UDC 665.613+617:547.83

DOI: 10.15372/CSD2024545

EDN: NDTGDA

Composition of the Compounds Occluded by Asphaltenes of Heavy Oils

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(Received 15.12.2023; revised 22.12.2023)

Abstract

The products of oxidative destruction of asphaltenes of heavy Paleozoic oils from the Ashalcha and Nurlat oilfields differing in the age of host sediments have been studied. It is shown that oxidation of the asphaltenes of both oils by hydrogen peroxide in the presence of acetic acid results in the release of occluded compounds. The compounds identified in their composition include *n*-alkanes, steranes, hopanes and methyl esters of *n*-alkane acids. A peculiarity of the asphaltenes of Nurlat oil occurring in the Devonian sediments is the presence of *n*-alkenes in the composition of occluded compounds. The presence of occluded compounds in the structure of asphaltenes is confirmed by the results of X-ray diffraction analysis.

Keywords: asphaltenes, oxidation, occluded compounds

INTRODUCTION

Asphaltenes of oil are macromolecules with a complicated multidimensional structure in which hollow cavities able to capture low-molecular compounds can be formed [1]. The captured (occluded) molecules are to a high extent protected from the effect of catalytic, microbial, and chemical processes that take place in an oil system, which makes them useful geochemical markers to characterize the conditions of oil-source rock sedimentation, to follow the routes of oil migration, and to reveal the processes involved in their transformation in reservoirs [1, 2]. In addition to the above-mentioned considerations, the information on the composition of compounds captured by asphaltene macromolecules is important for predicting the quality of products obtained in raw hydrocarbon processing.

The components that remained unaffected by various transformations may be characterised using asphaltene oxidation by chemical reagents [1, 3]. The oxidisers are to meet a number of requirements: they are to destroy the aromatic cycle of asphaltene aggregates [4], to cause no transformations of occluded compounds [1], to be efficient at room temperature or below [5], so that the losses causes by evaporation of occluded compounds might be avoided [6]. Among a broad range of reagents used in research practice, these requirements are most fully met by the 30 % solution of hydrogen peroxide in acetic acid.

Reaction mechanism is as follows: asphaltene molecules are destroyed under the action of the oxidiser due to destruction of inter-cluster bridges, which are oxidised to carboxylic groups. The compounds that are present between aromatic clusters are thus released [7].

The goal of the work was to study the composition of compounds occluded by the macromolecules of high-molecular asphaltenes of heavy Paleozoic oils from the Ashalcha and Nurlat oil-

fields differing from each other in the age of host sediments.

EXPERIMENTAL

Objects of investigation

The objects of investigation are high-molecular asphaltenes (HMA) of heavy oils from the Ashalcha and Nurlat oilfields, sampled from the Permian and Devonian pools, respectively, of the Paleozoic complex situated within the boundaries of the Volga-Ural oil and gas province.

The Ashalcha and Nurlat oils are high-sulphur (sulphur content is 3.89 and 4.70 wt%, respectively) and are characterised by the high asphaltene content (6.40 and 11.09 wt%, respectively).

Sample preparation procedure

The procedure of HMA sample preparation includes the stages of asphaltene precipitation with *n*-hexane taken in a 40-fold excess, extraction of thus obtained precipitates with *n*-hexane to remove co-precipitated maltenes, and subsequent extraction of the precipitates with hot acetone to remove adsorbed compounds [8, 9].

Characterisation of HMA samples subjected to oxidation is presented in [8].

High-molecular asphaltenes of oils were oxidised with a 30 % solution of hydrogen peroxide in acetic acid for 24 h at room temperature under permanent mixing. After the reaction was completed, weakly alkaline aqueous solution of potassium hydroxide (KOH) was added to neutralise residual acetic acid. The organic phase was separated, dried over sodium sulphate (Na_2SO_4), and separated by extraction with a 40-fold excess of *n*-hexane to obtain the soluble and insoluble components. The HMA sample after removal of occluded compounds is designated as HMA*. The soluble components were methylated using a 13–15 wt% BF_3 solution in methanol (CH_3OH) according to the procedure described in [9].

Methods of investigation

The composition of methylation products was analysed by gas chromatography – mass spectrometry (GC-MS) with the help of high-resolution mass spectrometer Thermo Scientific DFS (Germany) equipped with a gas chromatograph Trace GC Ultra. The conditions of chromatograms recording over the total ion current, their processing, and approached applied to identify the compounds are described in [10].

The relative content of different types of compounds in the samples under investigation was evaluated from the total areas of the identified peaks of fragment and molecular ions characteristic of each type of compound.

To characterise the conditions of sediment accumulation, thermal maturation and the degree of catagenic maturity of occluded compounds, we used geochemical parameters Pr/Ph, Ts/Tm, K_{mat}, respectively, where Pr is pristane ($C_{19}H_{40}$); Ph is phytane ($C_{20}H_{42}$); Ts is 22,29,30-trisnorhopane-17α-methyl, 18α; Tm is 22,29,30-trisnorhopane-18α-methyl, 17α; K_{mat} = (αββ, 20R + αββ, 20S) / (ααα, 20R) is the ratio of the sum of isosteranes C_{29} to α-steranes C_{29}.

The samples of HMA and HMA* were studied by X-ray diffraction analysis (XRD), which is widely used at present in the studies of macroarrangement of asphaltene substances [8, 10, 11].

X-Ray diffraction analysis was carried out using an X-ray diffractometer Bruker Discover D8 (CuK_α-radiation, λ = 0.154184 nm) equipped with a 2*D*-detector. Diffraction patterns within the region of 5–80° over 2θ were recorded at room temperature. The parameters of the crystallites of HMA and HMA* macromolecules were obtained from the recorded diagrams processed using the software packages EVA V.1.3 and TOPAS V.4.2. X-Ray diffraction studies were carried out with the diffractometer at the Multi-Access Centre, TSC SB RAS (Tomsk).

RESULTS AND DISCUSSION

General characterisation of asphaltene samples under investigation

According to the data reported in [8], HMA comprise the major part of asphaltene components of heavy oils. These compounds account for 94.1 % in the asphaltenes of oil from the Ashalcha oilfield and 95.0 % in the asphaltenes of oil from the Nurlat oilfield. With the close values of HMA relative content in initial asphaltenes, the samples under study differ from each other in the measured molecular masses, the H/C atomic ratios, and the distribution of heteroatoms. For instance, HMA of oil from the Nurlat oilfield are characterised by smaller molecular mass in comparison with HMA from the Ashalcha oilfield (1247 against 1700 a.m.u.), the macromolecules of the former

are less aromatic (H/C = 1.18 against 1.15), but they contain more nitrogen (1.68 against 1.56 wt%) and sulphur (7.45 against 5.38 wt%). As shown by the results of oxidative destruction, HMA of Nurlat oil contain twice as much occluded compounds than of oil from the Ashalcha oilfield (4.79 against 2.65 wt%).

Composition of the compounds occluded by high-molecular asphaltenes of heavy oils

According to the data of GC-MS analysis, the products of oxidation of the asphaltenes under investigation contain saturated hydrocarbons and heterorganic compounds.

In both HMA samples, occluded hydrocarbons (HC) are represented by *n*-alkanes, isoprenoid alkanes (pristane and phytane), hopanes and steranes. Among HC occluded in the asphaltenes of Nurlat (Devonian) oil, we additionally identified *n*-alkenes with the even number of carbon atoms in the chain (C_{16}, C_{18}, C_{20}, C_{22}). The authors of [2] have assumed that *n*-alkenes are the products of decomposition of the asphaltenes that captured these hydrocarbons at the early stages of organic matter transformation.

Comparison of the corresponding mass-chromatograms allowed us to reveal the similarities and differences in the composition of the same groups of compounds. One can see in Fig. 1, *a* that *n*-alkanes occluded in asphaltenes of Ashalcha oil from the Permian sediments are characterised by monomodal molecular mass distribution of homologues from C_{17} to C_{32} with maximum at C_{23}, while *n*-alkanes occluded in asphaltenes of oil from the Devonian sediments are characterised by the bimodal molecular mass distribution of homologues from C_{14} to C_{34} with the maxima at C_{18} and C_{25} (see Fig. 1, *b*). The presence of low-molecular homologues C_{14}–C_{16} in HC captured by HMA in Nurlat oil may evidence in favour of looser structure of its asphaltenes, which promotes occlusion of *n*-alkanes with low molecular mass [3]. A specific feature of HC in HMA of Nurlat oil is also a higher concentration of isoprenoid alkanes – pristane and phytane. Their ratio (Pr/Ph = 2.2) confirms that HC occlusion by asphaltenes of heavy Devonian oil proceeded under oxidative sedimentation conditions [2].

Hopanes that have been identified among occluded HC are represented in both cases by the homologous series from C_{27} to C_{33} (Fig. 2). Lower value of Ts/Tm ratio for HMA of Nurlat oil (0.94) in comparison with HMA of Ashalcha oil (1.09) may be evidence of the fact that occlusion of saturated HC in the case of Nurlat oil proceeded at earlier stages of the accumulation of initial organic matter [12]. Most probably, this difference is related to the structural features of asphaltenes of oil from the Nurlat oilfield, in particular their looser structure [10].

Steranes among HC occluded in HMA of both kinds of oil are represented by cholestanes (C_{27}), methylcholestanes (C_{28}) and ethylcholestanes (C_{29}). Maturation coefficient (K_{mat}), characterising the degree of thermal maturity of occluded compounds, is higher for HMA of Ashalcha oil (1.89) than for HMA of Nurlat oil (1.56). This may confirm the fact that HC occlusion in the structure of

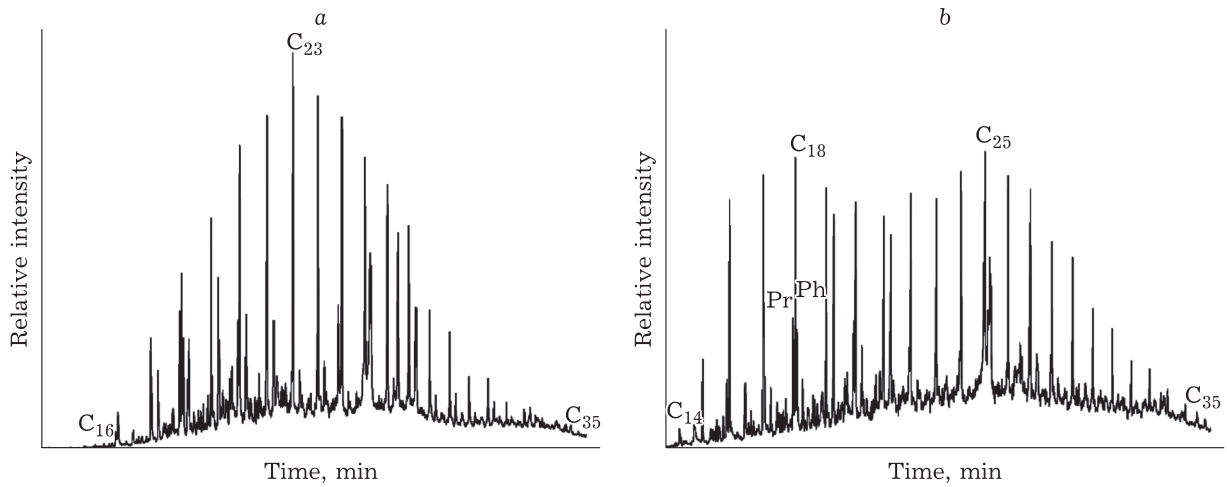

Fig. 1. Mass chromatograms of *n*-alkanes (*m*/*z* 71) occluded in the high-molecular asphaltenes of Ashalcha (*a*) and Nurlat (*b*) oils.

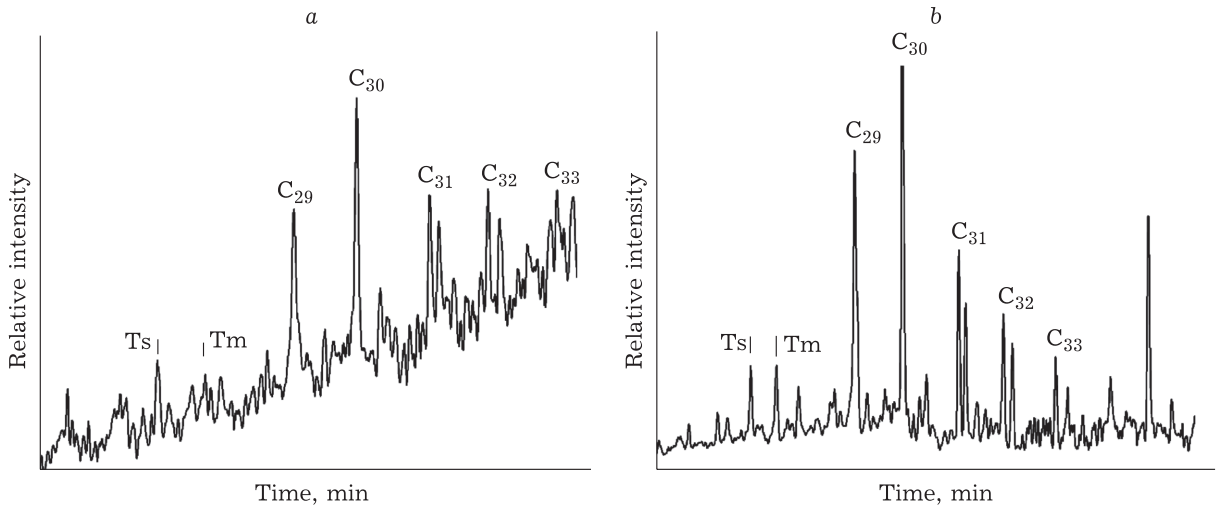

Fig. 2. Mass chromatograms of hopanes (m/z 191) occluded in the high-molecular asphaltenes of Ashalcha (*a*) and Nurlat (*b*) oils.

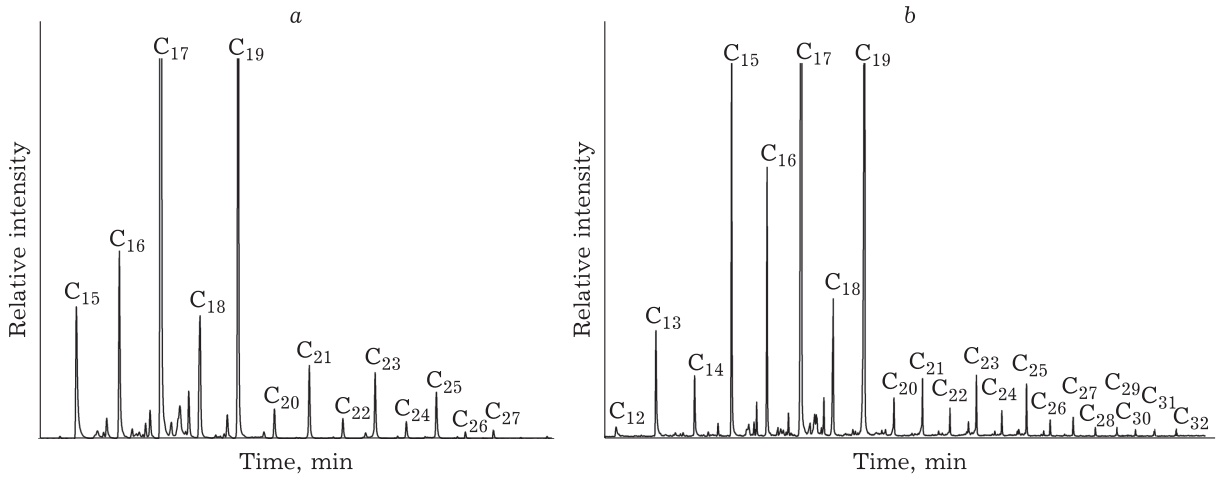

Fig. 3. Mass chromatograms of methyl esters of fatty acids (m/z 74) occluded in the high-molecular asphaltenes of Ashalcha (*a*) and Nurlat (*b*) oils.

asphaltenes of Nurlat oil occurred at earlier stages of organic matter transformation [13].

Among hetero-organic compounds captured in HMA of heavy oils, methyl esters of *n*-alkane acids have been identified. In the case of Nurlat oil, they are represented by the homologous series from C_{12} to C_{32}, and in the case of Ashalcha oil – from C_{15} to C_{27} with the maximal content of C_{17} and C_{19} homologues in both cases (Fig. 3).

Prevalence of the methyl esters of palmitic and stearic acids may be evidence of the substantial contribution from the fat of marine or lacustrine organisms (plankton or algae) into the formation of organic matter of oil [14, 15]. It cannot be excluded that methyl esters could be formed by methylation of *n*-alkane acids captured by asphaltenes at an early stage of the formation of their structure.

X-Ray diffraction of asphaltenes

Application of XRD allowed us to obtain the data on the structure of macromolecules of asphaltenes under investigation. It follows from Fig. 4 that the diffraction patterns of HMA and HMA* of heavy oils contain profiles with three broad peaks. The first peak (γ-line) within angle range 19–21° over 2θ corresponds to the presence of saturated (naphthenic and/or acyclic) fragments in the structure of asphaltene macromolecules, the second peak (002 line) within angle range 25–26° over 2θ relates to crystal-like pack formations, the third peak (100 line) within angle range

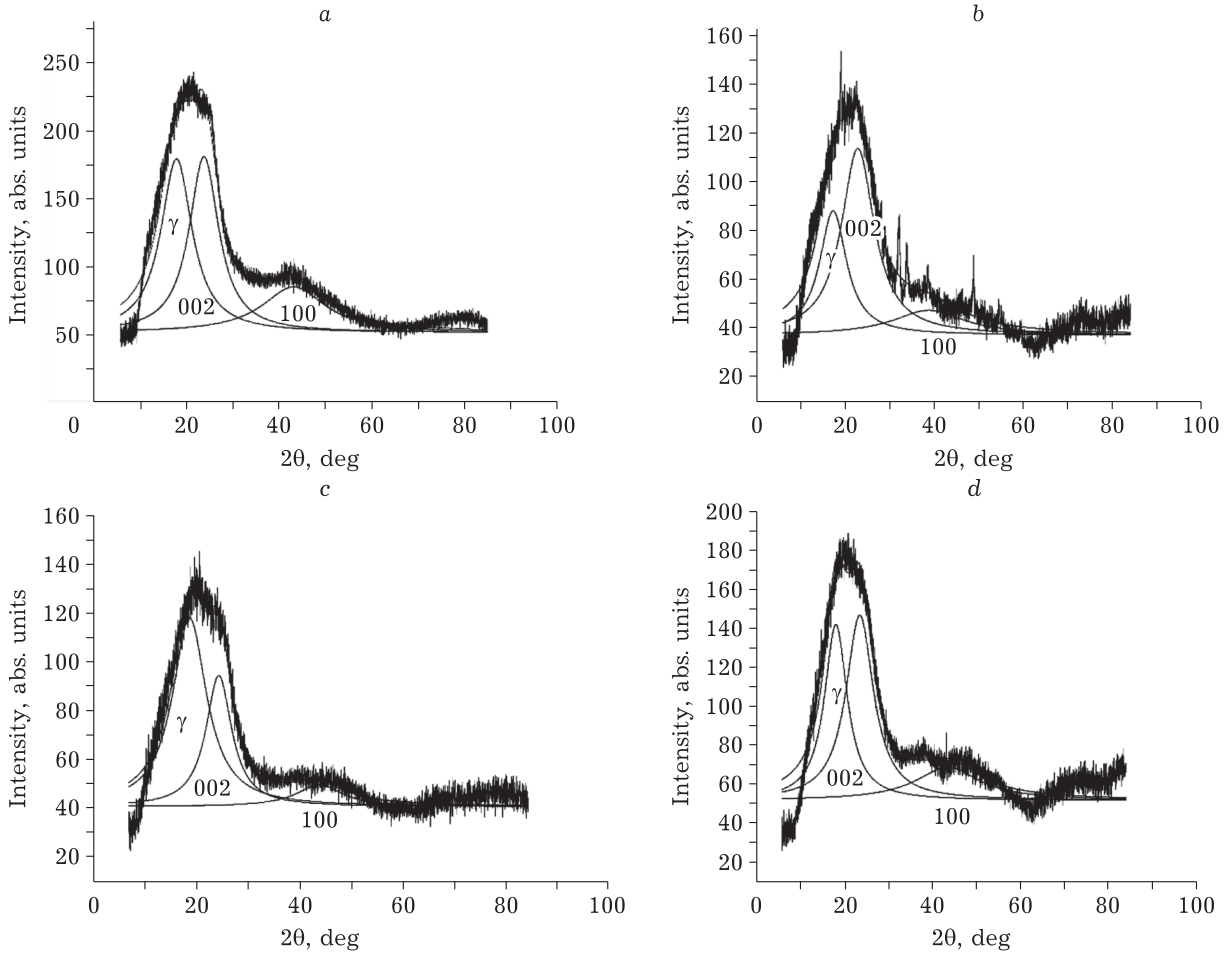

Fig. 4. Diffraction patterns and deconvolution curves of the main peaks for the high-molecular asphaltenes of Ashalcha (*a* and *b*) and Nurlat (*c* and *d*) oils before and after removal of occluded compounds, respectively.

40–45° over 2θ relates to the flat structure of aromatic plates in the nanoaggregates of asphaltene molecules [16, 17].

Comparison between the intensities of peaks on the curves obtained by deconvolution of the main peaks shows that the intensity of peaks related to saturated fragments decreases when passing from HMA to HMA*, and the intensity of peaks corresponding to the presence of crystal-like packed structures. The intensities of peaks characterising the presence of aromatic structures remain almost unchanged. A decrease in the intensities of peaks in the region of 19–20° over 2θ proves the presence of occluded saturated compounds in the macrostructure of HMA in heavy oil.

According to the data presented in Table 1, the packed core of the macromolecules of HMA from Ashalcha and Nurlat heavy oils has a close thickness of crystal-like pack (L_c) 10.50 and 13.47 Å, containing 4-5 aromatic layers (M = 3.83 and 4.69) with average diameter (L_a) equal to 10.59 and 16.17 Å, respectively. The distance between separate aromatic layers (d_m) is 3.72 and 3.66 Å, which does not exceed 4 Å. One layer includes four to six aromatic cycles, and the average number of aromatic rings in a layer (N_a) is equal to 3.94 and 6.06. Saturated fragments that enclose polyaromatic cores are located at a distance (d_r) 4.74 and 4.92 Å from each other; aromaticity degree (f_a) is equal to 0.34 and 0.49, respectively.

Removal of captured compounds causes changes in the structure of crystal-like packed HMA formations. It may be assumed (see Table 1) that the trend of changes in HMA* structure is related to an increase in the degree of asphaltene molecule aromaticity, an increase in the size of aromatic pack and the number of aromatic layers in it, an increase in the diameter of aromatic layer and the average number of aromatic rings in a layer, a decrease in the interlayer distance in the packs. The entire set of the parameters of HMA*

TABLE 1

Structural parameters of HMA and HMA* of Ashalcha oil (AO) and Nurlat oil (NO) according to the data of X-ray diffraction analysis

Sample	Parameter						
	d_m, Å	d_r, Å	L_c, Å	M	L_a, Å	N_a	f_a
HMA AO	3.72	4.92	10.52	3.83	10.50	3.94	0.49
HMA* AO	3.65	5.79	12.47	4.42	10.61	3.98	0.65
HMA NO	3.66	4.74	13.47	4.69	16.17	6.06	0.34
HMA* NO	3.58	5.64	20.20	6.64	20.36	7.63	0.56

Note. HMA and HMA* are high-molecular asphaltenes before and after removal of occluded compounds, respectively; d_m is the distance between the neighbouring aromatic layers in the pack; d_r is the distance between saturated structural fragments (the nearest alkyl chains or naphthelen cycles) in the packs; L_a is the average diameter of the aromatic layer; L_c is the average height of the pack of aromatic layers; M is the number of aromatic layers in the pack; N_a is the average number of aromatic rings in the layer; f_a is the degree of asphaltene molecule aromaticity.

macrostructure provides evidence that removal of occluded compounds leads to a more compact structure of the crystal-like pack, which is most probably due to mainly π–π-interactions (stacking interactions) between aromatic cores [18, 19].

CONCLUSION

The composition of compounds occluded by the macromolecules of high-molecular asphaltenes from heavy Paleozoic oils of the Ashalcha and Nurlat oilfields, differing from each other in the age of host sediments, has been investigated by oxidative destruction. It is shown that the compounds captured by the asphaltene components of heavy oils are represented by *n*-alkanes, hopanes, steranes and methyl esters of *n*-alkane acids. It has been established relying on geochemical indices that occlusion into the structure of asphaltenes in Nurlat oil embedded in Devonian sediments proceeded at earlier stages of organic matter transformation than occlusion into the structure of asphaltenes in Ashalcha oil from the Permian pool. The release of captured compounds causes changes in HMA macrostructure. According to XRD results, HMA* (in comparison with HMA) contains higher relative concentrations of crystal-like packed formations, which are characterised by larger size of the aromatic pack (L_c), an increased number of layers in a pack (M), increased diameter of the aromatic layer (L_a) and the average number of aromatic rings in a layer (N_a), and by decreased interlayer distance (d_m). The set of these parameters provides evidence that the release of occluded compounds leads to an increase in the degree of HMA molecule aromaticity due to the formation of a more compact structure of the crystal-like pack, which is caused mainly by π–π-interactions between arene fragments.

Acknowledgements

The work was carried out within the State Assignment for the Institute of Petroleum Chemistry SB RAS, financed by the Ministry of Science and Higher Education of the Russian Federation (NIOKTR No. 121031200185-6).

Authors thank researchers from the IPC SB RAS: P. B. Kadychagov for having recorded GC-MS spectra, and S. A. Perevezentsev for having recorded XRD spectra.

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