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Oxygen- and Nitrogen-Containing Structural Fragments of Resin and Asphaltene Macromolecules Inherent in Heavy Oil from the Usinsk Oilfield

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Abstract

The composition and structural features of the resin-asphaltene macromolecular fragments inherent in the substances from the Usinsk oilfield were investigated. It has been demonstrated that they contain ether and/or ester groups. Nitrogenous bases in the form of supramolecular structures are present only in the structure of the resinous components.

Key words: resins, asphaltenes, nitrogen bases, esters and ethers, composition

INTRODUCTION

Effective solving the problems associated with the processing of hydrocarbon raw material characterized by a high content of high molecular mass compounds depends to a considerable extent on the amount and profundity of information concerning the structure of resin-asphaltene substances (RAS). The fact is that the structural features of the macromolecules of resins and asphaltenes significantly affect the thermal stability and reactivity thereof.

This paper is devoted to the investigation of the characteristics of the RAS inherent in oil from the Usinsk oilfield (Republic of Komi), one of the largest deposits of heavy oil species in Russia currently being developed [1]. The authors of [2–5] studied in detail the hydrocarbon and sulphur-containing fragments of resin and asphaltene macromolecules inherent in this oil and demonstrated that the main representatives thereof are presented by paraffin chains, phenanthrenes, pyrenes, dibenzo- and benzonaphthothiophenes. Information obtained on the nitrogen- and oxygen-containing structures composing the RAS concerns mainly the compounds of carbazole and furan series. This paper presents the results of studying the composition and structural features of the macromolecular fragments of RAS containing basic nitrogen and ether/ester bonds.

EXPERIMENTAL

We studied the asphaltenes of the Usinsk oil and alcohol-benzene resins those constitute the bulk (73.8 rel. %) of the resinous components [6]. For the isolation of the samples under investigation we used a standard approach described in [7]. The elemental composition of the resulting products and functional composition of hetero compounds was analyzed according to procedures described in [8, 9].

The procedure of concentrating the organic nitrogen bases (NB) and the subsequent fractionation thereof into strongly and weakly basic components was carried out by means of acidic extraction [10] and liquid adsorption chromatography on silica gel modified with HCl [11].

In order to characterize the macromolecular fragments of RAS containing ether/ester bonds in the structure thereof, we used a scheme involving the stages of their destruction by boron tribromide and the reduction of alkyl bromides formed with the help of lithium aluminum hydride [12].

The IR spectra were registered using a NiTOlet 5700 spectrophotometer within the range of $4000-400\ \mathrm{cm}^{-1}$.

The mass spectra and GC-MS patterns were obtained using a DFS GC-MS unit (TERMO Scientific). The conditions of mass spectral analysis and calculation method are presented in [13, 14], the conditions of GC-MS analysis being reported in [15].

RESULTS AND DISCUSSION

Characterizing the nitrogen bases of the resin-asphaltene components of the Usinsk oil

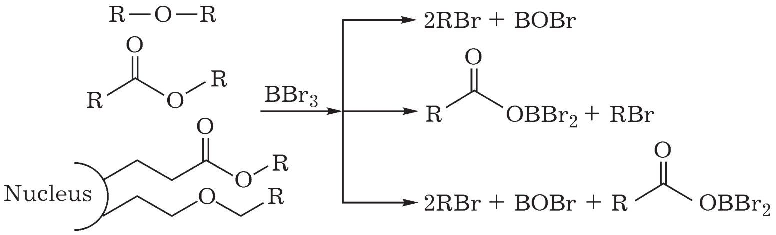
According to [16], the basic nitrogen determined in the composition of resins and asphaltenes, is predominantly included in the composition of high molecular compounds as structural elements due to the formation of σ-bonds. A smaller part of the RAS basic nitrogen is a part of the relatively low molecular mass compounds, those are adsorbed on the macromolecular entities of resins and asphaltenes due to donor-acceptor interactions. In order to isolate such bases we used a 25 % solution of sulphuric acid in 80 % acetic acid [10], whose use provides almost complete extraction of low molecular mass nitrogenous bases from complicated organic mixtures [17]. In the case of oil under investigation, with using this extractant we succeeded in the isolation of low molecular mass NB from resins only. A negative result in the extraction of asphaltenes might be caused, to all appearance, either by a higher strength of their supramolecular structures as to compare with the resins or by the absence of low molecular mass nitrogenous bases in the structure of asphaltene macromolecules.

According to the results of elemental analysis (N_{tot} = 3.5 mass %) and functional analysis, the nitrogen-containing components isolat-

TABLE 1

Structural-group composition of low molecular mass organic nitrogen bases inherent in alcohol-benzene resins from the Usinsk oil

Compounds	Content normalized to the sum of compounds identified, %
Strong nitrogenous bases	
Benzoquinolines (z = 17, 19)	20.4
Dibenzoquinolines (z = 23–27)	22.6
Tribenzoquinolines (z = 29, 31)	5.9
Thiophenoquinolines (z = 19)	5.8
Benzothiophenoquinolines (z = 21–25)	13.2
Dibenzothiophenoquinolines (z = 27, 29)	10.2
Benzoquinolinecarboxylic acid (z = 21, 23)	7.3
Dibenzoquinolinecarboxylic acid (z = 25–29)	11.8
Tribenzoquinolinecarboxylic acid (z = 31)	3.0
Weak nitrogenous bases	
Benzoquinolones (z = 19, 21)	23.7
Dibenzoquinolones (z = 23–27)	16.7
Tribenzoquinolones (z = 29, 31)	11.5
Dibenzothiaquinolones (z = 23–27)	17.3
Tribenzothiaquinolones (z = 29, 31)	8.0
Benzoquinolinecarboxylic acids (z = 21, 23)	13.9
Dibenzoquinolinecarboxylic acids (z = 25, 27)	8.6



Scheme 1.

ed from resins contain strong (N_b = 1.4 mass %) and weak $N_{w/b}$ = 2.1 mass %) nitrous basic compounds. The IR spectrum of the concentrate exhibit absorption bands inherent in pyridine benzologues (inflection at 1576 cm^{-1}) and in the carbonyl group of the amides (inflection at 1650 cm^{-1}) those are characteristic of strong and weak NB, respectively [17]. The absorption bands at 3211 and 1720 cm^{-1} indicate the presence of carboxyl-containing nitrogen compounds those, depending on the position of the carboxyl group with respect to the nitrogen atom could exhibit either strongly or weakly basic properties [18]. One should not exclude the presence of bases containing phenolic hydroxyl group in the structure (absorption of the free OH groups is located at 3600 cm^{-1}, that of the bound OH groups being at 3585 cm^{-1}), as well as sulphoxides (1037 cm^{-1}) in the mixture. The latter are similar in the properties to the weakly basic nitrogen compounds [9], and thus they could be extracted from complicated organic mixtures by means of the reagent we used [19].

The subsequent separation of the concentrate obtained on silica gel modified with hydrochloric acid, allows one to obtain products containing either a mixture of strong and weak bases, or strong bases only [11]. With the use of the mass spectral analysis, we demonstrated that the composition of the strong NB of the resins under investigation involves the alkyl and naphtheno derivatives of benzo-, dibenzo- and tribenzoquinolines, thiopheno- and benzothiophenoquinoline, benzo-, dibenzo- and tribenzoquinolinecarboxylic acids (Table 1). Prevailing compounds are presented by aza-arenes (48.9 rel. %), whose distribution maximum falls at dibenzoquinolines (22.6 rel. %). Among the strong sulphur-containing (29.2 rel. %) and carboxyl-containing (21.9 rel. %) nitrogenous bases, such compounds as benzothiophenoquinolines (13.2 rel. %) and dibenzoquinolinocarboxylic acid (11.8 rel. %) are characterized by a high content. The weak NB of the resins are presented by the derivatives of benzo, dibenzo and tribenzoquinolone, of dibenzo- and triben-

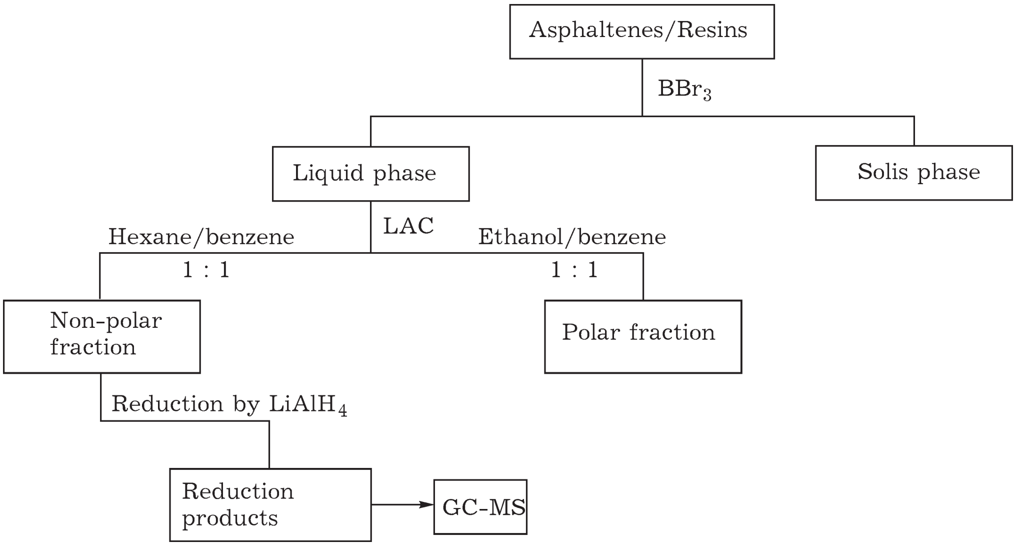


Fig. 1. Schematic diagram of studying the macromolecular fragments of resins and asphaltenes containing ether/ester bonds.

zothiaquinolone, as well as by the derivatives of benzo- and dibenzoquinolinecarboxylic acid. Prevailing compounds are presented by heterocyclic aromatic amides (52.0 rel. %), whose distribution maximum falls at benzoquinolones (23.7 rel. %). The most part of weak sulphur-containing (25.4 rel. %) and carboxyl-containing (22.5 rel. %) nitrogenous bases is presented dibenzothiaquinolones (17.3 rel. %) and benzoquinolinecarboxylic acid (13.9 rel. %).

Characterizing the oxygen-containing molecular fragments of the resin-asphaltene components of the Usinsk oil

The destruction of the ether and ester bonds by boron tribromide occurs *via* the reactions outlined in Scheme 1 [20].

In the case of interaction between the reagent and the resins or asphaltenes under investigation one can observe the formation of two phases, the liquid phase and solid phase (see Fig. 1). The IR spectra of the liquid bromination products exhibit distinct absorption bands inherent in C–Br bonds in alkyl bromides (622, 570, 550 cm^{-1}), which indicates the presence of fragments containing ether and/or ester groups in the RAS macromolecular structure. In addition, the IR spectra of the liquid phase of RAS exhibit absorption bands inherent in paraffinic chains (2922, 2852, 2729, 1462, 1378 cm^{-1}) aromatic rings (1602, 874, 805, 758 cm^{-1}) and sulphoxides (1029 cm^{-1}).

The set of absorption bands in the IR spectra of the solid phase indicates the presence of fragments containing aromatic (1589, 810, 780, 751 cm^{-1}) and aliphatic compounds (2919, 2849, 1440, 1377 cm^{-1}) in the macromolecular structure of resins and asphaltenes. Furthermore, they contain sulphoxides (1030 cm^{-1}) and fragments presented by carbazoles (stretching vibrations of the NH group at 3420 cm^{-1}) and acids (stretching vibrations of OH groups at 3235, 1700 cm^{-1}). The absorption bands inherent in alkyl bromides are almost absent. in the IR spectra of the solid phases These results allowed us to suggest that the ether/ester bonds are located in the end ("peripheral") parts of the macromolecules of resins and asphaltenes, thus the products of the destruction thereof enter the liquid phase.

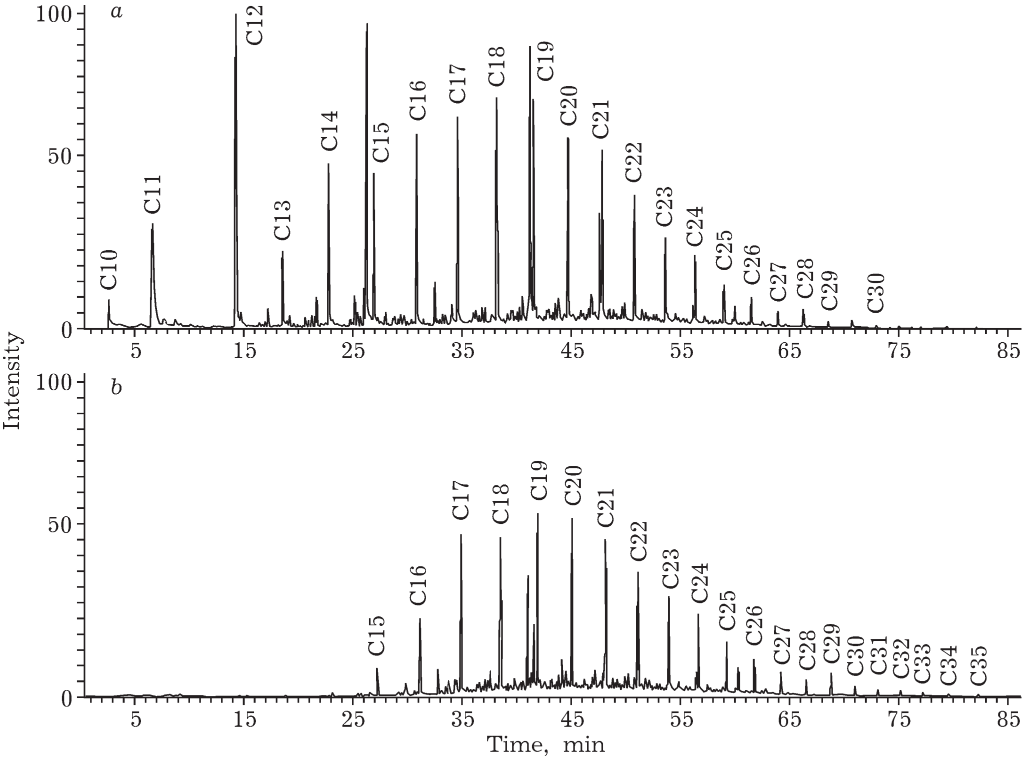


Fig. 2. Chromatography-mass spectral patterns for the reduction reaction products resulting from the alkyl bromides of the Usinsk oil resins (*a*) and asphaltenes (*b*) with respect to ions with m/z 57 (n-alkanes).

In order to investigate the composition of the resulting products the liquid phase was divided into a polar and non-polar fractions; the latter was reduced with lithium aluminum hydride, to analyze the products obtained by means of CMS.

According to the results of the CMS analysis, the structural fragments of resinous and asphaltene macromolecules containing ester groups include *n*-alkanes, aromatic hydrocarbons (AH) and heteroatomic compounds.

Alkanes with normal structure in the reduction products of resins are presented by C_{10}–C_{30} homologues (see Fig. 2, *a*), whereas those in the reduction products of asphaltenes are presented by C_{15}–C_{35} homologues (see Fig. 2, *b*). The maximum in the distribution thereof primarily falls at C_{18}–C_{20} compounds. A similar molecular mass distribution of *n*-alkanes is revealed for the reduction products of oil asphaltenes taken from a number of oilfields in China [20]. It should be also noted that there is a high content of C_{12} homologue observed in the *n*-alkanes of the resins.

Among the AH belonging to the reduction products of resins and asphaltenes there are mono-, bi- and tricyclic structures present with a maximum content (50.8–76.1 rel. %) of monocyclic compounds (Table 2). Among those there were identified monoalkylbenzenes (*m*/*z* 91) alkyltoluenes (*m*/*z* 105), alkylxylenes (*m*/*z* 119), 1-alkyltrimethylbenzenes (*m*/*z* 133). The resins are characterized by an increased content of monoalkylbenzenes, whereas the asphaltenes are characterizes by an increased content of alkyltoluenes (see Table 2).

TABLE 2

Content of aromatic hydrocarbons in the products of resin and asphaltene reduction, % with respect to the sum of aromatic hydrocarbons identified

Compounds	Content	
	Resins	Asphaltenes
Monoalkylbenzenes	21.6	23.2
Alkyltoluenes	18.2	28.8
Alkylxylenes	6.6	13.2
1-Alkyltrimethylbenzenes	4.4	10.9
Naphthalenes	27.3	14.0
Diphenyl	14.9	–
Phenanthrenes	7.1	9.9

Monoalkylbenzenes (*m*/*z* 91) inherent in the resins (Table 3 and Fig. 3) are presented by homologues C_{14}, C_{17}, C_{18}, C_{19}, those we assigned by us to phenylalkane isomers with different positions of the phenyl substituent in the alkyl chain [21, 22]. The mass chromatograms of alkylbenzenes inherent in asphaltenes do not exhibit peaks *1*, *2* and *10*, which indicates the absence octylbenzene, 1-butylheptylbenzene, 1-methyldodecylbenzene in their structure. In both cases, the most of monoalkylbenzenes are presented by C_{18} and C_{19} isomers.

The alkyl substituted alkylbenzenes with *m*/*z* 105, 119, 133 inherent in the reduction products of resin contain a lower number of carbon atoms than the respective structures of

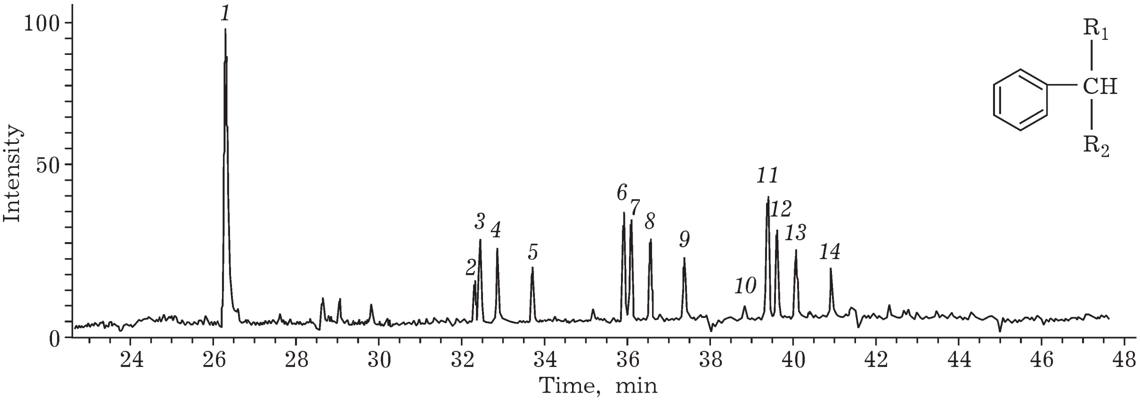


Fig. 3. Chromatography-mass spectral patterns for the reduction reaction products resulting from the alkyl bromides of the Usinsk oil resins, with respect to ions with *m*/*z* 91 (alkylbenzenes): *1* – octylbenzene, *2* – 1-butylheptylbenzene, *3* – 2-propyloctylbenzene, *4* – 1-ethylnonylbenzene, *5* – 1-methyldecylbenzene, *6* – 1-pentylheptylbenzene, *7* – 1-butyloctylbenzene, *8* – 1-propylnonylbenzene, *9* – 1-ethyldecylbenzene, *10* – 1-methyldodecylbenzene, *11* – 1-pentyloctylbenzene, *12* – 1-butylnonylbenzene, *13* – 1-propyldecylbenzene *14* – 1-ethylundecylbenzene.

TABLE 3

Content of alkylated benzene derivatives in the products of resin and asphaltene reduction, % with respect to the sum of aromatic hydrocarbon types identified

Total number of C atoms in alkyl substituents	Monoalkylbenzenes *m/z* 91		Alkyltoluenes *m/z* 105		Alkylxylenes *m/z* 119		1-Alkyltrimethylbenzenes *m/z* 133	
	Resins	Asphaltenes	Resins	Asphaltenes	Resins	Asphaltenes	Resins	Asphaltenes
C_5	–	–	–	–	12.3	–	–	–
C_6	–	–	4.1	–	9.6	–	16.1	–
C_7	–	–	6.5	–	12.4	–	12.4	–
C_8	–	–	17.8	–	11.4	–	24.3	–
C_9	–	–	4.8	5.0	7.5	–	15.6	15.5
C_{10}	–	–	6.2	5.0	5.5	4.2	12.6	20.2
C_{11}	–	–	13.1	15.8	7.3	12.7	7.2	21.7
C_{12}	–	–	16.3	22.9	7.7	25.3	11.8	15.4
C_{13}	–	–	15.3	21.7	16.2	25.6	–	7.3
C_{14}	24.7	–	7.3	12.6	10.1	17.5	–	13.3
C_{15}	–	–	4.8	10.1	–	7.8	–	6.6
C_{16}	–	–	3.8	6.9	–	6.9	–	–
C_{17}	17.8	20.8	–	–	–	–	–	–
C_{18}	29.3	42.0	–	–	–	–	–	–
C_{19}	28.2	37.2	–	–	–	–	–	–

Note. Dash denotes the compound to be absent.

asphaltenes (see Table 3). So, among the alkyltoluenes of resins there are compounds with an alkyl chain length of from 6 to 16 carbon atoms, among the alkylxylenes there are chains having from 5 to 14 carbon atoms, among the trimethylbenzenes there a those having from 6 to 12 carbon atoms. The maximum content is exhibited by alkyltoluenes C_8, C_{12}, C_{13}, alkylxylenes C_5, C_7, C_{13} and alkyltrimethylbenzenes C_6 and C_8.

In the case of asphaltenes, for toluenes the alkyl chain length amounts to C_9–C_{16}, for xylenes – C_{10}–C_{16}, for trimethylbenzenes C_9–C_{15} carbon atoms. The bulk thereof is presented by C_{12}, C_{13} alkyltoluenes, C_{12}–C_{14} alkylxylenes and C_9–C_{11} alkyltrimethylbenzenes.

The bicyclic AH of resins are presented by biphenyl, naphthalene and C_1–C_4 alkyl derivatives of the latter (see Table 2, Fig. 4, *a*). Among the asphaltene reduction products there were only C_3 and C_4 alkyl naphthalenes identified. The maximum in the distribution of resinous alkyl naphthalenes falls at C_2 homologues, that of asphaltenes falls at C_3 homologues.

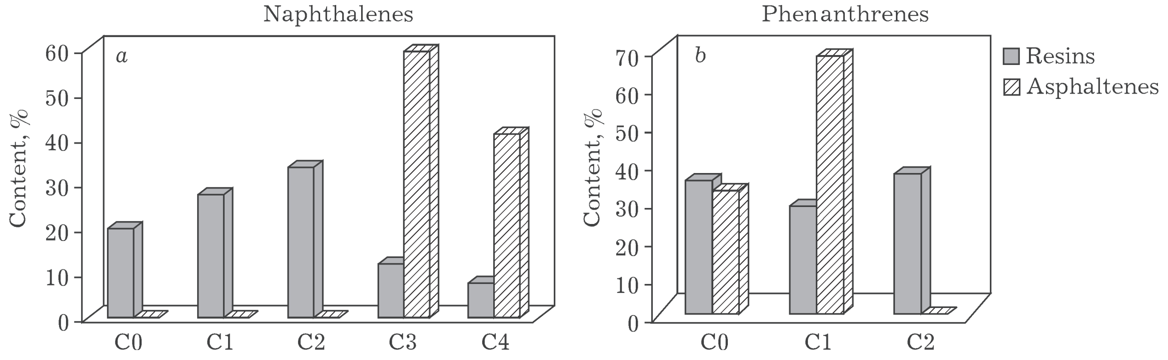


Fig. 4. Distribution of the compounds belonging to naphthalene (*a*) and phenanthrene (*b*) series.

TABLE 4

Content of aromatic sulphur compounds in the products of resin reduction, % with respect to the sum of sulphur compounds identified

m/z	Compounds	Empirical formula	Content
	Benzothiophenes		
162	C_2	$C_{10}H_{10}S$	6.9
176	C_3	$C_{11}H_{12}S$	1.9
190	C_4	$C_{12}H_{14}S$	1.1
204	C_5	$C_{13}H_{15}S$	3.3
	Dibenzothiophenes		
184	C_0	$C_{12}H_8S$	18.8
198	C_1	$C_{13}H_{12}S$	23.3
212	C_2	$C_{12}H_{14}S$	22.6
226	C_3	$C_{13}H_{15}S$	13.2

Among resinous tricyclic AH there are phenanthrene and C_1, C_2 alkyl derivatives thereof (see Table 2, Fig. 4, *b*). No obvious differences in the content of the compounds identified were observed. In the case of asphaltenes the tricyclic AH are presented by phenanthrene and its monomethyl substituted structures with a maximum content of the latter.

Heteroatomic components were detected only in the reduction products of alkyl-bromide resins. They are presented by aromatic sulphur compounds those are composed of C_2–C_5 alkylbenzothiophenes, dibenzothiophene and C_1–C_3 alkyl-substituted structures (Table 4). Sulphur-containing structures (77.8 rel. %) are mainly presented by dibenzothiophenyl. The maximum in the distribution of alkylbenzothiophenes are accounted for homologues of C_3 that in the distribution of alkyldibenzothiophenes is determined by the homologues of C_1 and C_2. Among the composition of alkyl-substituted structures there were identified dimethyl, trimethyl, ethyl, methylethyl, dimethylethyl, diethyl, ethylpropyl-, methyldiethyl-, methylbutylbenzothiophenes, as well as methyl, dimethyl, trimethyl, ethyl, and ethylmethyldibenzothiophenes.

CONCLUSION

The results of our investigations have demonstrated that the structural fragments containing ether group and/or ester groups are involved in the structure of the macromolecules of the resins and asphaltenes of heavy oil. Nitrogenous bases in the form of supramolecular structures are present only in the structure of the resinous components.

Ether/ester bonds could be located in the end ("peripheral") parts of RAS macromolecules. The structural fragments of of resinous and asphaltene macromolecules with ester groups contain *n*-alkanes, phenylalkanes, alkyltoluenes, alkylxylenes, trimethyl substituted alkylbenzenes, alkyl derivatives of naphthalene and phenanthrene.

Aromatic and aliphatic hydrocarbons inherent in asphaltenes are characterized by a great number of carbon atoms in paraffinic chains. The macromolecules resins of contain biphenyl, holonuclear naphthalene as well as alkyl-substituted benzo- and dibenzothiophenes.

The most part of the nitrogenous bases of the resins studied consists of alkyl- and naphthene-substituted dibenzoquinolines, benzothiophenoquinolines, benzoquinolones, dibenzothia- quinolones, benzoquinolino- and dibenzoquinolinecarboxylic acids.

The data obtained append the concepts concerning the structural features of resinous and asphaltene macromolecules inherent in heavy oils, being of importance when dealing with the issues related to the processing thereof.

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REFERENCES

1 Ruzin L. M., Chuprov I. F., Tekhnologicheskiye Printsipy Razrabotki Zalezhey Anomalno Vyazkikh Neftey Bitumov, Izd-vo UGTU, Ukhta, 2007.

2 Grinko A. A., Min R. S., Sagachenko T. A., Golovko A. K., *Neftepererab. i Neftekhim.*, 4 (2012) 24.

3 Grinko A. A., Min R. S., Sagachenko T. A., Golovko A. K., *Chem. Sustain. Dev.*, 20, 5 (2012) 205.
URL: http://www.sibran.ru/en/journals/KhUR

4 Grinko A. A., Min R. S., Sagachenko T. A., Golovko A. K., *Neftekhim.*, 52, 4 (2012) 249.

5 Antipenko V. R., Grinko A. A., Melenevskiy V. N., *Izv. Tom. Politekhn. Un-ta*, 319, 3 (2011) 129.

6 Cheshkova T. V., Kovalenko E. Yu., Vseros. Nauchn. Molodezh. Shk.-Konf. "Khimiya pod Znakom SIGMA" (Treatises), Izd-vo SO RAN, Novosibirsk, 2012, pp. 117–119.

7 Bogomolov A. I., Temyanko M. B., Khotyntseva L. A. (Eds.), Sovremennye Metody Issledovaniya Neftey (Handbook), Nedra, Leningrad, 1984.

8 Chumachenko M. N., Khandik T. A., Sosnina N. P., Vorotnikova V. A., *Khim. Tekhnol. Topl. Masel*, 5 (1983) 39.

9 Galpern G. D., Bezinger N. N., Metody Analiza Organicheskikh Soyedineniy Nefti, Ikh Smesey i Proizvodnykh, Izd-vo AN SSSR, Moscow, 1960, pp. 141–169.

10 Gerasimova N. N., Sagachenko T. A., Beiko O. A., Ogorodnikov V. D., *Neftekhim.*, 27, 1 (1987) 32.

11 Kovalenko E. Yu., Gerasimova N. N., Sagachenko T. A., Golushkova E. B., *Khim. Tekhnol. Topl. Masel*, 4 (2001) 33.

12 Peng P., Morales-Izquierdo A., Hogg A., Strausz O. P., *Energy Fuels*, 11, 6 (1997) 1171.

13 Turov Yu. P., Sagachenko T. A., Unger F. G., *Zh. Analit. Khim.*, 43, 8 (1988) 1406.

14 Polyakova A. A., Molekulyarny Mass-Spektralny Analiz Organicheskikh Soyedineniy, Khimiya, Moscow, 1983.

15 Kovalenko E. Yu., Gerasimova N. N., Sagachenko T. A., Min R. S., *Neftepererab. i Neftekhim.*, 4 (2012) 42.

16 Galpern G. D., *Usp. Khim.*, XLV, 8 (1976) 1395.

17 Beiko O. A., Golovko A. K., Gorbunova L. V., Khimicheskiy Sostav Neftey Zapadnoy Sibiri, Nauka, Novosibirsk, 1988.

18 Jewell D. M., Petroleum in the Marine Environment, Adv. Chem., NY, 1980, ser. 185, pp. 219–232.

19 Kshirtsev V. A., Kovalenko E. Yu., Min R. A., Sagachenko T. A., *Khim. Tv. Topl.*, 4 (2009) 3.

20 Peng P., Morales-Izquierdo A., Lown E. M., Strausz O. P. // Energy Fuels. 13, 2 (1999) 248.

21 Tuo Juncai, Chen Ru, Zhang Mingfeng, Wang Xianbin, *J. Asian Earth Sci.*, 39 (2010) 770.

22 Antipenko V. R., Golubina O. A., Goncharov I. V., Nosova S. V., Ostroukhov S. B., *Neftekhim.*, 47, 3 (2007) 172.