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Organonitrogen Highly Paraffinic Oil Bases and Asphalt-Resin-Paraffin Deposits Formed Therefrom

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Abstract

Being natural surfactants, organonitrogen bases affect the behaviour of oil disperse system *in situ* conditions and upon technogenic exposure on oil fluids. In this regard, characteristics of major compounds of highly paraffinic oils and resulting asphalt-resin-paraffin deposits are important for understanding participation of these compounds in the formation of organic deposits. The work studies the distribution and composition of organonitrogen bases in highly paraffinic oil and a model of asphalt-resin-paraffin deposits obtained from oil under laboratory conditions. Concentrates of high and low molecular mass bases are isolated using sedimentation techniques, extraction, and liquid adsorption chromatography on impregnated oil and sediment sorbents. High molecular mass compounds with a strongly developed alkyl skeleton prevail among highly paraffinic base oils. The fraction of these compounds is higher in sediment than in oil, which indicates their predominant participation in deposit formation. The composition of the isolated bases was characterized by IR and ^1H NMR spectroscopy, and chromatography-mass spectrometry. According to the structural-group analysis, average molecules of organonitrogen bases of oil and residue consist of polycyclic nucleus involving aromatic and saturated cycles with various alkyl skeletons. Average molecules of high molecular mass compounds with strongly developed alkyl substitution (the number of carbon atoms in the alkyl chain (29–32)) may contain 2–3 aromatic and 4–5 saturated cycles. Weakly alkylated (three to five carbon atoms in the alkyl chain) high molecular mass bases are more cyclical due to the development of both aromatic ($K_a = 6–9$) and naphthene rings ($K_n = 10–13$). Alkyl substituents in the structure of their average molecules are presented by methyl groups only. According to the results of chromatography-mass spectrometry studies, the composition of low molecular mass compounds of oil and asphalt-resin-paraffin deposits is characterised by identical sets of alkyl-substituted quinolines, benzo-, dibenzoquinolines, and azapyrenes, among which alkylbenzoquinolines prevail.

Key words: highly paraffinic oil, asphalt-resin-paraffin deposits, organonitrogen compounds, content, composition, IR and ^1H NMR spectroscopy, chromatography-mass spectrometry

INTRODUCTION

An increase in the proportion of highly paraffinic oils in the total level of resources of liquid hydrocarbons sets a number of complex tasks for the oil industry. They are related to the development of new technologies of rational use of these non-traditional raw materials [1]. A high concentration of paraffins contributes to their falling out from oil solutions and the formation of asphalt-resin-paraffin depo-

sits (ARPD) that decrease the efficiency of technologies used for oil extraction and transportation, jointly with resins and asphaltenes [2]. When developing ways to combat ARPD the information of the chemical nature of sediment and oil components, from which they are obtained, is required. It is known that the bulk of heteroatomic oil compounds, in particular, organonitrogen bases that are natural surfactants and exert significant effects on the behaviour of oil disperse system *in situ* conditions and upon

TABLE 1
Characteristic of study objects

Objects	Content, mass %				
	P	Asphaltenes	Resins	N_{tot}	N_b
Oil	9.2	1.2	6.5	0.26	0.017
ARPD	22.9	1.3	9.5	0.30	0.034

technogenic exposure on oil fluids [3–5]. In this regard, the study of characteristics of organonitrogen bases in highly paraffinic oils and ARPD formed in them is important for understanding of the role of these compounds in the formation of organic sediments. This paper presents the results of the study of the composition and distribution of organonitrogen bases in highly paraffinic oil and ARPD formed therefrom.

EXPERIMENTAL

Samples of highly paraffinic oil of West Siberia and ARPD obtained therefrom were studied by cold rod method under laboratory conditions (yield is 17.5 mass %) [6]. From the data of Table 1 it follows that oil and ARPD are almost not different by asphaltene content. Organic deposition is distinguished by higher paraffin content (P), resinous components of total (N_{tot}) and basic (N_b) nitrogen.

Organonitrogen bases were isolated from deasphalted samples of oil and ARPD in ac-

cordance with the scheme (Fig. 1) that included deposition of high molecular mass bases with gaseous hydrogen chloride (K-1), extraction of low molecular mass organonitrogen bases with sulphuric-acetic acid mixture (K-2) and concentration of high molecular mass organonitrogen bases not precipitated by hydrogen chloride by the of liquid adsorption chromatography techniques on silica impregnated with hydrochloric acid (K-3) [7, 8]. Compounds K-1 were separated by the extraction method on components soluble (K-1^{HS}) and insoluble (K-1^{HI}) in hexane [9], K-2 compounds – by liquid adsorption chromatography techniques on silica modified with KOH into nitrogen- (K-21) and nitrogen- and oxygen-containing structures (K-22) [8].

Analysis of concentrates of organonitrogen bases and the products of their separation was carried out using the equipment of the Tomsk Scientific Centre of the SB RAS.

The elemental composition of these samples was defined using Vario EL Cube CHNS-analyser, N_b content – by non-aqueous potentiometric titration method [10], the average molecular mass (MM) – by the cryoscopic method in benzene [11].

Infrared spectra were obtained using Nicolet 5700 FT-IR spectrometer in the 4000–400 cm^{-1} region. The samples were dissolved in CCl_4 , applied on KBr plates, the resulting films were dried.

Proton NMR spectra were recorded using Bruker Avance AV 300 FT-NMR spectrometer

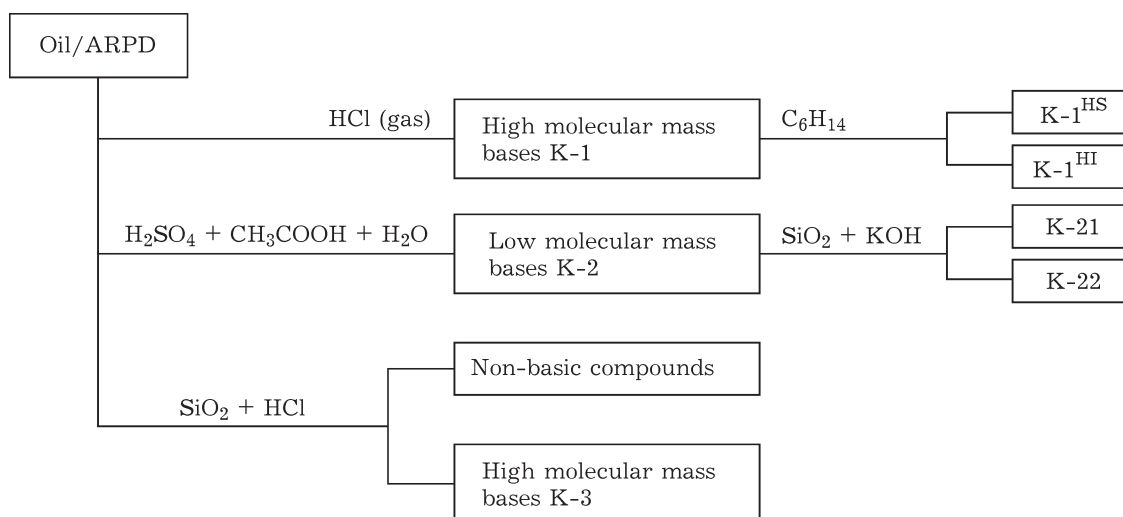


Fig. 1. Scheme for isolation and separation of organonitrogen bases.

at 300 MHz in CDCl_3 solutions. Tetramethylsilane was an internal standard. The relative number of protons in various structural fragments was calculated by ^1H NMR spectra on the assumption of peak areas in appropriate spectrum regions (ppm): H_{ar} (the proportion of protons contained in aromatic structures) 6.6–8.5; H_{α} (the fraction of protons at the carbon atoms in the α -position to aromatic rings); 2.2–4.0; H_{β} and H_{γ} (the proportion of protons in methylene and terminal methyl groups of aliphatic fragments of species, respectively), 1.1–2.1, 0.3–1.1, respectively.

The totality of data about the elemental composition, average molecular masses and proton distribution in ^1H NMR spectra of the samples was carried out to calculate the average structural parameters of species by the methods set out in [12, 13]. The following parameters were defined: the total number (K_{tot}), the number of aromatic (K_{a}) and naphthene cycles (K_{n}) in the average molecule, the number of carbon atoms in paraffinic structural fragments of the average molecule (C_{p}), the number of atoms that are found in terminal methyl groups (C_{r}) not connected with aromatic nuclei.

Gas chromatography-mass spectrometry (GC-MS) analysis of organonitrogen bases was performed on DFS Thermo Scientific instrument. A TR-5MS quartz capillary column with a 30 m length and a 0.25 mm internal diameter was used in the gas chromatograph. Chromatography was carried out in the programmed temperature rise mode from 80 to 300 °C at a 4 °C/min rate and then for 30 min at the final temperature. The carrier gas is helium. Scanning of mass spectra was carried out every second in the mass range up to 500 amu. The results of the CMS analysis were processed using Xcalibur program. To identify individual compounds the data from [14, 15] and the NIST 02 mass

spectral library were used. The relative abundance of every individual compound was assessed as the ratio of its content to the total content of all identified compounds.

RESULTS AND DISCUSSION

As follows from the data of Table 2, oil and ARPD obtained therefrom differ slightly on the total content of the isolated compounds (6.7 и 7.6 mass %, respectively) and the proportion of basic nitrogen bound to them (65.7 and 61.0 rel. %, respectively), the bulk of which (57.2 and 55.8 rel. % for oil and ARPD, respectively) comprises high molecular mass bases K-1 and K-3. Herewith, in the both cases, the relative content of basic nitrogen in K-1 is lower compared to that in K-3. This difference is related to the structure of high molecular mass organonitrogen bases.

According to the method used [7], compounds presented by polycyclic condensed structures with poorly developed alkyl substitution are isolated as hydrochloric salts insoluble in hydrocarbon medium. Differentiation results of high molecular mass compounds K-1 of oil and ARPD on the products soluble and insoluble in hexane demonstrated that they were presented by a mixture of compounds with various MM. This is mainly (61–76 rel. %) bases (K-1^{HI}) insoluble in hexane, close to high molecular mass bases K-3 (907 and 868 amu, respectively) by MM (956 and 1243 amu for oil and ARPD, respectively). The components soluble in hexane (K-1^{HS}) are close to low molecular mass organonitrogen bases (K-2, 354–365 amu, respectively) isolated by acid extraction method by average MM (484 and 538 amu, respectively). Comparative results of isolation of more alkylated structures of high molecular mass organonitrogen bases indicate that the proportion of bases K-3 in the

TABLE 2

Distribution of organonitrogen bases in oil and asphalt-resin-paraffin deposits

Samples	MM, amu		Yield, mass %		Fraction of N_{b} , rel. %	
	Oil	ARPD	Oil	ARPD	Oil	ARPD
K-1	836	793	0.7	0.8	24.8	9.2
K-2	354	365	0.1	0.2	8.5	5.2
K-3	907	868	5.9	6.6	32.4	46.6

TABLE 3

Calculated values of the key structural parameters of organonitrogen base species

Parameters	Oil			ARPD		
	K-1 ^{HS}	K-1 ^{HI}	K-3	K-1 ^{HS}	K-1 ^{HS}	K-3
Number of alkyl carbon atoms:						
C _p	10.0	4.5	31.5	10.1	3.0	29.5
C _r	3.0	4.5	4.6	2.8	3.0	5.0
Ring composition:						
K _{tot}	5.6	21.8	7.2	6.3	17.0	6.6
K _a	2.3	9.2	2.5	2.1	6.4	1.9
K _n	3.3	12.6	4.7	4.2	10.6	4.7

Note. K_{tot}, K_a, and K_n are the total number, the number of aromatic and naphthene rings in the medium-sized molecules, respectively; C_p is the number of carbon atoms in paraffin structural fragments of the average molecules; C_r is the number of carbon atoms found in terminal methyl groups not bound to aromatic rings.

composition of ARPD is higher compared to its proportion in oil that is 46.6 and 32.4 rel. %, respectively. Therefore, mainly high molecular mass highly alkylated organonitrogen bases mainly take part in the formation of ARPD.

This conclusion is consistent with the data of the structural group analysis (SGA) for high molecular mass organonitrogen bases and ARPD. Analysis of calculated values for the main structural parameters of species of K-3 compounds and the products of differentiation of compounds K-1 for the components soluble and insoluble in hexane demonstrated that the medium-sized species of compounds K-1^{HS}, K-1^{HI}, and K-3 of oil and ARPD consisted of aromatic, naphthene and paraffin structural fragments (Table 3). High molecular mass bases K-1^{HI} are characterised by the maximum total cyclicity (K_{tot}). There are more aromatic (K_a) and unsaturated (K_n) rings in the polycyclic system of their medium-sized species than in the struc-

ture of the medium-sized species K-1^{HI} and K-3. The medium-sized species of high molecular mass compounds K-3 and lower molecular mass bases K-1^{HS} are comparable between each other on parameters K_{tot}, K_a, and K_n. Herewith, saturated rings prevail over aromatic in all cases. The medium-sized molecules of bases K-1^{HI} are also characterised by the smallest number of carbon atoms in aliphatic fragments that are presented by only methyl groups (3–5). This follows from the ratio of the total number of alkyl carbon atoms to that in CH₃ groups distant from aromatic rings (C_p/C_r). The medium-sized molecules of compounds K-3, in the structure of which the presence of alkyl substituents with the number of carbon atoms to 6–7 is possible, are distinguished by most developed alkyl substitution. The presence of long alkyl substituents in species of compounds K-3 is confirmed by the data of qualitative IR spectroscopy. The IR spectra of these samples contain

TABLE 4

Structural composition of organonitrogen bases K-1^{HS}

Compounds	Empirical formula	Homologs		Content relatively to the identified structures, %	
		Oil	ARPD	Oil	ARPD
Quinolines	C _n H _{2n-11} N	C ₄ -C ₁₀	C ₆ -C ₁₀	3.2	19.7
Benzoquinolines	C _n H _{2n-17} N	C ₁ -C ₈	C ₁ -C ₈	90.8	61.5
Dibenzoquinolines	C _n H _{2n-23} N	C ₁ -C ₇	C ₁ -C ₇	2.6	7.6
Azapyrenes	C _n H _{2n-21} N	C ₃ -C ₉	C ₃ -C ₉	3.4	11.2

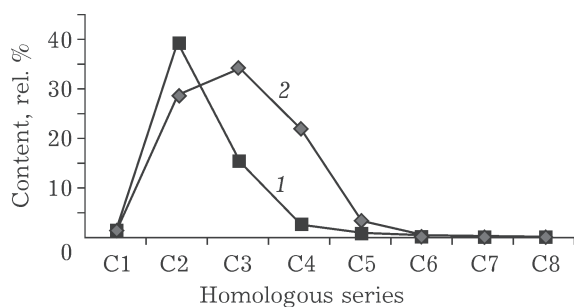


Fig. 2. Distribution of alkylbenzoquinolines in K-1^{HS} of ARPD (1) and oil (2).

relatively intense adsorption bands at 722–721 cm^{-1} typical for alkyl fragments with the number of carbon atoms over 4. The medium-sized species of bases K-1^{HS} occupy the intermediate position on C_p values and the substituent sizes (3–4 carbon atoms).

With the overall trends of a change in the structure of the medium-size molecules of K-1^{HS}, K-1^{HI}, and K-3 bases of oil and ARPD, the medium-sized molecules of organic deposits are characterised by a smaller number of aromatic and saturated rings and carbon atoms in alkyl substitution. K-1^{HS} compounds of ARPD and oil

are slightly different on calculated K_a , K_n , C_p , and C_r values.

The structural similarity of K-1^{HS} bases of oil and ARPD is confirmed by the study results of their individual composition using GC-MS method. Alkyl derivatives of quinoline, benzoquinoline, and azapyrene with the maximum content of alkylbenzoquinolines are present among bases of these samples (Table 4). Molecular mass distributions of similar types of compounds are alike.

Distribution curves of alkylbenzoquinolines in K-1^{HS} of oil and ARPD are given as an example in Fig. 2. Distribution maxima in both cases fall on C₂–C₃ homologs, in the composition of which 2,4-dimethylbenzo[h]quinoline was identified. Figure 3 presents the mass fragmentogram of C₂-benzoquinoline in K-1^{HS} of oil on an m/z 207 ion and the mass spectrum (retention time is 51.5 min) of 2,4-dimethylbenzo[h]quinoline in the NIST-02 mass spectral library.

Bases K-2 present a complex mixture of benzo derivatives of pyridine, a part of which contains a carboxyl group. This is testified by the presence of adsorption bands in sample IR spec-

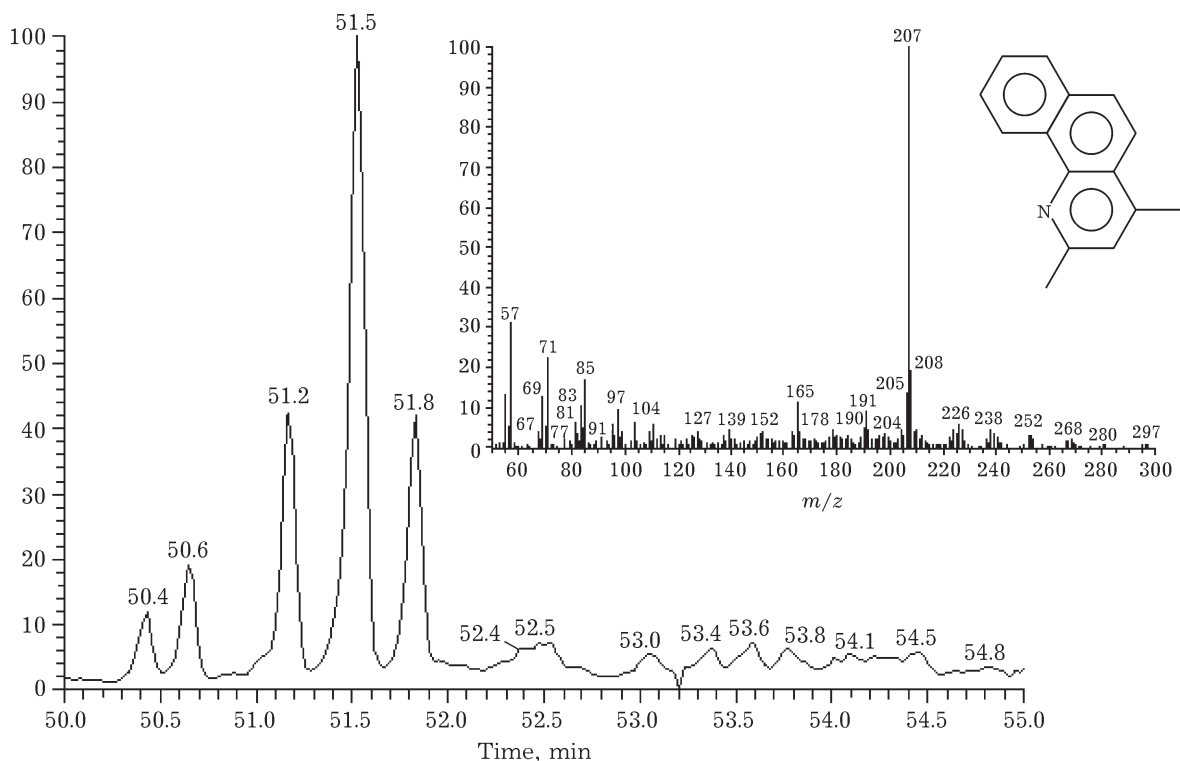


Fig. 3. Mass fragmentogram of C₂-benzoquinoline for ion m/z 207 in K-1^{HS} of oil and the mass spectrum of the peak with 51.5 min retention time.

tra typical for stretching vibrations of C=N bonds of the pyridine ring ($1500\text{--}1580\text{ cm}^{-1}$), of C=C bonds polycyclic aromatic system (1600 cm^{-1}), C=O stretching vibrations ($1720\text{--}1700\text{ cm}^{-1}$) and OH fragments ($3271\text{--}3100\text{ cm}^{-1}$) of acid groups [18]. Products K-21 and K-22 were obtained using a sorbent impregnated with KOH resulting from separation of K-2. According to IR data, there are no nitrogen-containing acids in the composition of compounds K-21. Adsorption bands typical for carboxyl groups appear only in IR spectra of compounds K-22 that comprise the bulk of bases K-2 (60 and 66 % in K-2 of oil and ARPD, respectively). Therefore, low molecular mass polyfunctional bases mainly take part in the formation of organic deposits.

CONCLUSION

Thus, it was found that highly paraffinic oil and ARPD obtained therefrom contained high molecular mass organonitrogen bases with strongly and weakly developed alkyl substitution, and also low molecular mass bases. High molecular mass highly alkylated compounds prevail in both cases; however, their fraction is higher in ARPD than in oil. It was determined by SGA that the medium-sized molecules of high molecular mass compounds with strongly developed alkyl substitution ($C_p = 29\text{--}32$) might contain 2–3 aromatic and 4–5 saturated rings. Weakly alkylated ($C_p = 3\text{--}5$) high molecular mass bases are more cyclical due to the development of aromatic ($K_a = 6\text{--}9$) and saturated fragments ($K_n = 10\text{--}13$). Alkyl substituents in

the structure of their medium-sized molecules are presented only by methyl groups. Alkyl derivatives of quinoline, benzo, dibenzoquinoline, and azapyrene are present among low molecular mass bases of oil and ARPD. Similar types of compounds have the analogous characters of molecular mass distribution. Low molecular mass bases play a significant part in the formation of organic deposits.

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