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ADAMANTOIDS IN OILS AS INDICATORS OF PRESENCE OF THE DEEP SOURCE ROCKS, ABSHERON ARCHIPELAGO, SOUTH CASPIAN BASIN, AZERBAIJAN

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Petroleum is the only natural source for adamantane and its isomers. It is rigid and at same time stress-free molecule with three connected cyclohexane rings arranged in the "armchair" configuration and has high degree of symmetry. The spatial arrangement of carbon atoms in the adamantane molecule is the same as in the diamond crystal, that is why adamantane type hydrocarbons are also called "diamond type hydrocarbons". Detailed geochemical analysis, including Gas-chromatography and Chromatography-mass-spectrometry were run on the oil samples from the fields located in Absheron archipelago. Biomarkers, including adamantanes and its homologs have been identified in the oils analyzed; distribution of adamantine C_{10}-C_{14} and the role of adamantine on the genesis of the hydrocarbons have been studied as well. Analyses of the chromato-mass spectrometry data suggest that adamantine and its methyl substitution compounds are present in the sequence of increasing of the thermodynamic resistance in the following order: 2-MAd > 1-MAd > 3-MAd > Ad. This indicates formation of the adamantine as a result of thermal transformations of normal alkanes. Oil samples with higher continental input source characterized by lower concentration of tricyclic terpanes C_{19-30} in comparison with the same age oils but with marine source of sediment. Interpretation and analyses of the geochemical data, including concentration of diamondoids indicates presence of deep source rocks in the South Caspian basin.

Keywords: *oil, biomarkers, adamantoids, chromato-mass spectrometry*

There are number of publications dedicated to the crystal structure, properties, methodologies to synthesize and practical application of "diamond type hydrocarbons" [1-15]. Physical and chemical properties as well as crystal structure of the "diamond type hydrocarbons" are similar to the dicaterpanes. Adamantane is the chemical name for the "diamond type hydrocarbons" [15] (Fig.).

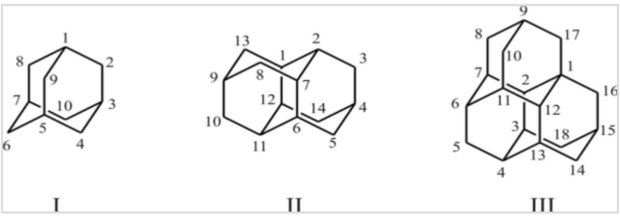

Fig. Adamantoids

I - adamantane $C_{10}H_{16}$, II - diamantane $C_{14}H_{20}$, III- triamantane $C_{18}H_{24}$

Understanding of the genesis of the adamantanes always has been in the focus of the researchers around the world. Successful research projects that helped to develop methodologies to synthesize adamantane in the laboratory conditions suggest that the source of adamantane in petroleum is cyclic hydrocarbons. Most likely, the potential precursors of alcyladamantanes in oil are condensed tricyclic hydrocarbons - fragments that occur during the destruction of the relict compounds of oil - steranes, triterpanes and others [2, 5, 6-9]. Shales and aluminosilicates may act as catalysts to support the process of transformation of the tricyclic hydrocarbons into adamantanes, to be more precise, as these condensed tricyclic hydrocarbons interact with shale rocks they transfer into proto-adamantanes which later form adamantane hydrocarbons. It has been reported that diamond-like hydrocarbons like adamantanoids are also present in the oils generated by carbonate sediments (Giruz, doctoral thesis «Алмазоподобные углеводороды в нефтях и моделирование процессов их образования», 2015).

These relict hydrocarbons have been found in the oil and rock samples from sedimentary basins as well as basement rocks [5].

Objective and work scope

The purpose of this work is to study the composition and distribution of adamantanes, its derivatives and other biomarkers in the oils from Azerbaijan, as well as evaluate the role of adamantanoids in the process of hydrocarbon formation.

Adamantanoids have not yet widely used in the assessment of various geochemical indicators, although they are unique due to high resistance to the high temperatures and biodegradation. As organic matter matures the informativeness of steranes and terpanes decreasing. That is due to thermodynamically equilibrium that builds between certain types of biomarkers, and thus the total amount of the biomarkers in the hydrocarbons decreases. That suggests that in a case of high mature oils it is more beneficial and diagnostic to use diamondoids instead of standard set of biomarkers. Therefore, identification of new geochemical indicators, including adamantane type of biomarkers, is a very important task.

Study objects, methods and results

Oil samples taken from various depths and stratigraphic formations of the fields in the Absheron archipelago such as: Darvin-kupesi, Pirallahi, Palchig Pilpilesi, Neft Dashlari, Guneshli, Chilov, Sangachal-deniz fields are the subject of the current study.

There are a wide range of instrumental methods, which include: gas chromatography, chromato-mass spectrometry, high resolution liquid chromatography, infra-red spectroscopy, supercritical fluid chromatography, thin-layer chromatography, ultraviolet and fluorescent spectroscopy, isotopic mass spectrometry, thermogravimetry and dynamic light dispersion scattering (DRS). The most widely used one is gas chromatography-chromato-mass spectrometry (GC- MS). Recent technological advances have made it possible to solve more complicated tasks – identification of the specific biomarkers and polycyclic aromatic hydrocarbons in the oils using capillary GC-MS. The GC-MS data are used to compare oil samples based on the distribution and height of the peaks for the carbon numbers from C_{15} to C_{25}.

Chromatograms of hydrocarbons were obtained by total ion current (TIC) and specific ion fragments (SIR). Identification of the individual hydrocarons was carried out through a computer search of the National Institute of Standards NIST-08 library (more than 130,000 mass-spectrums of organic compounds), according to published data and based on reconstruction of ion fragments that been identified. Adamantane HC is detected by scanning fragmented ions m/z 136, 135, 149, 163. It is known that the amount of adamantane in oils directly depends on the chemical composition of it. The highest content of adamantane is typical for the naphthenic class of oils whereas paraffinic oils contain much smaller concentration of adamantanes. The concentration of the adamantanes in the oils from Surakhany field is given in the table 1. Data clearly shows direct relationship between the concentration of the naphthenic hydrocarbons and adamantanes in the oils, i.e as the concentration of the naphthenic hydrocarbons in the oil samples decreases the amount of the adamantanes decreasing as well. It indicates that the degree of transformation of the polycyclic hydrocarbons into adamantanes and its isomers is much higher in naphthenic type of oils.

More than 250 individual hydrocarbons have been identified in the oil samples analyzed. The important ones are the biomarkers – isoprenoids hydrocarbons, i.e. terpanes, steranes, hopanes, adamantanes. The composition of adamantanes C_{10}-C_{13} in the oils from Guneshli and Neft Dashlari fields is given in the tables 2 and 3. It shows that highest amount of alkyl-adamantanes corresponds to its dimethyl-transitioned homologs whereas concentration of the adamantanes that not been transformed is the lowest.

High content of 2-monomethyl-adamantanes (2-MAd) in C_{12} suggests continental depositional environment. At the same time it is possible that organic matter was deposited at the continent that was later covered by the water. For example, oil from the well 2194 is either was degraded during catagenesis or biodegraded as it has highest concentration of the diamantanes. Adamantanoid hydrocarbons may help in understanding of the transformations of the organic matter that take place in deeper strata. The distribution of the adamantanes identified in the oils from various oil fields of Absheron archipelago is presented below (Table 4).

Table 1

Adamantane content in the oils from Surakhany field

Formation	TD, m	Alkanes	Cycloalkanes	Aromatic HC	Adamantane amount, mass %
QUQ	710	3,7	88,7	7,6	0,0013
QS	1302	7,6	77,0	15,0	0,0010
QA	2324	45,0	39,0	16,0	0,0004

Table 2

Distribution of adamantanes (C10 – C13) - Guneshli Field

Guneshli Field, Well#	Adamantanes % $C_{10} : C_{11} : C_{12} : C_{13}$	C_{11} / C_{10}	C_{12} / C_{11}	C_{13} / C_{12}	C_{11} / C_{13}	C_{12} / C_{13}
135	10 : 35 : 40 : 25	3.5	1.14	0.63	1.4	1.6
250	7 : 31 : 36 : 27	4.43	1.16	0.75	1.15	1.33
136	5 : 27 : 40 : 27	5.4	1.48	0.67	1	1.48
293	23 : 29 : 30 : 17	1.26	1.03	0.56	1.7	1.76
244	5 : 37 : 25 : 33	7.4	0.68	1.32	1.12	0.76
212	3 : 19 : 37 : 37	6.3	1.94	1	0.51	1

Table 3

Distribution of Adamantoids - Neft Dashlari Field

Well#	Formation	Depth, m	C10, %	C11, %	C12, %	C13, %	C14, %	C15, %
2188	Fasila	1285	0.44	15.7	37.31	23.65	3.48	5.4
2285	Fasila	2475	0.46	14.4	37.5	47.64	-	-
1795	Fasila	2740	3,8	14,89	28,56	18,22	7,28	27,25
2122	VIII	2230	-	16.53	40.02	43.45	-	-
2292	VIII	2326	0.92	10.18	50.38	23.4	7.74	4.33
2194	PK	2192	5.95	31.16	41.54	21.35	-	-

Table 4

Biomarkers in the oils - Absheron Archipelago Fields

Field, Well#	Depth m, Formation	Adamantanes C_{10}-C_{13}	Triterpanes	Hopanes	Regular steranes	i-steranes	Seskviterpanes	Total biomarkers %
Neft Dashlari 2285	2475 Fasila	0,012	0,04	0,13	0,14	0,05	0,008	0,38
Neft Dashlari 1795	2740 Fasila	0,04	0,07	0,36	0,02	0,11	0,02	0,61
Neft Dashlari 2122	2230 XIII	0,02	0,06	0,11	0,13	0,04	0,04	0,37
Neft Dashlari 2292	2326 XIII	0,0004	0,001	0,001	0,001	0,0003	0,0003	0,004
Neft Dashlari 2194	2192 QA	0,009	_	0,018	0,026	0,01	0,005	0,068
Guneshli 244	2998 Fasila	0,004	0,0033	0,04	0,0046	0,0024	0,0007	0,055
Guneshli 250	3024 Fasila	0,00012	0,00057	0,001	0,00085	0,003	0,00018	0,00572
Guneshli 293	2987 IX	0,06	0,005	0,02	0,01	0,02	–	0,115
Guneshli 212	3000 IX	0,025	0,024	0,056	0,095	0,21		0,416
Guneshli 136	2990 X	0,042	0,02	0,01	0,005	0,001	–	0,078
Guneshli 135	3148 X	0,003	0,003	0,009	0,007	0,003	–	0,025
Palchig Pilpilesi 1300	697 Gala	0,00006	0,0016	0,012	0,009	0,006	0,00006	0,02872
Palchig Pilpilesi 1172	543 Gala	–	0,013	0,0212	0,173	0,0555	–	0,2627
Darvin Kupesi 633	1021	0,000007	0,001	0,003	0,0015	0,0006	0,00002	0,00619
Chilov 112	1384	0,013	0,01	0,046	0,044	0,032	0,013	0,158
Pirallahi-deniz 1023	759 Gala	–	0,0113	0,033	0,015	0,0086	_	0,0679
Sangachal- deniz 405	VII	0,00016	0,0027	0,0067	0,0053	0,0027	0,00084	0,0184

Conclusions

- There is direct relationship between concentration of low-molecular steranes (C_{21-22}) and paleoenvironmental conditions as well as between distribution of tricyclic terpanes C_{19-30} – cheilanthanes and geological age of the oil samples analyzed;
- Oil samples with higher continental input characterized by lower concentration of pregnanes and cheilanthanes compared to the same age oils generated from the source rocks deposited in marine environment.
- Distribution of the biomarkers in the range C_{19}-C_{30} and C_{21-22} shows mixed depositional environment - from sapropelic to sapropelic – humus type of OM;
- Analysis of the chromato-mass spectrometry data shows following distribution of the adamantane and its methyl substitutions: 2–MAd>1-MAd>3-MAd>Ad. It indicates the formation of adamantane as a result of thermal transformation of normal alkanes.
- Interpretation and analyses of the geochemical data, including concentration of diamondoids indicates presence of deep source rock (at the depth of 13km, or deeper) in the South Caspian basin.

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ABŞERON ARXİPELAQI NEFTLƏRİNDƏ ADAMANTOİDLƏR – DƏRİN QATLARDA ANA SÜXURUN MÖVCUDLUĞUNUN GÖSTƏRİCİSİ KİMİ. CƏNUBİ XƏZƏR HÖVZƏSİ, AZƏRBAYCAN

İ.S.Quliyev, Q.S.Martınova, F.R.Babayev, A.S.Cavadova

Xromato-mass-spektrometriya üsulu ilə Abşeron arxipelaqı neftlərində biomarkerlər müəyyənləşdirilib, o cümlədən adamantan və onun homoloqları, adamantoidlərin C_{10}-C_{14} tərkibində paylanma xüsusiyyətləri və onların neftin genezisində rolu haqqında araşdırılma aparılıb. Xromato-mass-spektrometrik nəticələrin hesablanmalarına görə, adamantan və onun metiləvəzolunan birləşmələri termodinamik davamlılığın artma qaydasında aşağıdaki kimi yerləşir: 2-MAd >1-MAd > 3-MAd > Ad, bu isə adamantanın neftlərdə normal alkanların termiki çevrilmələr nəticəsində əmələgəlməsini göstərir. Geokimyəvi tədqiqatların təsviri Cənubi Xəzər hövzəsinin dərin qatlarında (13km və hətta daha dərin) ana süxurunun mövcud olmasını göstərir.

Açar sözlər: *neft, biomarkerlər, adamantoidlər, xromato-mass-spektrometriya*

АДАМАНТОИДЫ В НЕФТЯХ АБШЕРОНСКОГО АРХИПЕЛАГА КАК ПОКАЗАТЕЛИ НАЛИЧИЯ НЕФТЕМАТЕРИНСКИХ ПОРОД НА БОЛЬШИХ ГЛУБИНАХ. ЮЖНО-КАСПИЙСКАЯ ВПАДИНА, АЗЕРБАЙДЖАН

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В нефтях Абшеронского архипелага методом хромато-масс-спектрометрии идентифицированы биомаркеры, в том числе адамантан и его гомологи, исследованы особенности распределения адамантоидов состава C_{10} - C_{14} и их роль в генезисе нефти. Расчеты по данным хромато-масс-спектрометрии показали, что адамантан и его метилзамещенные соединения располагаются в порядке увеличения термодинамической устойчивости следующим образом: 2-МАд > 1-МАд > 3–МАд > Ад, что в свою очередь свидетельствует в пользу генезиса адамантана в нефтях путем термического превращения нормальных алканов. Комплексная интерпретация геолого-геохимических данных позволяет сделать выводы о возможном залегании нефтематеринских пород на больших глубинах (порядка 13 км и, возможно, глубже) Южно-Каспийской впадины.

Ключевые слова: *нефть, биомаркеры, адамантоиды, хромато-масс-спектрометрия*