Adamantane Hydrocarbons as Indicators of Oil Genesis in the Open System

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Abstract. Hydrocarbons of the adamantane structure are referred to as hydrocarbon biomarkers. However, they differ from other biomarkers in that no analogues of hydrocarbons of adamantane structure in wildlife have been found. These hydrocarbons are assumed to have been formed because of structural rearrangements and at the polycyclic naphthenic hydrocarbons molecules fragmentation. Adamantane hydrocarbons, regardless of the deposit location, are featured by the pronounced nonequilibrium composition. This is, although in laboratory experiments at sufficiently low temperatures (180–220°C) equilibrium is reached within a few days. All these testify to the fact that the formation of adamantane structures has proceeded very fast, in the kinetic regime, and is most likely to associate with the processes of hydrocarbons migration into the deposit. Researchers of adamantane hydrocarbons indicate the option of adamantane structures formation in migration processes, though not specifying the mechanism of their development. It has been suggested that the formation of adamantane hydrocarbons proceeds dynamically in a stream of deep fluids in the supercritical state. The isomeric composition of alkyl adamantanes is determined by the time of contact with the rocks, as well as their catalytic activity. This can confirm the earlier assumption on oil genesis in thermodynamically open system.

1. Introduction

The adamantane hydrocarbons are the hydrocarbons of carcass structure and contain at least one adamantane fragment. Adamantane is a tricyclo [3,3,1,1³,⁷]decane-tricyclic saturated bridged hydrocarbon of the C₁₀H₁₆ composition, consisting of three cyclohexane rings in the "armchair" conformation [1-4]. Adamantane was first isolated by S. Landa in 1932 when studying the composition of high naphthene oils of the Godoninskoye deposit. In addition to the adamantane itself, its mono-, di-, and trimethyl and ethyl homologues of the C₁₁-C₁₅ composition were found in oils [2, 3]. Adamantanes have unique stability both in the processes of thermal and catalytic cracking, and in conditions of biodegradation of oils [5]. Many researchers of adamantanes believe that the study of these hydrocarbons would give critical data for clarifying the origin and mutual transformations of oil hydrocarbons.

We find it interesting to consider the features of composition and distribution of hydrocarbons of adamantane structure in various oils and condensates from the point of view of oil genesis [3, 5-7].
2. Adamantane hydrocarbons
Adamantane hydrocarbons belong to bridged hydrocarbons of the diamond-like structure. Adamantane has a highly symmetrical structure, completely free of internal stresses [1-3]. Stereochemical features of the adamantane structure largely determine the high thermodynamic stability of both adamantane itself and its alkyl-substituted homologues [1-3]. Thus, in the reactions of tricyclic hydrocarbons isomerization, from the point of view of thermodynamics, the most stable are the hydrocarbons of adamantane series [2, 3]. Among the homologues of alkyl adamantanes, the isomers containing methyl groups at the nodular positions of the nucleus (1-methyl-, 1,3-methyl-, 1,3,5, -trimethyl- and 1,3,5,7-tetramethyladamantanes) are featured by the highest thermodynamic stability [2, 3].

2.1. Adamantanes in oils
As already mentioned above, in addition to the adamantane itself, numerous mono- di- and trimethyl and ethyl homologues of the C₁₁-C₁₄ composition have been found in oils. The highest relative content falls precisely on the proportion of polymethyl-substituted alkyl adamantanes. An important feature of the isomeric composition in the alkyladamantanes mixtures observed for all studied oils is the presence of less stable isomers (with bridge substituents) in concentrations significantly exceeding the equilibrium along with the most stable compounds (substituents at the nodal carbon atoms) [2-10]. Of interest is the presence in oil of high concentrations of thermodynamically unstable structures: ethyl-, and methyl-substituted adamantanes, where one of the substituents is located not in the head of the bridge (1,2-dimethyl-, 1,3,4-trimethyladamantanes, etc.).

Studies of adamantanes have shown that these hydrocarbons are present in oils of different ages, of varying degrees of transformation, generated in different lithologic-facies environment. The amount of adamantane hydrocarbons in oils depends on the oil chemical nature. The oils of naphthenic type have the highest content [3, 5-7].

2.2. Features of composition and distribution of adamantanes in the oils and condensates of Yakutia
The content, composition, and nature of the distribution of adamantane hydrocarbons in various genetic types of oils and condensates in Western Yakutia were studied: the condensate of the Sredneviliuysk deposit from the T₁,-III horizon, the oil from the Mastakh deposit from the J₁,-I horizon, genetically related to the organic matter of the sapropelite-humites of continental facies, and the Vendian-Cambrian oil of the Talakan and Irellyakh deposits, generated by the organic matter of marine facies [11].

As a result of the studies [11], adamantane and its homologues were found in all the fluids studied. The quantitative content of adamantanes was mainly determined by the chemical type of oil and the source of their generation. The highest content of adamantane hydrocarbons (0.28%) was found in the naphthenic oil of the Mastakh deposit, the lowest (0.04%) was found in the alkane oils of the Talakan and Irellyakh deposits; in the Sredneviliuysk condensate, the content of adamantanes was 0.08%. In all the fluids studied, the thermodynamically nonequilibrium character of the distribution of alkyl-substituted adamantanes was revealed, which was typical for oils.

2.3. Characteristic features inherent in adamantane hydrocarbons of the oil origin
The review of the literature data and studies carried out by the authors confirmed the following:
- the content of adamantane hydrocarbons in oil depends on its chemical type - maximum concentrations are noted in naphthenic oils and naphthene-type condensates;
- the distribution of homologues of adamantane hydrocarbons has a strongly pronounced nonequilibrium character and does not depend on the oil age, the varying degree of transformation of organic matter, and the generation in different lithologic-facies conditions. Thermodynamically more stable hydrocarbons: 1-methyl-, 1,3-dimethyl-, 1,3,5-trimethyl- and 1,3,5,7-tetramethyladamantanes, although present in appreciable concentrations in oils, are still not the main components oil mixtures, while the equilibrium mixtures of adamantanes of C₁₁-C₁₄ composition contain over 90% of methyl-substituted isomers with methyl radicals located in the head of the bridge [3, 7].
3. Formation of adamantane hydrocarbons of oil

S. Landa, the discoverer of adamantane, has already suggested that cyclic hydrocarbons are the source of adamantane in oil. Natural clays and aluminosilicates can play the role of catalysts for these transformations. The catalytic activity of natural clays that cause polymerization reactions, hydrogen disproportionation and isomerization of unsaturated hydrocarbons at temperatures of ~ 200 °C is well known [2, 3]. The comparison of the results of studies of various oils showed that although the total content of alkyl adamantanes varies, the ratios of individual isomers are very close to each other. The presence of the common distribution of alkyl adamantane isomers in the oil fields of the regions very far from each other allowed [3] to conclude that there exists a common pathway for the formation of hydrocarbons of the adamantane series.

3.1. Known (existing) models for the formation and isomerization of adamantane hydrocarbons

In [3, 4] it is shown that the conversion of hydrogenated aromatic tricyclic hydrocarbons to alkyl adamantanes easily proceeds over aluminium oxide impregnated with dilute solutions of certain mineral acids (sulfuric acid in particular) and over amorphous silica-alumina catalysts at relatively moderate temperatures (180-220°C). Since these conditions are comparable to the natural conditions of oils occurrence and development, such a reaction, in their opinion, can be considered as a model for the formation of alkyl adamantanes under natural conditions.

As mentioned above, equilibrium mixtures of adamantanes of the C_{11}-C_{14} composition contain over 90% of methyl-substituted isomers with methyl radicals located in the head of the bridge, i.e., respectively, 1-methyl-, 1,3-dimethyl-, 1,3,5- trimethyl-, 1,3,5,7-tetramethyladamantanes [3, 7]. However, the composition of adamantane hydrocarbons in oils is far from equilibrium: along with more stable isomers, a significant content of less stable structures is noted. These thermodynamically unstable structures are usually formed primarily in the isomerization of non-adamantane tricyclic hydrocarbons to hydrocarbons of the adamantane series [2, 3]. Among the adamantane hydrocarbons, they are kinetically more preferred and, due to their low isomerization rate, accumulate in the reaction products. As suggested by [2, 3], obviously, the same holds true for oils.

The author [2] proposed the following multi-stage pattern for the formation of hydrocarbons of the adamantane series in oils: initial tricyclic hydrocarbons → a pseudo-equilibrium mixture of proto-adamantane tricyclanes → kinetically favorable adamantanes (2-methyl-, 1,2-dimethyl-, 1-ethyladamantanes, etc.) → thermodynamically stable adamantanes (1-methyl-, 1,3-dimethyl-, 1,3,5-trimethyladamantanes).

The potential for the formation of hydrocarbons of the adamantane series in oils is large, since any tricyclic saturated hydrocarbon can transform into such hydrocarbons (at appropriate conditions, catalyst, etc.). Studies [2, 7] of the relationships between adamantane hydrocarbons and other tricyclanes of the C_{11}-C_{14} composition showed that in oils, non-adamantane tricyclanes constitute 80-90% of the total tricyclanes sum. Adamantane hydrocarbons in oils are only part of the potential resources of adamantane tricyclanes. Since adamantanes are usually absent in bioorganic compounds, the presence of these hydrocarbons in oils indicates the occurrence of catalytic reactions requiring the participation of acid catalysts. In natural conditions, the only real catalysts are aluminosilicates (clays) [2, 3].

However, the authors of [6] believe that, from the viewpoint of the considered mechanism for the formation of adamantane hydrocarbons, it is difficult to explain the presence of carcass structures in oils and organic matter of rocks generated by carbonate sequences lacking catalytic activity; the presence of these hydrocarbons in organic matter with a low degree of maturity, as well as in the organic matter of the crystalline basement. In addition, according to these authors, it is problematic to assume that in such biopolymers as asphaltenes and, especially, kerogen, isomerization occurs with the formation of adamantanes. The conclusion is made about the possibility of the existence of other, so far unknown, pattern of the formation of carcass hydrocarbons in oil.

In [3, 6] it was shown that adamantane hydrocarbons can be formed not only in the reactions of isomerization of saturated tricyclic hydrocarbons, but also in the result of destructive isomerization of...
high-molecular polycyclones. Adamantanes are also formed by thermal cracking (450°C) of high n-alkanes [5], the saturated fractions [12] and polar components [13] of oil. The authors [14, 15] managed to experimentally obtain adamantane hydrocarbons by catalytic thermolysis of bacterial biomass. On this basis, a conclusion is made about the possibility of such a mechanism for the formation of carcass hydrocarbons in oil. To perform all of the above mentioned processes high temperatures are required and therefore it is unlikely that they would take place in the oil.

3.2. The formation of adamantane hydrocarbons in an open system in a supercritical deep fluid flow

Under laboratory conditions [3, 4], the isomerization reactions leading to the formation of adamantane hydrocarbons take place at quite low temperatures (180-220 °C), comparable to those of the main phase of oil formation, and the equilibrium state of the adamantane hydrocarbon mixture is reached within hours/days. The absence of equilibrium concentrations of isomeric hydrocarbons of the adamantane series in oil seems to indicate that the formation of these hydrocarbons proceeds in a kinetic regime, i.e. in conditions when thermodynamic equilibrium simply does not have time to establish itself. Such conditions, most likely, can be realized in the process of hydrocarbon migration to the reservoir. The possible occurrence of reactions of the formation of adamantane structures in oil in the kinetic regime was indicated [3]. It is assumed there that these processes could be associated with the migration of hydrocarbons, but their mechanism is not specified.

In our opinion, many issues arising in connection with the mechanism of formation of adamantane hydrocarbons in oil find their explanation, if the genesis of gas-oil fields takes place in the thermodynamically open system. According to the proposed model of gas-oil formation [16-18], the migration of hydrocarbons to the reservoir occurs in a stream of deep fluids in the supercritical state. Supercritical fluids are characterized by high penetrating, dissolving capacity and chemical activity [19]. The main components of deep fluids are carbon dioxide, methane, water. We believe that the deep fluid can completely or partially penetrate the oil-bearing rocks, dissolve organic matter and carry them further along the conducting rocks into the reservoir. In the process of primary migration through dense oil-bearing rocks, organic substances undergo strong strain stresses, so they can undergo mechanochemical transformations. Especially it concerns high-molecular compounds. In case of polycyclones destruction with the formation of tricyclic fragments, it is inevitable to expect the formation of adamantanes in certain amount, as the most thermodynamically stable structures, even in the strata of rocks that do not possess catalytic activity (carbonates). In the clay rocks of further isomerization, the catalytic activity of the rock walls will also contribute. With a low gas permeability of the overlying rocks, a deep fluid can fill the cracks in the basement, bringing there bituminous substances, including adamantanes. Thus, the proposed mechanism for the formation of adamantane structures in a dynamic regime allows to come to conclusions in good agreement with the previously established regularities of the content and distribution of adamantane hydrocarbons in oil. The quantitative content of adamantanes depends on the type of organic matter; the higher the content of saturated polycyclic hydrocarbons (naphthenes), the higher the concentration of adamantane structures. The distribution of isomeric structures is due to the length of contact of hydrocarbons with the walls of rocks during migration, the type of rock, and its catalytic activity.

4. Geochemical significance of adamantane hydrocarbons (Conclusion)

Hydrocarbons of the adamantane structure are found in oils and are referred to as biomarker hydrocarbons. However, they differ from other biomarkers in that no analogs of these hydrocarbons have been found in wildlife. Consequently, the hydrocarbons of the carcass structure bear information on the mutual transformations of oil hydrocarbons. Also, as the most stable structures, they can act as biomarkers in the case of destruction of other high-molecular polycyclic structures. We believe that the proposed mechanism for the adamantanes formation can cast light on the processes of oil and gas formation.

At present, the ratios between the isomeric hydrocarbon isomers of the C11-C14 adamantium series have been used to characterize the degree of maturity of the organic matter of sedimentary rocks and
oils [5, 20, 21], ignoring the fact that the process of formation of these hydrocarbons in oil is likely to proceed in a kinetic regime. Besides, the maturity of organic matter, determined by the ratio of the isomers of the adamantane series hydrocarbons, do not always coincide with those determined by other biomarkers [5]. Unfortunately, the process of formation of adamantane hydrocarbons has been regarded as static, tied with catagenetic transformations of organic matter. Under static conditions, the formation of adamantanes is possible, though higher temperatures are required for these processes to occur (thermal cracking at 450°C) [5, 12, 13]. Due to high temperatures, it is unlikely that these processes would develop in oil.

In our opinion, very little attention is paid to the possibility of transforming organic matter in hydrocarbon migration processes. As was shown earlier on the example of supercritical carbon dioxide [17], mechanochemical processes (destruction, isomerization of organic matter) occur even at room temperatures. We believe that the formation of adamantane hydrocarbons in oil is most likely to occur dynamically in a stream of deep fluid in a supercritical state. Such the mechanism makes it possible to explain all the features of the content and composition of adamantane hydrocarbons and can also serve as a confirmation of the proposed model of oil genesis in a thermodynamically open system.

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