphaltene molecules of heavy and light oils are almost not different according to total cyclicity ($K_o^* = 8.0$ and 7.9), and also to the number of aromatic ($K_a^* = 3.3$ and 2.8), naphthenic ($K_n^* = 4.7$ and 5.1), and alkyl ($C_{alk}^* = 1.7$ and 1.5) moieties.

Regardless of the oil type, asphaltenes have a similar nature of compound distribution according to MW. The main contribution to the composition of asphaltenic components is made by HMA (MW of 1009 and 1500 amu for oils I and II, respectively). The fraction of LMA (MW of 550 and 770 Da) and maltenes (MW of 500 and 700 Da) is much lower. Oil II is different from oil I by a higher content of HMA (92.2 against 87.1 rel. %).

A feature of oil I is a higher content of LMA (5.4 against 3.7 rel. %) and the almost twice higher content of maltenes (6.7% against 3.4 rel. %). The most different fractions of asphaltenes (HMA and maltenes) were used for comparative characteristics of asphaltenic components of oils of different nature.

TABLE 1
Characteristics of research objects

Samples	Yield, %	Density, kg/m ³	Content, mass %			
			S	N	N _b [*]	O
Oil I		867	1.05	0.35	0.03	4.42
Resins	8.8		3.78	0.56	0.25	5.45
Asphaltenes	2.6		2.34	0.89	–	3.86
Oil II		1008	1.98	0.62	0.19	3.24
Resins	19.1		2.96	1.08	0.55	6.34
Asphaltenes	11.2		3.42	1.14	–	9.66

* As determined by non-aqueous potentiometric titration [11].

High molecular weight asphaltenes

As determined, in molecules of the HMA investigated, fragments linked *via* sulphide (sulphur-bound) and ether/ester bridges are presented by saturated and aromatic hydrocarbons (AHC), and also by heteroorganic compounds (HOS). Normal and branched alkanes, alkylcyclopentane and alkylcyclohexane derivatives, sterane, terpane, alkylbenzene, and alkyltoluene compounds were determined as a part of the bound components in both cases [12 and 15]. Herewith, the same representatives of saturated and aromatic HC in the composition of HMA in oil I are characterised by a greater number of carbon atoms in the main chain or alkyl substituents. This is exemplified by the distribution of *n*-alkanes as a part of rupture products of ether/ester bonds in molecules of high-molecular-weight oils I and II in Fig. 1, *a* and *b*.

A distinguishing feature of HMA molecules of oil I is the presence of sulphur-bound components of C₁₆–C₃₄ 1-alkenes with an even number of carbon atoms in a molecule (Fig. 2, *a*), unsaturated C₃₀ hopanes, C₁–C₄ naphthalenes, C₀–C₁ anthracenes, C₀–C₄ phenanthrenes, C₀–C₂ fluoranthenes and pyrenes, C₀–C₂ triphenylenes and chrysenes, C₀–C₂ perylenes, benzofluoranthenes, and benzo[*a*]pyrenes, C₀–C₂ benzo[*g,h,i*]perylene, dibenzochrysenes, and also C₀–C₁ dibenzopyrenes [15].

Among HOC of breakdown products of S–C and C–O bonds in HMA molecules of oil I, C₀–C₃ dibenzothiophenes together with C₁₃ and C₁₅ aliphatic alcohols were determined. In HOC of breakdown products of S–C and C–O bonds of HMA molecules of oil II, C₁₄–C₂₂ alkylthiophenes and dibenzothiophene, and also some C₁₄–C₁₈ aliphatic acids and ethyl esters of C₁₆–C₂₀ aliphatic acids were identified. The presence of alkylthiophenes in the composition of asphaltenes was found by the authors of [16] in the products of thermolysis of Athabasca asphaltene components. The determined ethyl esters are most likely occluded by HMA, as chemical decomposition may lead not only to the rupture of covalent bonds but also to the release of compounds inside asphaltene structures [17]. It should be noted that upon a relatively high content of total nitrogen in asphaltenes (see Table 1) within rupture products of C–S and C–O bonds, organonitrogen compounds of neutral and basic nature (carbazole and pyridine derivatives, respectively) were not found. Therefore it can be assumed that the listed components are not bound to the nucleus of molecules of the investigated asphaltenes by sulphide or

ether/ester bridges but are mainly located in their condensed polycyclic components.

Maltenes

As demonstrated by the GC-MS research of compounds from the low-polar fraction of asphaltenic components of oils I and II, these systems contain the following compounds. The latter are the following: normal and branched alkanes, alkylcyclopentanes, alkylcyclohexanes, steranes, terpanes, *n*-alkylbenzene and fetanyl benzene compounds, alkyltoluenes, alkylsilanes, naphthalene, phenanthrene, benzo- and dibenzothiophene homologues, and also benzocarbazole and dibenzofuran derivatives. Systems of similarly named compounds have the same mass distribution. A distinguishing feature of the low-polar fraction of maltenes in oil II is that the latter contains more tricyclic terpanes, phenylalkanes with different locations of the phenyl substituent in the alkyl chain, tetra- and pentacyclic aromatic hydrocarbons (AHC), including phenyl and naphthalene derivative, and also naphthobenzothiophenes, carbazoles, fluorenones and ethyl esters of higher fatty acids with an even number of carbon atoms. The low-polar fraction of maltenes in oil I is notable for the presence of 1- and 2-alkenes with an even number of carbon atoms in a molecule (see Fig. 2, *b*), and dibenzocarbazoles. As demonstrated by comparative analysis data, some compounds determined in low-polar fractions of maltenes, mainly, *n*-alkanes, naphthenes, HC compounds are a part of the structure of HMA molecules. Compounds of the same name have a similar molecular mass distribution but are different in the nature of the concentration distribution.

Resins

Sufficiently high concentrations of heteroatoms are typical for the investigated resins (see Table 1). The content of S, N and O in resins of oil I is 3.6, 2.7, and 1.2 times higher, respectively, than that in crude oil. In resins of oil II, the content of these heteroatoms is 1.5, 1.7 and 2.0 times higher, respectively, than in crude oil.

Hence, the fraction of resins in the oil I has 32, 14, and 11 % of S, N, and O atoms, whereas that of resins of oil II contains 29, 33, and 37 % of S, N, and O atoms as determined in crude oil. Compounds in resins of oil I that contain the N atom are represented by NC by 45 %, whereas resin concentration in oil II is 51 %. The measured values of MW of oil II resins is higher than those of

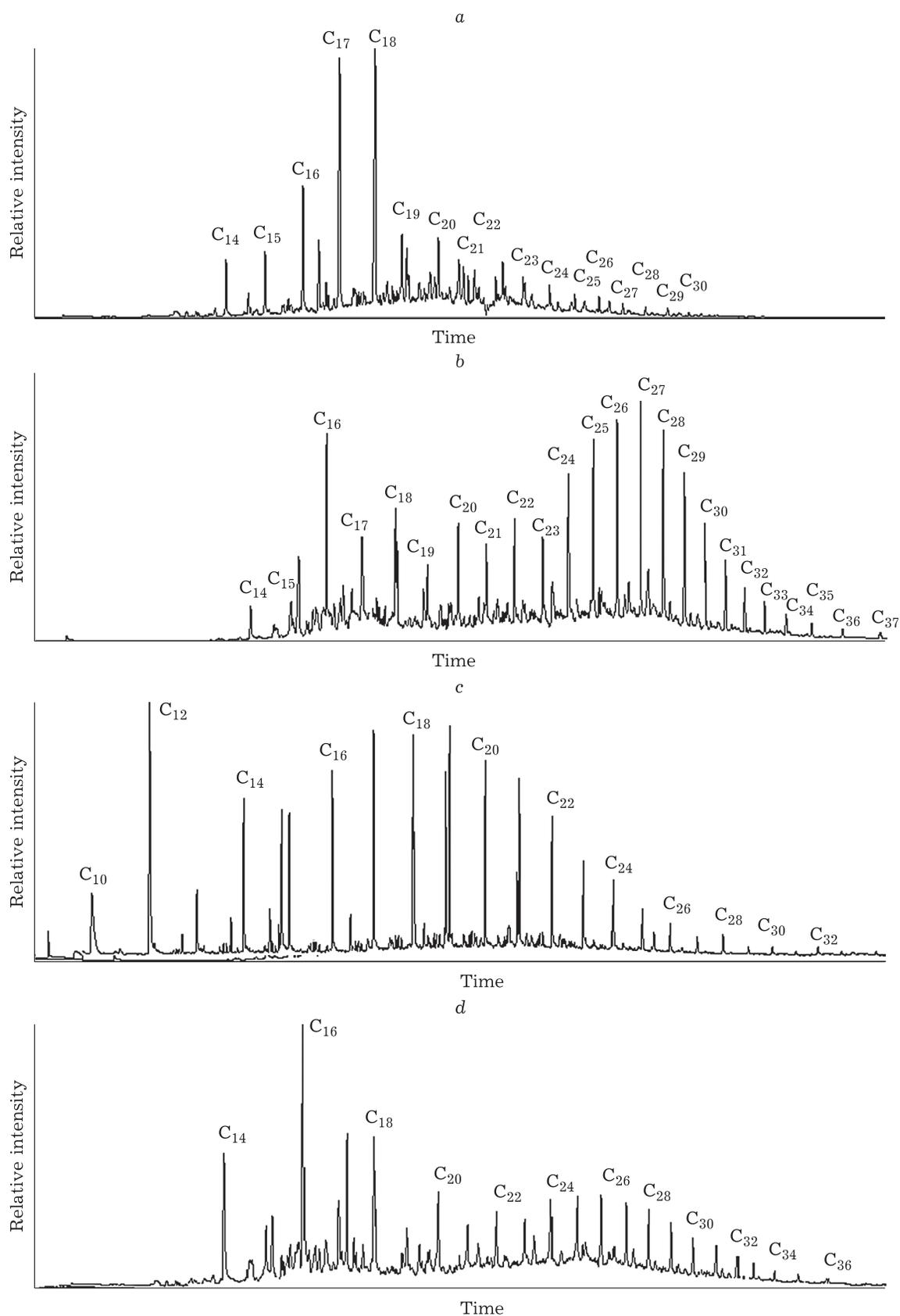


Fig. 1. Mass chromatograms of rupture products of ether/ester bonds by ion m/z 71: *a* and *b* – in molecules of heavy and light oils, correspondingly; *c* and *d* – in molecules of resins of heavy and light oils, respectively.

C₁₄–C₃₇ – number of paraffinic carbon atoms.

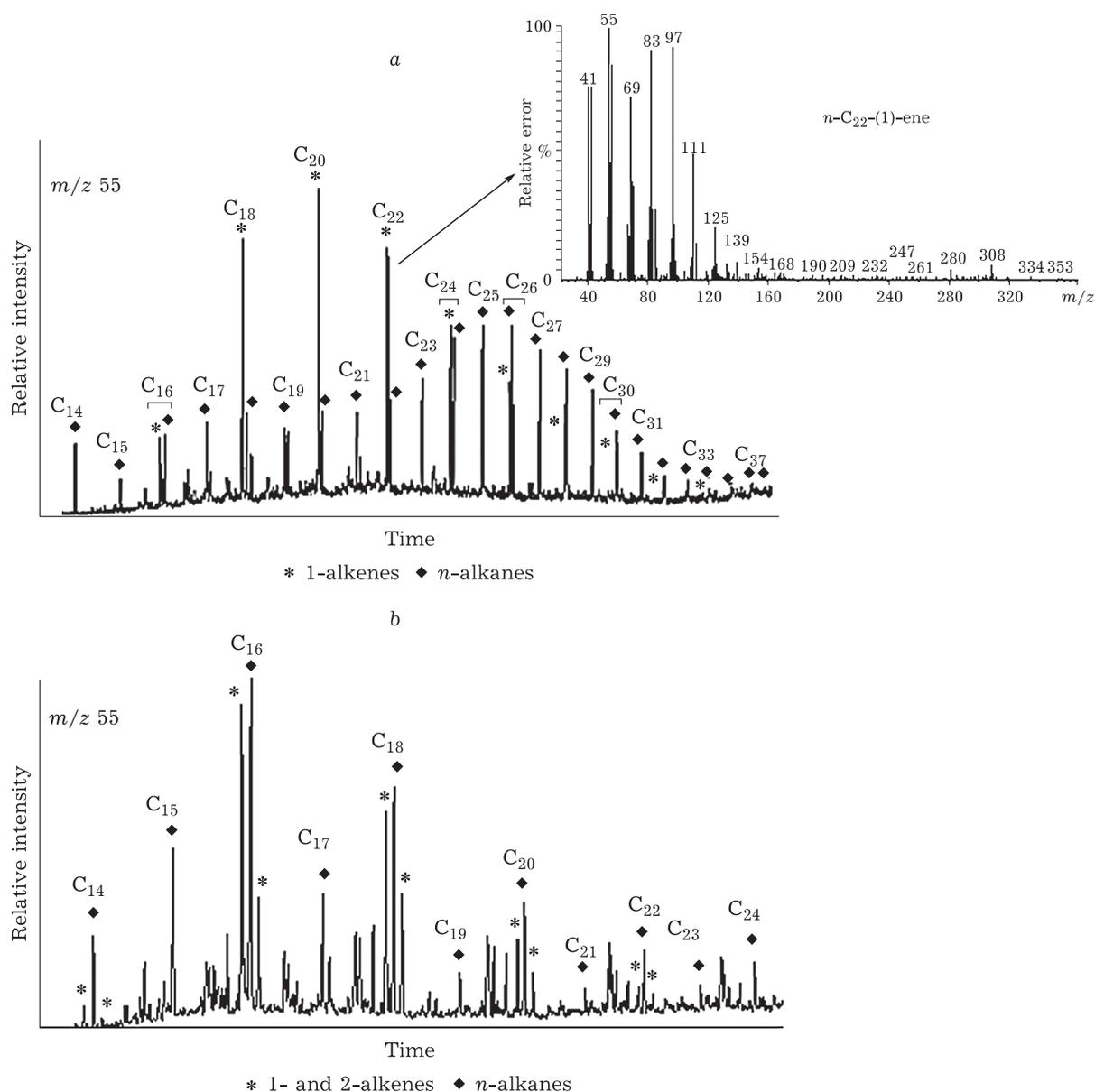


Fig. 2. Mass chromatograms of rupture products of sulphide bonds in molecules of HMA (a) and maltenes (b) of light oil according to the ion with m/z 55.

oil I (877 and 480 amu, correspondingly). Carbon atoms in the average species of resins in oils I and II form one and two structural units, respectively ($m_a = 1.2$ and 1.8). Herewith, the average species are larger due to a higher development of aromatic ($K_a^* = 2.4$ against 1.5) and naphthenic ($K_n^* = 3.1$ against 2.5) compounds and alkyl moieties ($C_a^* = 10.8$ against 8.5). In both cases, most C_a^* are found in long weakly branched alkyl substituents ($C_\gamma^* = 2.0$ and 2.6).

According to the data of GC-MS analysis, in soluble products of the chemical breakdown of ether/ester bonds in molecules of resins of both types, there are *n*-alkanes, methyl-substituted alkanes

with varying locations of the substituting radical, isoprenoids (2,6,10-trimethylalkanes, pristane, and phytane), alkylcyclopentanes, alkylcyclohexanes, steranes, hopanes, phytanylbenzenes, and also mono-, di-, tri-, and tetraalkylbenzenes [6 and 13].

When the qualitative composition of saturated and aromatic HC is similar, resins of oils I and II are different according to the molecular content of separate representatives of ether/ester moieties. Figure 1, c and d reports an example of the distribution of *n*-alkanes in the rupture products of C–O-bonds in molecules of the investigated resins. There are also differences in the molecular mass distribution of bound monoarenes. In molecular

crystals of resins of oil I, these fragments are characterised by a large number of carbon atoms in the alkyl substituent of *n*-alkylbenzenes, alkylmethylbenzenes, alkyl-dimethylbenzenes, and alkyl-tetramethylbenzenes. A feature of resin molecules of oil II is the presence of ether/ester moieties of pregnanes (low-molecular-weight steranes) and chelanthenes (tricyclic terpanes), C₀-C₄ naphthalenes and C₀-C₂ phenanthrenes, C₂-C₅ benzothiophenes, C₀-C₄ dibenzothiophenes and normal aliphatic alcohols with the composition of C₁₂, C₁₄, C₁₆, and C₁₈ [6]. Among ether/ester moieties of resin molecules of oil I, there are no polycyclic AHC and GOS were not found.

Common sulphur-bound moieties in molecules of resins of oils I and II are *n*-alkanes, monomethyl-substituted alkanes with varying locations of the substituting group, isoprenoids (2,6,10-trimethylalkanes, pristane, and phytane), alkylcyclopentanes, alkylcyclohexanes, phenylalkanes, monoarenes, and monobasic aliphatic acids. As well as in case of ether/ester compounds, sulphur-bound moieties of resins of oil I stand out. For example, *n*-alkanes and monocycloalkanes are characterised by a wider molecular mass distribution and monoarenes – by a greater number of atoms in the aliphatic substituent. A feature of molecules of resins in oil I is also the presence of steranes, tri- and pentacyclic terpanes close in composition to ether/ester analogues, ethyl esters of *n*-alkanoic acids, aliphatic alcohols and bicyclic sulphides as a part of sulphur-bound moieties [13].

Nitrogenous bases of resins

As demonstrated by the analysis results reported in Table 2, the type of oil has an effect on the quantity of NB isolated from resins and the nature of the distribution of the latter according to the corresponding concentrates. For example, the total yield of NB compounds from resins of oil II is significantly higher (40.8 mass %) than that using resins of oil I (26.1 mass %). The main isolated compounds in both cases are K-1 and K-2 components. However, K-1 components are prevailing in resins of oil II, whereas in resins of oil I the quantities of high-molecular-weight components K-1 and K-2 are comparable. The content of the extracted compounds K-3 in the composition of resins of both oils is insignificant. The oils are almost not different according to the relative content of N_b in the composition of compounds isolated from resins (84.3 rel. % for resins of oil I and 85.9 rel. % for resins of oil II). However, in the case of resins of oil II, the main N_b amount

(79.9 rel. %) is a part of the K-1 component structure. The K-2 and K-3 components account for only 3.6 and 2.4 rel. %, respectively. In case of resins of oil I, the N_b fraction in the composition of K-1 components is significantly lower (31.8 rel. %) and that in the structure of components K-2 and K-3 is much higher (38.1 and 14.4 rel. %).

With the common trend of changing MM in a series of the concentrates isolated (K-1 > K-2 > K-3), NB of oil resins are different by higher values of average MW. The magnitudes are driven by structural features of the average species of NB of the investigated resinous components. The average species in nitrogenous bases of resins in light oil contain more structural entities (*m_a*) than NB of resins of heavy oil (see Table 2). In this case, the structural entities of similar concentrates are close according to the total number of rings (*K_t^{*}*). However, the former are different in the composition of the polycyclic system, the number of carbon atoms in paraffinic components of structural entities (*C_p^{*}*), and the distribution nature of the latter in aliphatic moieties. Naphthoaromatic compounds of structural entities of average species of NB of oil I resins contain more aromatic rings (*K_a^{*}*), and those of oil II – naphthenic ones (*K_n^{*}*).

It has turned out that the number of paraffinic carbon atoms is higher in the average structural entities than that in average structural units of NB of concentrates K-1 and K-2 in resins of oil II. A feature of BS of resins in oil II is a large number of paraffinic carbon atoms in structural entities of average species of low-molecular-

TABLE 2
Physicochemical characteristics and average structural parameters of nitrogen base molecules

Parameters	Samples					
	Oil resins I			Oil resins II		
	K-1	K-2	K-3	K-1	K-2	K-3
Yield, %	10.93	13.21	1.94	38.6	2.2	2.3
MW, Da	1018	607	383	844	519	365
N	1.29	1.73	2.20	1.36	1.36	1.30
N _b	0.73	0.72	1.86	1.86	0.90	1.22
<i>m_a</i>	2.3	1.6	1.2	1.9	1.3	1.0
<i>K_b[*]</i>	5.8	4.7	3.4	6.0	5.4	3.5
<i>K_a[*]</i>	2.8	2.2	1.4	2.5	1.6	1.1
<i>K_p[*]</i>	3.0	2.5	2.0	3.5	3.8	2.4
<i>C[*]</i>	30.6	25.0	20.9	29.7	27.6	24.1
<i>C_p[*]</i>	6.8	5.6	6.6	5.0	5.0	9.2
<i>C_α[*]</i>	4.7	4.0	3.7	4.3	3.6	3.2
<i>C_γ[*]</i>	1.7	1.5	1.8	2.4	2.4	2.9

weight compounds K-3. As it follows from the comparison of average values of the C_7^* parameter, the average structural entities of NB molecules of resins in oil I contain less relatively long or branched paraffinic chains than that in structural entities of NB molecules of resins of oil II.

Low-molecular-weight nitrogenous bases of resins

According to GC-MS analysis, there are C_2 - C_3 quinoline and C_2 - C_5 benzoquinoline homologues in low-molecular-weight NB of concentrates K-3. The nature of mass-spectra of intensive peaks in mass-chromatograms (the maximum intensity of the molecular ion peak, a low ratio of $[M-H]^+/M^+$ ions, and the lack of peaks of rearrangement ions) indicate that azaarenes determined are mainly presented by methyl-substituted compounds [18]. Among alkyl-substituted quinoline derivatives, there are 2,3,4-trimethyl- and 2,4,6-trimethylquinoline compounds. There were unambiguously determined 2,4-dimethylbenzo(h)- and 2,4,6-trimethylbenzo(h)quinoline compounds in benzoquinoline homologues.

CONCLUSION

As demonstrated by the analysis results of the research on the composition and structure of resinous-asphaltene materials in light and heavy oils, features of asphaltene and resins of heavy oil are higher values of average molecular masses, the number of the bound structural units and mean sizes of polyarene rings. Herewith, there is a lower development of aromatic moieties condensed with the aromatic ring of the molecules, and the prevalence of bulky aromatic substituents.

Heavy oil is characterised by an increased content of high-molecular-weight asphaltene (HMA), light one – by a higher concentration of low-molecular-weight asphaltene (LMA) and maltene. As determined, sulphur-bound and ether-bound moieties in the molecules of the investigated HMA are represented by saturated and aromatic hydrocarbons and heteroorganic compounds (HOS). Herewith, the same representatives of saturated and aromatic hydrocarbons in the structure of HMA in light oil contain a greater number of carbon atoms in the main chain or alkyl substituents. Hydrocarbons (HC) of the same classes are found in the composition of low-polar maltenic compounds as in the composition of bound moieties. The feature of maltene of heavy oil is the presence of a wider set

of polycyclic naphthenes and aromatic hydrocarbons (AHC) in the maltenic composition.

Among compounds bound by both ether/ester and sulphide bridges in molecules of resins in oils of both types, there are normal and branched alkanes, phenyl-substituted alkanes, alkylcyclopentane and alkylcyclohexane derivatives, and also mono-, di-, tri-, and tetraalkyl-substituted benzene homologues. A distinctive feature of molecules of resins in heavy oil is the presence of ether/ester bound moieties and polycyclic AHC and HOC in their composition, whereas that of resins in light oil – sulphur-bound moieties of polycycloalkanes, ethyl esters of *n*-alkanoic acids, aliphatic alcohols, and bicyclic sulphides.

Nitrogenous compounds in molecules of the investigated resinous-asphaltene materials (RAM) are not bound *via* sulphide and ether/ester bonds to the core of molecules but are present in condensed polycyclic components of the latter. Nitrogenous bases (NB) in resins of oils of both types are presented by high- and low-molecular-weight components, the total content of which in resins of heavy oil is higher than that in light one. Herewith, NB of resins in light oil are notable for higher values of average MW. In the structure of the average species of these systems, the contribution of aromatic fragments is more apparent, whereas that in the composition of the average species of NB of resins in heavy oil – naphthenic moieties. There are similar alkyl-substituted homologues of quinoline and benzoquinoline in the structure of low-molecular NB of the investigated resins.

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