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Distribution and Composition of Low Molecular Mass Nitrogen-Containing Bases in Highly Resinous Paraffinic Petroleum Oil Species

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Abstract

Low molecular mass nitrogen bases inherent in highly resinous paraffinic oil species were studied. It is demonstrated that the structural-group composition thereof does not depend on the content of resin-asphaltene substances and paraffins in the oil and substances being characterized by a set of compounds typical for the bulk of the oil species produced.

Key words: oil, resins, paraffins, nitrogen-containing bases

INTRODUCTION

The reserves of oil species with the content of solid paraffins greater than 6 mass % represent the most important part of the raw material base of the world oil industry [1, 2]. So, in 2011 they accounted for more than 70 % of the total oil produced in Russia. High paraffin content complicates the processes of the production, transportation and processing of liquid hydrocarbons. In connection with this, studying the composition and properties of highly paraffinic oil species are becoming urgent. The data published in the scientific literature mainly concern studying the physical and chemical properties thereof and the distribution of high molecular mass alkanes [3, 4]. Therewith, heteroatomic, in particular, nitrogen-containing compounds of highly paraffinic oil species remain to a considerable extent uninvestigated. At the same time it is known that low molecular mass nitrogenous bases (NB) represent naturally-occurring surfactants participating in the different type interactions of the oil system [5, 6].

In addition, the NB exhibit a high chemical and thermal stability, thereby they adversely affect the catalytic processing of distillate fractions and the operating parameters of commodity petroleum products [7].

We studied the characteristics of low mass molecular mass NB inherent in highly paraffinic oil species. We investigated the distribution and the structural-group composition thereof in low resinous highly paraffinic oil and demonstrated [8] that the oils under investigation differs from low resinous paraffinic oils (the paraffin content being less than 6.0 %) in a lower concentration of low molecular mass NB. At the same time, low resinous highly paraffinic crude oil has a set of these compounds typical for the reference oil species.

The present work was devoted to studying a quantitative content and composition of low molecular mass NB in highly resinous paraffinic oil species.

TABLE 1

Characteristics of oils under investigation and reference oils

Samples	Oils	Content, mass %			
		P	RAS	N_{tot}	N_{bas}
	Oils under investigation (highly resinous paraffinic oil)				
1	Mamurino oilfield	20.9	25.5	0.26	0.08
2	Ashchisay oilfield	18.9	19.7	0.23	0.07
3	Emlichheim oilfield	10.0	26.9	0.18	0.05
	Reference oil				
4	Low resinous paraffinic oil (25)*	≤6.0	5.5	0.11	0.02
5	Highly resinous paraffinic oil (2)*	≤6.0	17.4	0.14	0.03
6	Low resinous highly paraffinic oil	15.3	7.6	0.11	0.01

Note. P – paraffins, RAS – resin-asphaltene substances, N_{tot} – nitrogen content, N_{bas} – the content of organic nitrogen bases.

* Parenthesized is the number of samples presented, those were used for averaging.

EXPERIMENTAL

As the objects of investigation, we chose highly resinous paraffinic oil species from the oilfields of Mamurino (Povolzhye), Ashchisay (Kazakhstan), and Emlichheim (Germany) (Table 1).

We determined the total nitrogen content (N_{tot}) in a Pokrovsky reactor [9], the total content of sulphur (S_{tot}) using a Sheniger flask method [10], the content of organic nitrogen bases (N_{bas}) *via* non-aqueous potentiometric titration with a solution of perchloric acid in dioxane as described by the authors of [11].

Low molecular mass NB were extracted using an acetate solution of sulphuric acid with the mass ratio between the mineral acid, organic acids and water equal to 25 : 37.5 : 37.5, respectively [12]. The compounds isolated were fractionated using silica gel modified with alkali at a mass ratio sample/adsorbent equal to 1 : 100 [13]. Comprehensive desorption was performed using the solvents with the eluting power (ε^0_{AB}) equal to 0.20 and 0.60 [14].

The IR spectra were registered using a Nicolet 5700 FTIR spectrometer within the wave number region of 4000–400 cm^{-1}. The mass spectra and GC-MS spectra were obtained using a Thermo Scientific chromatograph-mass spectrometer. The conditions of mass spectral analysis and the technique of calculation were presented by the authors of [15, 16], the conditions of chromatography-mass spectrometry were described by the authors of [17].

The results of the investigation performed were compared with similar data obtained for low resinous paraffinic oil species [18], the main raw material for refineries, as well as with the data obtained for highly paraffinic but low resinous oil (Festivalnoye oil field, West Siberia) [8] and those obtained for highly resinous paraffinic oil species taken from the Nizhne-Tabaganskoye and Novoyutymskoye oilfields (West Siberia) [19] in order to determine an effect of the content of resin-asphaltene substances (RAS) and paraffins on the distribution and composition of the NB.

RESULTS AND DISCUSSION

As it can be seen from Table 1, the content of N_{tot} and N_{bas} in the oil species under investigation ranges within 0.18–0.26 and 0.05–0.08 %, respectively. For the reference oil species these values are lower, although highly resinous paraffinic samples are much closer to the oil species under investigation in the content of the total (average 0.14 %) and of the basic nitrogen (average 0.03 %) than low resinous paraffinic oil (mean values 0.11 and 0.02 %,

TABLE 2

Characteristics of low molecular mass nitrogenous bases (NB) inherent in oil species under investigation and reference oils

Samples No.	NB concentrate yield, mass %	Content in concentrate, %		
		N_{tot}	N_{bas}*	S_{tot}
1	0.06	3.47	3.44/2.5	2.37
2	0.06	3.96	3.94/3.6	1.55
3	0.07	2.68	2.68/3.8	3.36
4	0.05	3.36	3.34/8.8	n./d.
5	0.04	3.65	3.63/4.8	3.06
6	<0.01	3.78	3.77/1.9	2.60

Note. n. d. – no data.

* The denominator presents the content with respect to the original oil.

respectively) and low resinous highly paraffinic oil (0.11 and 0.01 %, respectively). Such a distribution of the total and the basic nitrogen indicates the absence of any connection between the paraffin content in the oil and the content of nitrogenous compounds therein. At the same time, a direct interrelation between the content of N_{tot} and N_{bas} and the resin content in the samples is quite natural, since the bulk of the nitrogen compounds in the oils is concentrated in the RAS [19].

The amount of compounds extracted from oil samples, including the reference samples ranges from <0.01 to 0.07 % (Table 2). The yield of NBs isolated ranges from 1.9 to 8.8 rel. % of basic nitrogen contained in the original oil.

The content of resins in oil species affects the yield of NB, whereas the paraffin content therein influences the fraction of basic nitrogen bound with them. So, the content of low molecular mass NB in highly resinous oil species is higher (0.04–0.07 mass %) as compared to low resinous oil species (0.01–0.05 mass %). At the same time, regardless of the RAS content, the paraffinic oil species typically exhibit a greater level of extraction for basic nitrogen (4.8–8.8 rel. %) than it is for highly resinous paraffinic oil (1.9–3.8 rel. %). Most likely, this could be caused by the structural features of NB inherent in highly paraffinic and paraffinic oil.

According to IR spectroscopy, the qualitative composition of low molecular mass NB inherent in oil species under investigation is similar to the composition of these components inherent in reference oil species [8]. In all the cases, the extractable NB are presented by pyridine benzo derivatives (a characteristic doublet within the wave number range of 1580–1520 cm^{-1}), those partially contain carboxyl groups (absorption bands at 3211–3203, 1734–1722 cm^{-1}) and sulphur atoms (see Table 2).

In the course of the chromatographic separation of concentrates isolated from highly resinous paraffinic oil species on modified silica gel, the NB are distributed throughout the two fractions: F-1 and F-2 (Table 3). The amount ranging from 50.0 to 93.3 rel. % of the bases are eluted into the fraction of F-1 and, according to IR spectroscopy, the bases do not contain nitrogen-containing acids in the composition. The carboxyl-containing NB are eluted into a more polar fractions of F-2. A similar pattern of NB fractionation is noted for low resinous highly paraffinic reference oil [8]. The analysis of data presented in Table 3 allows us to conclude that the yield of the fractions depends on the content of paraffins in oil species being not connected with the resin content therein. The maximum yield of the least polar fraction is inher-

TABLE 3

Results of the separation of the concentrates nitrogenous bases inherent in oils under investigation and reference oils with the use of SiO_2/NaOH

Fractions	ε^0_{AB}	Yield, rel. %			
		Samples			
		1	2	3	6
F-1	0.20	93.3	81.6	50.0	61.6
F-2	0.60	6.7	18.4	50.0	38.4

TABLE 4

Structural-group composition of low molecular mass nitrogenous bases for oils under investigation and reference oils

Compounds	z	Content, rel. % (with respect to the sum of compounds identified)					
		Samples					
		1	2	3	4	5	6
$C_nH_{2n-z}N$		**64**	**65**	**62**	**66**	**64**	**66**
Pyridines	9–13	9	10	11	5	9	10
Quinolines	11–19	17	17	14	18	20	16
Benzoquinolines	17–23	13	13	12	18	15	13
Dibenzoquinolines	23–29	9	8	8	9	7	9
Azapyrenes	21–25	10	10	9	10	9	10
Benzoazapyrenes	27–31	6	7	8	6	4	8
$C_nH_{2n-z}NS$		**36**	**35**	**38**	**34**	**36**	**34**
Benzothiazoles	9–15	10	12	12	8	11	10
Thiophenoquinolines	15–19	12	11	11	10	11	10
Benzothiophenoquinolines	21–27	9	10	10	11	10	9
Dibenzothiophenoquinolines	27–33	5	4	5	5	4	5

Note. For designations, see Table 1.

ent in the most highly paraffinic oil taken from the Mamurino oilfield (sample No. 1), whereas the minimum yield of that is characteristic of oil taken from the Emlichheim oilfield (sample No. 3), wherein the paraffin content is minimal (see Table 1). Such a distribution of low molecular mass bases throughout the products of chromatographic separation indicates the fact that the composition of low molecular mass NB inherent in the oil species with a high content of paraffins exhibit a higher percentage of the structures developed alkyl substitution.

The composition of NB those are the most representative with respect to the yield of the fraction F-1 was studied using mass spectrometry and gas chromatography-mass spectrometry. In accordance with the results of mass spectrometric analysis, the low molecular mass NB from oil species under investigation are mainly presented by the identical sets of compounds with empirical formulas $C_nH_{2n-z}N$ and $C_nH_{2n-z}NS$, where z is the level of unsaturation with respect to hydrogen (Table 4). The types of bases revealed are also inherent in reference oil species. The character of distribution for the compounds identified does not depend on the resin content and paraffinic content of the oil. Both oil species under investigation and oil species exhibit azaarenes (62–66 rel. %) to prevail presented by the alkyl and naphthene derivatives of pyridine, quinolone, benzo- and dibenzoquinolines, azapyrene and benzoazapyrene. All the oil samples are characterized by an increased content of quinoline (14–20 rel. %) and benzoquinoline (12–18 rel. %). The content of sulphur-containing NB ranges from 34 to 38 rel. %. All oil the species contain the alkyl and naphthene derivatives of benzothiazole thiophenoquinoline, benzo- and dibenzothiophenoquinolines, the most of those is presented by benzothiazoles (8–12 rel. %), thiopheno- (10–12 rel. %) and benzothiophenoquinolines (9–11 rel. %).

The GC-MS analysis allowed us to identify among the quinolines and benzoquinolines of the oil species under investigation any alkyl-substituted structures those contain 2–8 and 1–6 carbon atoms respectively in the aromatic ring substituents. Among them, there were identified 3- and 8-ethyldimethylquinolines (m/z 185), 8-ethyltrimethyl-2-ethyltrimethylquinolines and 2,4-dimethyl-8-isopropylquinoline (m/z 199), 2,3,4-trimethyl-8-isopropylquinoline (m/z 213), 8-isopropyltetramethylquinoline (m/z 227), 2-methyl- (m/z 193), 2,3-dimethyl-, 2,4-dimethyl- (m/z 207) and 2,4,6-trimethylbenzo(h)quinoline (m/z 221).

The comparison of the results obtained with earlier studies demonstrate that according to the set of homologues in the composition of alkylquinolines and alkylbenzoquinolines and the presence of the compounds identified the highly resinous paraffinic oil species under investigation differ almost neither from reference highly resinous paraffinic oil species, nor from reference low resinous highly paraffinic oil species [8, 19], nor from the main amount of low resinous oil species produced in Russia with the paraffin content lower than 6.0 mass % [8, 18].

CONCLUSION

Thus, the structural-group composition of low molecular mass NB inherent in highly resinous paraffinic oil species does not depend on the content of resin-asphaltene and paraffinic compounds therein being characterized by a set of compounds typical for the bulk of the oil species produced. The main representatives of the low molecular mass NB in all the oil species are presented by alkyl and naphthene derivatives of pyridine, quinoline, benzo- and dibenzoquinolines, azapyrene, benzoazapyrene, benzothiazole, thiophenoquinoline, benzo- and dibenzothiophenoquinolines.

Differences are observed in the quantitative content of the NB, isolated from the oil by means of acidic extraction. The oil species with a higher content of resin-asphaltene substances exhibit a higher content of such compounds, whereas in oils species with a higher content of paraffins demonstrate the structures with a developed alkyl substitution to prevail.

The similarity of the qualitative composition of low molecular mass NB for highly resinous paraffinic oil species and for the bulk of the oil species produced comprises the use of unified technological schemes for upgrading the distillate fractions thereof.

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