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Composition of Organosulphur and Organonitrogen Compounds Contained in Yakutian Oil Shale

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Abstract

The composition of sulphur and nitrogen compounds contained in the bitumenoid isolated from Cambrian rocks oil shale formation was studied. It has been demonstrated that the sulphur compounds contain benzo-, dibenzo-, naphthobenzothiophenes and dibenzothiophene sulphoxides. Nitrogen compounds are presented by weak bases and neutral components. Among the weak bases, there are predominately alkyl homologues of dibenzoquinolone, dibenzothiaquinolone, dibenzoquinolinecarboxylic acids. The maximum in the distribution of neutral nitrogen-containing components corresponds to the alkyl derivatives of benzocarbazole and benzothiophenecarbazole as well as mononaphtheno derivatives of carbazolecarboxylic acids.

Key words: oil shale, bitumenoid, sulphur compounds, nitrogen compounds, composition, structure

INTRODUCTION

At the present time, oil and natural gas are considered to be the main source of raw materials for energy and chemical industry. However, for the sustainable development of our country, the raw materials base should involve interchangeably different types of organic materials. From this point of view, of great practical importance are shale oil species, whose processing can result in obtaining liquid fuel and valuable products [1].

In Russia, the proven reserves of shale oil are amounting to dozens billion tons, the most part of those is concentrated in the deposits of the Kuonamka complex in Eastern Siberia [1, 2]. The results of studying the hydrocarbon composition of Kuonamka oil shale [3, 4] indicate that there is possibility of using them as a potential source of fuel and energy resources. However, for general use and processing of oil shale in Eastern Siberia one need information about the chemical nature of their heteroatomic components, in particular sulphur and organonitrogen compounds whose presence complicates the catalytic processing of oil shale [5, 6], causing the quality and stability of fuel materials to worsen, with a negative influence upon the environment [1]. At the same time, basing on the mentioned heteroatomic compounds one could obtain products those are widely used in medicine, veterinary medicine, in various industries and agriculture (ichthyol and its homologues, thiophene and its derivatives) [7].

This paper describes sulphur and nitrogen components inherent in the organic matter of Kuonamka Cambrian oil shale deposits (Yakutia).

EXPERIMENTAL

Organic matter was isolated from oil shale using a technique described in [8]. Rock was grinded mechanically up to obtaining particle

size within the range of 0.2–0.5 mm, weighed, placed in a sleeve made of filter paper and extracted with 7.0 % (by volume) ethanol solution in chloroform with the use Tecator Coxtec HT system during 2 h. Finishing the extraction was performed by placing the sleeve into a flask with the same solvent. The solutions were joined together and the solvent was then evaporated; the residue was adjusted to obtain constant mass under vacuum.

For obtaining information concerning organosulphur compounds, bitumenoid was deasphalted using an excess of petroleum ether. From the malthenes part, using chromatographic separation on ASK silica gel, we isolated oil fraction to examine then by gas chromatography/mass spectrometry (GCMS).

The concentration of nitrogen compounds (NC) was performed via extraction [9] and gel filtration chromatography [10]. As an extracting agent we used sulphuric acid solution in acetic acid at a mass ratio between the mineral acid, the organic acid and water equal to 25 : 60 : 15, respectively. The use of the mentioned extracting agent allows one to quantitatively extract low molecular nitrogen components of basic and weak basic character [9] from organic mixtures. Non-extractable bitumenoid NC were subjected to a gel chromatographic separation on SDV-p · 10^3 cross-linked polystyrene gel. The elution was performed using benzene at a flow rate of 1 cm^3/min. The fractions with volume amounting to 5 cm^3 were sampled.

The IR spectra were registered with the help of a Nicolet 5700 FTIR spectrometer in the range of 4000–400 cm^{-1}.

The mass spectra were obtained with the use of a MX-1320 mass spectrometer with direct sample introduction into the ion source at electron energy value amounting to 70 eV. The optimum temperature of sample evaporation (at a heating rate of 7 °C/min) was determined from the strength of total ion current, whose maximum value corresponds to registering the mass spectra [11]. For the calculation of the structural-group composition of the samples we used the ratio between the peak intensities of molecular ions and pseudomolecular ions in monoisotopic mass spectra [12].

The chromatography/mass spectrometry study was performed using a Shimadzu QP 5050A chromatograph/mass spectrometer. For the oil fraction of the bitumenoid, the GLC analysis was carried out in the mode of programmed temperature increase from 35 to 310 °C at a rate of 2 °C/min, with further holding at the final temperature within 70 min. For the concentrate of low molecular NC the chromatographing was performed using a programmed temperature increase from 80 to 290 °C at a rate of 2 °C/min with further holding for 25 min at the final temperature. In both cases, the separation was carried out on DB-5-MS+D6 quartz capillary column 30 m long, the inner diameter being of 0.25 mm, with dimethylpolysiloxane phase thickness amounting to 0.25 μm. Helium was used as a carrier gas.

The identification of sulphur and nitrogen compounds being the part of the samples analyzed was carried out basing on the retention time and via comparison of mass spectra with the fragmentograms borrowed from the NIST 157 and Wiley 229 databases as well as with those published in the scientific literature. The quantitative evaluation was performed from peak areas. The relative abundance of each type of compounds was calculated as a ratio between its total intensity and the sum of peak areas corresponding to all the compounds.

RESULTS AND DISCUSSION

As it follows from the data of oil fraction GCMS analysis, the sulphur-containing components of the bitumenoid under investigation are presented by a wide range of compounds belonging to benzo-, dibenzo- and naphthobenzothiophene series (Table 1).

The most part of the compounds identified (81.3 rel. %) is presented by dibenzothiophenes (DBT). The first term of the series represents alkyl- and naphthene-substituted structures. The dominated are alkyldibenzothiophenes (68.1 rel. %) among those there are derivatives from C_1 to C_5 with a maximum content of C_1 and C_2 homologues (see Table 1). For the C_1-DBT, 1-, 2-, 3- and 4-methyldibenzothiophenes (MDBT) are observed.

Among DBT naphthene derivatives, we identified 8,9,10,11-tetrahydronaphtho[1,2-b]- or 8,9,10,11-tetrahydronaphtho[2,1-b]- and

TABLE 1

Analysis of thiophene compounds containing in the oil fraction of chloroform bitumenoid from Kuonamka oil shale

m/z	Compound	Empirical formula	Content*, rel. %
176		*Benzothiophenes (BT)*	
	C_3-BT	$C_{11}H_{12}S$	0.4
		Dibenzothiophenes (DBT)	
184	C_0-DBT	$C_{12}H_8S$	11.9
198	C_1-DBT	$C_{13}H_{10}S$	25.8
212	C_2-DBT	$C_{14}H_{12}S$	23.1
226	C_3-DBT	$C_{15}H_{14}S$	13.5
240	C_4-DBT	$C_{16}H_{16}S$	4.3
254	C_5-DBT	$C_{17}H_{18}S$	1.4
Total			80.0
		Tetrahydronaphthobenzothiophenes (THNBT)	
238	8,9,10,11-THNBT	$C_{16}H_{14}S$	0.5
252	C_1-THNBT	$C_{17}H_{18}S$	0.8
Total			1.3
		Naphthobenzothiophenes (NBT)	
234	C_0-NBT	$C_{16}H_{10}S$	4.7
248	C_1-NBT	$C_{17}H_{12}S$	7.5
262	C_2-NBT	$C_{18}H_{14}S$	3.7
276	C_3-NBT	$C_{19}H_{16}S$	2.2
290	C_4-NBT	$C_{20}H_{18}S$	0.2
Total			18.3

*Total concentration of thiophene compounds is taken to be 100 %.

7,8,9,10-tetrahydronaphtho[2,3-b]benzothiophene, C_1 and C_2 naphthenol-DBT.

The fraction of naphthobenzothiophenes (NBT) amounts to 3.18 rel. %. In this series, the first term of the series and its alkyl homologues from C_1 to C_4 were identified. Methyl NBT are dominating (see Table 1). Holonuclear NBT could have the structure of naphtho[1,2-b]-, naphtho[2,1-b]- and naphtho[2,3-b]benzothiophene.

Among benzothiophenes (BT), we revealed only C_3-BT, whose content is insignificant (0.4 rel. %).

As it follows from Table 2, extractable compounds are connected only with 6.18 rel. % of nitrogen in the bitumenoid under investigation. According to the set of data concerning the elemental [13] and functional [14] analysis of NC extract is almost entirely represented by weak bases, whose structure, alongside with the nitrogen atom could include sulphur atom or a carboxyl group. The IR spectrum of such bases exhibits absorption bands corresponding to amide carbonyl group (1700–1600 cm^{-1}) and

TABLE 2

Characteristics of nitrogen compounds (NC) containing in the bitumenoid of Kuonamka oil shale

Products	Yield,	Content in the sample, mass %					
	mass %	S_{total}	N_{total}	N_{base}	$N_{weak/base}$	N_{neutr}	$COOH^-$
Bitumenoid	0.37	1.06	0.59	Abs.	0.17	0.42	3.00
NC concentrate	2.62	2.67	4.20	Abs.	4.10	Abs	4.00
Residue after extraction	88.80	ND	0.48	Abs.	0.07	0.41	ND

Note. ND – not determined, Abs. – absent.

TABLE 3

Structural-group composition of weakly basic nitrogen compounds contained in the bitumenoid of Kuonamka oil shale

Compound types	*Z*	Molecular mass of the first term of the series	Content against the total amount of identified compounds, %
$C_nH_{2n-z}NO$			
Quinolones	15	225	1.2
Benzoquinolones	17	195	1.7
	19	235	9.8
	21	275	5.2
Total			16.7
Dibenzoquinolones	23	245	12.4
	25	285	8.8
	27	325	5.1
Total			26.3
Tribenzoquinolones	29	295	4.3
Lactams	17	237	0.2
	19	277	0.1
Total			0.3
Sum total			**48.8**
$C_nH_{2n-z}NO_2$ (acids)			
Quinolinecarboxylic acids	15	213	1.3
	17	253	0.5
Total			1.8
Benzoquinolinecarboxylic acids	19	223	0.7
	21	263	6.3
	23	303	4.6
Total			11.6
Dibenzoquinolinecarboxylic acids	25	273	8.9
	27	313	5.1
	29	353	3.4
Total			17.4
Sum total			**30.8**
$C_nH_{2n-z}NS$			
Thiaquinolones	15	241	0.8
Benzothiaquinolones	17	211	1.3
	19	251	0.5
	21	291	5.8
Total			7.6
Dibenzothiaquinolones			
	23	261	6.4
	25	301	5.5
Total			11.9
Sum total			**20.3**

nitrogen-containing acids (1710 cm^{-1}), as well as vibrations of the C=S double bond (1120 cm^{-1}) in the compounds of thiaquinolone series.

The main part of nitrogen contained in the bitumenoid (72.2 rel. %) is included in non-extractable nitrogen compounds those, according to the elemental analysis and potentiometric titration, represent weakly basic and neutral substances (see Table 2). The latter are dominating. In the course of gel-chromatography separation, the mixture components are distributed over 17 fractions. According to the authors of [10], the first four fractions contain the compounds, whose molecular mass exceeds the limit of fractionation inherent in the sorbent used. In this connection, the mentioned fractions were not investigated. The analysis of the IR spectra for the further fractions demonstrated that the set of characteristic bands of the IR spectra for fractions Nos. 5–11 and 12–17, and are almost indistinguishable, so they were combined to obtain products A and B, respectively. The feature of the IR spectrum of fraction A consists in a high intensity of the absorption bands inherent in weak bases. The IR spectrum of fraction B exhibits absorption bands inherent in weak bases and in the compounds of the carbazole series (3460 cm^{-1}) those could be attributed to neutral nitrogen-containing components [15].

According to data obtained from the mass spectrometric investigation of the NC concentrate and fractions A and B, weak bases of the shale oil under investigation are presented by aromatic heterocyclic amides of quinolone type and their hydrogenated analogues such as lactams ($C_nH_{2n-z}NO$), thiaquinolones ($C_nH_{2n-z}NS$), quinolinecarboxylic acids ($C_nH_{2n-z}NO_2$) as well as alkyl- and naphthene-substituted structures (Table 3). Compounds with general formula $C_nH_{2n-z}NO$ (48.8 rel. %) are prevailing. Most of heterocyclic amides represent mononaphthenebenzoquinolones (9.8 rel. %) and alkyldibenzoquinolones (12.4 rel. %). The concentration of quinolones (1.2) and tribenzoquinolones (4.3) are to a considerable extent lower, whereas the concentrations of lactams are negligible (0.3 rel. %). Carboxylic acids those demonstrate weak basic properties (30.4 rel. %) are presented by compounds containing in the structure either quinoline or benzo-and dibenzoquinoline nucleus. The maximum of their distribution falls at dialkyl-substituted benzoquinolinecarboxylic acids (8.9 rel. %). Among the compounds with the general formula $C_nH_{2n-z}NS$ (20.3 rel. %) there are thiaquinolones, benzo- and dibenzothiaquinolones. The maximum abundance is inherent in alkyldibenzothiaquinolones (6.4 rel. %).

Thus, among all the types of weak bases there are alkyldibenzo derivatives observed to prevail. The maximum of their distribution falls, as a rule, at the compounds whose aliphatic chains contain eight carbon atoms.

The investigation of the NC concentrate using the GCMS technique made it possible to obtain information about an individual composition of the weak bases. We analyzed compounds eluted with chloroform-in the course of separating NC concentrate on alumina, deactivated by 3.75 % of water. It was found that among low molecular mass weak bases contained in the oil shale under investigation there are benzoquinolones (BQ) and dibenzoquinolones (DBQ) present. Among the BQ we identi-

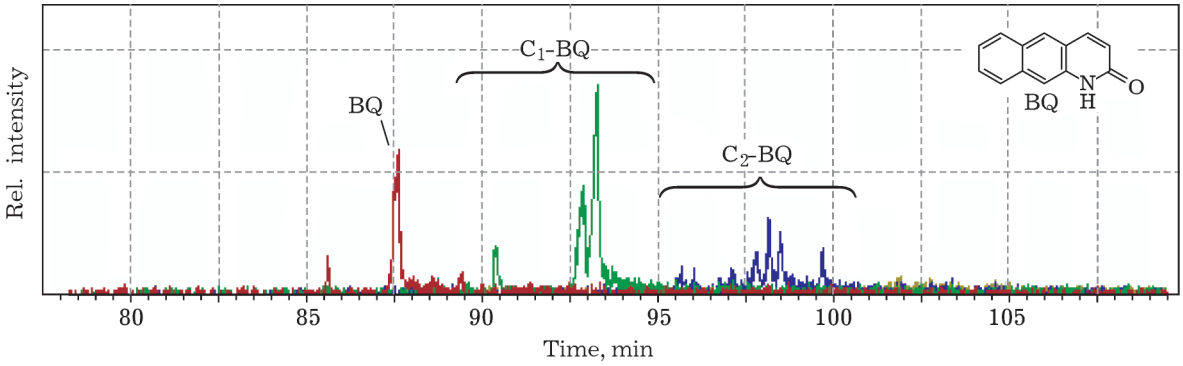

Fig. 1. Mass fragmentograms of benzoquinolone (BQ, m/z 195) and its C_1–C_2 alkyl homologues (m/z 209, 223).

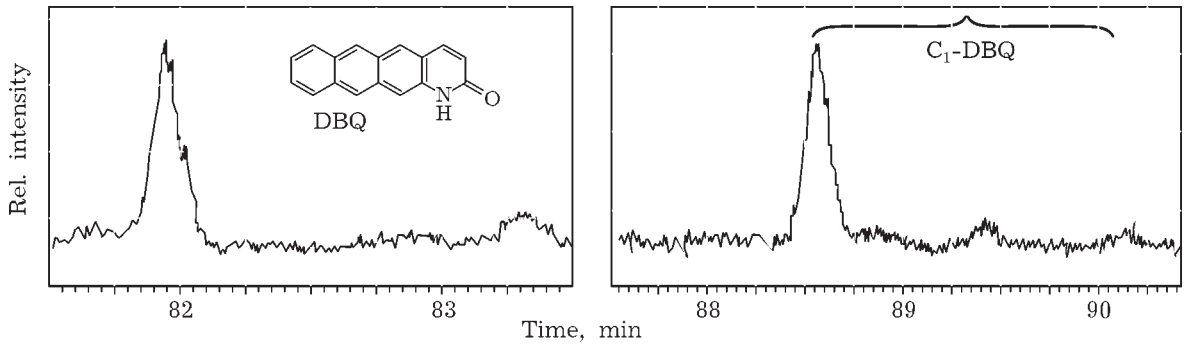

Fig. 2. Mass fragmentograms of dibenzoquinolone (DBQ, m/z 245) and methyldibenzoquinolones (C_1-DBQ, m/z 259).

fied the first term of the series ($C_{13}H_9NO$, m/z 195) and its C_1 ($C_{14}H_{11}NO$, m/z 209) and C_2 ($C_{15}H_{13}NO$, m/z 223) homologues (Fig. 1). Dibenzoquinolones are presented by holonuclear ($C_{17}H_{11}NO$, m/z 245) and methyl substituted structures ($C_{18}H_{14}NO$, m/z 259) (Fig. 2). A limited set the identified structures of weak nitrogen bases, is most likely connected with a lack of information concerning the mass spectra inherent in these bases, both in the literature and in digital libraries.

As far as the composition of the fraction studied is concerned, we also revealed holonuclear dibenzothiophene sulphoxide and its methyl homologues (Fig. 3). The simultaneous presence of the derivatives of sulphoxides and quinolones in the NC concentrate could be, to all appearance, caused be the fact that the compounds of sulphur and nitrogen exhibit a similar chemical activity with respect to the process of isolating and concentrating them.

Basing on the results of mass spectral analysis for fraction B, the neutral components of the bitumenoid under investigation were considered among the isobaric-homologous series of the derivatives of carbazole (38.1 rel. %) thiophenecarbazole (27.0 rel. %) and carbazolecarboxylic acids (35.0 rel. %) (Table 4). Among the first type of compounds we revealed alkyl and naphthene derivatives of benzo- (22.1 rel. %) and dibenzocarbazole (16.0 rel. %), with a maximum content of alkyldibenzocarbazoles (z = 27).

The structures containing nitrogen and sulphur are presented by benzo- (19.6 rel. %) and naphthothiophenecarbazoles (7.4 rel. %). Alkylbenzothiophenecarbazoles (z = 25) are most abundant. Among the compounds with the general formula $C_nH_{2n-z}NO_2$ we identified carbazole (22.1 rel. %) and benzocarbazolecarboxylic acids (12.9 rel. %), with the maximum content of mononaphthene carbazolecarboxylic acids (z = 19). The maximum in the distribution of predominant types of neutral compounds falls at the structures, whose aliphatic chain contains from 4 to 8 carbon atoms.

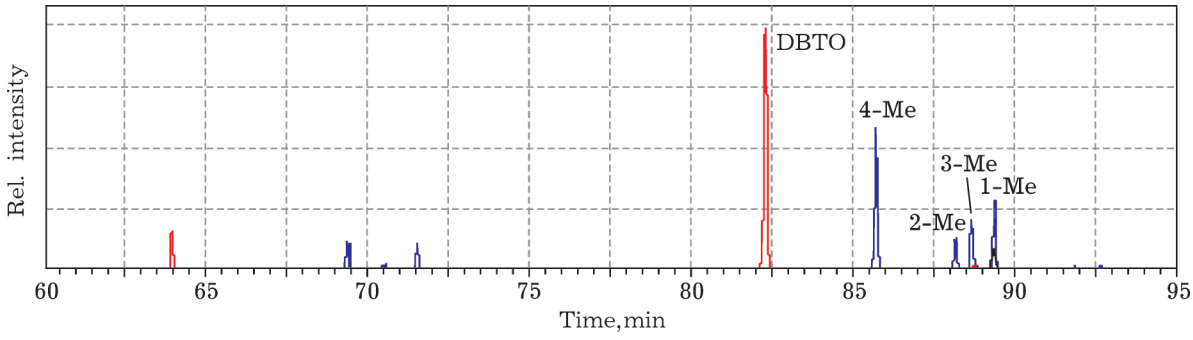

Fig. 3. Mass fragmentograms of dibenzothiophene sulphoxide (DBTO, m/z 200) and methyl-substituted (Me) (m/z 214) compounds.

TABLE 4

Structural-group composition of neutral nitrogen compounds contained in the bitumenoid of Kuonamka oil shale

Compound types	Z	Molecular mass of the first term of the series	Content against the total amount of identified compounds, %
$C_2H_{2n-z}N$			
Benzocarbazoles	23	257	13.5
	25	297	8.6
Total			22.1
Dibenzocarbazoles	27	267	16.0
Sum total			**38.1**
$C_nH_{2n-z}NS$			
Benzothiophenecarbazoles	25	273	10.4
	27	313	4.3
	29	353	4.9
Total			19.6
Naphthothiophenecarbazoles	31	323	7.4
Sum total			**27.0**
$C_nH_{2n-z}NO_2$			
Carbazolecarboxylic acids	19	251	12.9
	21	291	9.2
Total			22.1
Benzocarbazolecarboxylic acids	23	261	12.9
Sum total			**35.0**

CONCLUSION

Thus, the organosulphur and organonitrogen components of Kuonamka oil shale are presented by a complex mixture of aromatic heterocyclic compounds. Among sulphur compounds, there are benzo-, dibenzo-, naphthobenzothiophenes and dibenzothiophene sulphoxides detected. The nitrogen compounds represent weak bases and neutral components. Among the weak bases, predominate the alkyl homologues of dibenzoquinolones, dibenzothiaquinolones, and dibenzoquinolinecarboxylic acids. The most part of the neutral nitrogen-containing components represent the alkyl derivatives of benzocarbazole, benzothiophenecarbazole and mononaphthene derivatives of carbazolecarboxylic acids.

These data are important for the creation of a unified database for the composition and physicochemical properties of Eastern Siberia shale oil as non-traditional hydrocarbon sources. The results of the investigation could be used in order to solve the problems connected with the development of novel technologies and with the improvement of existing ones concerning the processing of oil shale, as well with extending the range of valuable chemical products.

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