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Composition of Compounds Occluded by Asphaltenes of Oils of Different Chemical Nature

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Abstract. Compounds occluded by asphaltenes of methanonaphthenic oil from the Krapivinskoye field and naphthenoaromatic oil from the Usinskoye field are investigated using the hydrogen peroxide-acetic acid system. The study has found that their composition contains normal and branched alkanes, n-alkylcyclohexanes, n-alk-1-enes, steranes, terpanes and n-alkanoic acids which are similar in structure. The presence of alkyl-substituted benzenes and alkylnaphthalenes in the composition of captured compounds is a distinguishing feature of naphthenoaromatic oil asphaltenes.

Keywords: asphaltenes, oxidation, occluded compounds.

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Состав соединений, окклюдированных асфальтенами нефтей различной химической природы

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Аннотация. С использованием системы перекись водорода – уксусная кислота изучены соединения, окклюдированные асфальтенами метанонафтенной нефти Крапивинского месторождения и нафтеноароматической нефти Усинского месторождения. Показано, что в их составе присутствуют близкие по строению нормальные и разветвленные алканы, *n*-алкилциклогексаны, *n*-алк-1-ены, стераны, терпаны и *n*-алкановые кислоты. Особенностью асфальтенов нафтеноароматической нефти является наличие в составе захваченных соединений алкилзамещенных бензолов и алкилнафталинов.

Ключевые слова: асфальтены, окисление, окклюдированные соединения.

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Introduction

Asphaltenes are the most high-molecular and complicated components of dispersed oil systems. The structural fragments of their macromolecules are aromatic, naphthenic and heteroaromatic rings with alkyl side substituents, which can be condensed into a single polycyclic system or linked to each other through C–S–, C–O– and C_{ar.} – C bridges [1, 2]. The hollow cells of these structures contain compounds captured by the macromolecular skeleton of asphaltenes during their formation [3–5]. Captured (occluded) compounds are practically unaffected by catalytic, microbial and chemical processes occurring in the oil reservoir. This feature of occluded compounds gives rise to interest in studying their composition, since the results obtained are important for solving a number of fundamental and applied problems related to the genesis of oils, the formation of their composition and, as a consequence, the processing of oil stock [3, 5, 6].

In the practice of scientific research, the method of mild oxidation of asphaltenes by a 30 % solution of hydrogen peroxide in glacial acetic acid is widely used to characterize blocked compounds [5, 8, 9]. The method is aimed at the chemical destruction of intercluster bridges inside asphaltene macromolecules, which makes it possible to “weaken” the interactions responsible for their aggregation, thereby facilitating the release of mechanically trapped compounds.

In this work, the hydrogen peroxide – acetic acid system was used in a comparative study of the composition and structure of compounds occluded by macromolecules of asphaltene components of oils of different chemical types. The interest in such investigations is due to the fact that the chemical nature of oils largely determines the composition and structure of their asphaltene agglomerates [3].

Objects and methods of research

The objects of the study were asphaltenes (A) of methanonaphthenic oil from the Krapivinskoye field in Western Siberia (I) and asphaltenes of naphthenoaromatic oil from the Usinskoye field in Komi Republic (II).

The samples under study were isolated according to a procedure that included the stages of precipitation of asphaltenes with a 40-fold excess of n-hexane, extraction of the precipitated products with n-hexane to remove coprecipitated maltenes, and subsequent extraction of the precipitates with hot acetone to remove adsorbed compounds [10].

Oxidation was carried out at room temperature by constant stirring of a mixture of asphaltenes (0.15 g), benzene (50 mL), hydrogen peroxide (4 mL) and acetic acid (14 mL) for 24 hours. At the end of reaction, the remaining acetic acid was neutralized with an aqueous solution of KOH. The organic phase was separated, dried over sodium sulfate and separated with a 40-fold excess (by volume) of n-hexane into soluble and insoluble components. Hexane-soluble components were methylated with a BF_3/MeOH solution (12 %) according to the method described in [11].

The composition of methylation products was determined by IR spectroscopy and gas chromatography-mass spectrometry (GC–MS).

For this purpose, samples of asphaltenes as thin films obtained from a solution in chloroform were analyzed. IR spectra of asphaltene samples were registered using a Nicolet 5700 FT-IR spectrometer in the range of 4000–400 cm^{-1} and then processed using OMNIC 7.3 Thermo Nicolet Corporation software.

To assess differences in the relative content of structural fragments in the molecules of occluded compounds, the ratios of the optical densities of some absorption bands were used. The values of spectral coefficients indicating the relative content of aromatic ($C_1 = D_{1600}/D_{720}$) and aliphatic ($C_2 = D_{720} + D_{1380}/D_{1600}$) structures were calculated. The proportion of fragments containing carbonyl ($C_3 = D_{1710}/D_{1465}$) and sulfoxide ($C_4 = D_{1030}/D_{1465}$) functional groups was also found [12].

GC–MS analysis was performed using a Thermo Scientific DFS gas chromatography-mass spectrometer equipped with a Trace GC Ultra gas chromatographer. The separation of compounds was carried out using a quartz capillary column ($l=30$ m, $d=0.25$ mm, carrier gas – helium) with a 0.25 μm thick DB-5MS stationary phase in the mode of programmed temperature rise from 800 (isotherm for 3 min) to 300 $^{\circ}\text{C}$ at a rate of 4 degrees/min. A final hold time at this temperature was 30 minutes. Mass spectra were obtained at an ionizing voltage of 70 eV and a source temperature of 250 $^{\circ}\text{C}$. The mass spectra were scanned every second in the mass range from 50 to 500 amu. Mass spectral data were

processed using the Xcalibur software. To identify individual compounds, the literature data and the computer library of mass spectra of the National Institute of Standards and Technology (NIST Mass Spectral Library) were used.

Results and discussion

The results of oxidative destruction suggest that A of methanonaphthenic (A I) and naphthenoaromatic (A II) oils differ in the content of compounds occluded by their macromolecules. Their content is higher (5.06 %) in A II than that (2.77 %) in A I. However, the qualitative composition of methylation products of hexane-soluble occluded compounds A I and A II is virtually the same. Some absorption bands in their IR spectra correspond to aliphatic (2970...2800, 1462, 1377 cm^{-1}), aromatic (3050, 1603, 880...730 cm^{-1}), oxygen-containing (3500...3150, 1732 cm^{-1}) and sulfoxide (1040 cm^{-1}) structural fragments. The IR spectra of both samples are characterized by high intensity of absorption bands, which suggest the presence of aliphatic (2925–2854 and 1461–1377 cm^{-1}) and oxygen-containing (3500...3300, 1732 cm^{-1}) structures.

A comparative analysis of the data presented in Table 1 allowed us to assess the differences in the relative content of structural fragments in the samples under study.

Table 1. Characteristics of compounds occluded by AI and AII according to Fourier transform infrared spectroscopy data

Samples	Spectral indices*			
	C ₁	C ₂	C ₃	C ₄
A I	0.92	3.86	1.26	0.38
A II	1.04	3.45	0.99	0.34

*C₁ = D 1600/D 720; C₂ = D 720+D 1380/D 1600; C₃ = D 1710/D 1465; C₄ = D 1030/D 1465

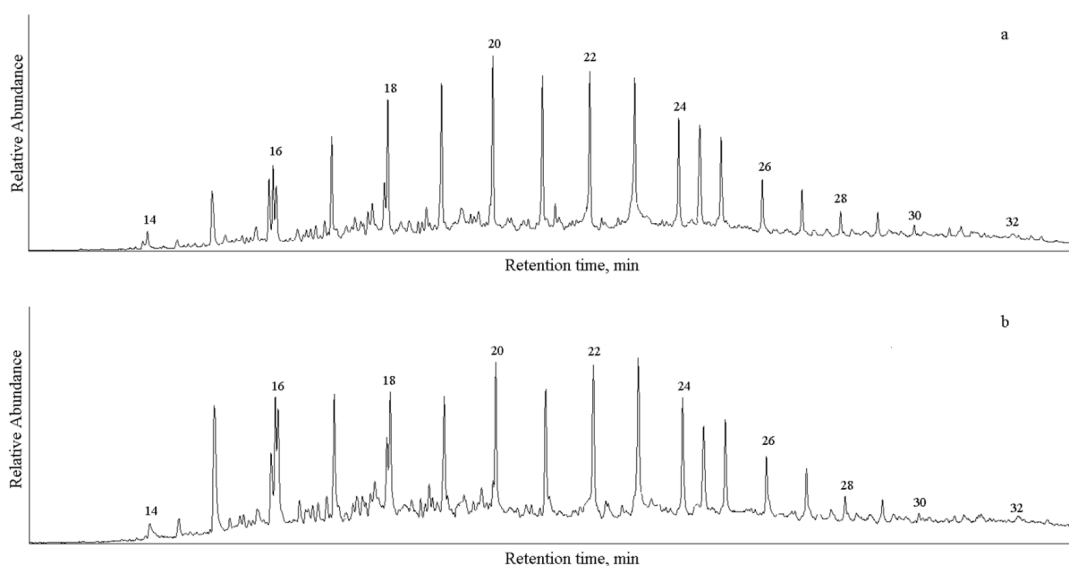
It follows from a comparison of the values of spectral coefficients that compounds occluded by A I are characterized by a higher relative content of aliphatic (C₂) and oxygen-containing fragments (C₃), while compounds occluded by A II are characterized by a higher relative content of aromatic structures (C₁). The content of sulfoxide groups (C₄) of compounds occluded by A I and A II differs slightly.

The results of GC–MS analysis of the methylation products of hexane-soluble occluded compounds suggest the presence of compositionally similar normal, branched and isoprenoid alkanes, n-alkylcyclohexanes, steranes, pentacyclic terpanes (hopanes) n-alk-1-enes with an even number of carbon atoms, phenylalkanes with different positions of the phenyl substituent and n-alkanoic acids identified as methyl esters in the compounds captured by macromolecules of A of methanonaphthenic and naphthenoaromatic oils (Table 2). A distinctive feature of compounds occluded by A of naphthenoaromatic oil is the presence of a fairly wide range of aromatic hydrocarbons in their composition. In addition to phenylalkanes and alkylbenzenes, n-alkylmethyl, n-alkyldimethyl-, n-alkyltrimethylbenzenes and alkyl-naphthalenes have been identified among them.

A comparison of mass chromatograms of the same compounds made it possible to establish that n-alkanes, methyl alkanes, steranes and hopanes, identified in the composition of compounds

Table 2. Composition of compounds occluded by macromolecules of asphaltenes from methanonaphthenic and naphthenoaromatic oils

Compound, m/z	Asphaltenes	
	A I	A II
n-alk-1-enes, 55	C ₁₆ , C ₁₈ , C ₂₀ , C ₂₂	C ₁₆ , C ₁₈ , C ₂₀ , C ₂₂
n-alkanes, 71	C ₁₄ –C ₃₃	C ₁₄ –C ₃₂
methylalkanes, 57, 71	C ₁₅ –C ₃₃	C ₁₅ –C ₃₄
isoprenoid alkanes	C ₁₈ –C ₂₀	C ₁₈ –C ₂₀
n-alkylcyclohexanes, 82, 83	C ₁₅ –C ₂₉	C ₁₄ –C ₂₈
hopanes, 191	C ₂₇ –C ₃₃ ,	C ₂₇ –C ₃₃
steranes, 217	C ₂₇ –C ₂₉	C ₂₇ –C ₂₉
n-alkylbenzenes, 92	non-identified	C ₁₄ –C ₂₄
n-alkylmethylbenzenes, 105	non-identified	C ₁₇ –C ₂₀
n-alkyldimethylbenzenes, 119	non-identified	C ₁₇ –C ₂₀
n-alkyltrimethylbenzenes, 133	non-identified	C ₁₁ –C ₁₆
phenylalkanes, 91	C ₁₇ –C ₁₉	C ₁₇ –C ₁₉
alkylnapthalenes, 142+14	non-identified	C ₁ –C ₃
methyl esters of n-alkanoic acids, 74	C ₁₃ –C ₃₁	C ₁₃ –C ₂₇

Fig. 1. Mass chromatograms of n-alkanes (m/z 71) occluded by asphaltenes of oils A I (a) and A II (b)

occluded by asphaltenes of methanonaphthenic and naphthenoaromatic oils, practically do not differ in the nature of their molecular weight distribution. The structural similarity of these hydrocarbons may indicate their common biological precursor. As an example, the Fig. 1 shows the distribution of n-alkanes found in compounds occluded by macromolecules of A I and A II.

The revealed similarities and differences in the composition of compounds occluded by asphaltenes of oils of different chemical natures are most likely due to the mechanism of formation of asphaltene

components at different stages of the formation of an oil disperse system. Hence, some of them are captured by asphaltenes – structural fragments of kerogen – at the stage of its thermal decomposition. These occluded compounds inherit the nature of the original biomass. Typical representatives of relic compounds traditionally include n-alkanes, n-alkylcyclohexanes, steranes, terpanes and n-alk-1-enes [4, 5, 7, 13].

Another part of occluded compounds can be captured during the later formation of the macrostructure of asphaltenes, which occurs at the stage of thermal transformation of the oil fluids themselves [4, 14]. The most prominent representatives of these occluded compounds are aromatic hydrocarbons. The presence of alkylbenzenes and alkyl-naphthalenes of different composition in compounds occluded by A of naphthoaromatic oil may suggest a greater degree of its catagen maturity.

Conclusions

A comparative study of the composition of compounds occluded by asphaltenes of methanonaphthenic oil from the Krapivinskoye field and naphthoaromatic oil from the Usinskoye field has been carried out using the hydrogen peroxide – acetic acid oxidative system.

It has been found out that

- the content of occluded compounds in the macrostructure of asphaltenes of naphthoaromatic oil is higher than in the macrostructure of asphaltene components of methanonaphthene oil.
- the composition of compounds occluded by asphaltenes of both oils contains alkanes of normal and branched structure, similar in composition, n-alkylcyclohexanes, terpanes, steranes, n-alk-1-enes, phenylalkanes and n-alkanoic acids. A distinctive feature of the compounds occluded by asphaltenes of naphthoaromatic oil is a wider range of aromatic hydrocarbons, represented by n-alkylbenzenes, n-alkylmethyl-, n-alkyldimethyl-, n-alkyltrimethylbenzenes and alkyl-naphthalenes.
- the identified features of the composition of occluded compounds are due to the mechanism of formation of asphaltene components at different stages of the formation of an oil dispersed system.

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