Gas chromatographic-mass spectrometric investigation of n-alkanes and carboxylic acids in bottom sediments of the northern Caspian Sea

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Abstract

Prior to the start of experimental oil production in the Kashagan field (northern part of the Caspian Sea), n-alkanes and carboxylic acids contained in samples obtained from bottom sediments in the area of artificial island "D" were investigated by gas chromatography–mass spectrometry. Concentrations of 10 n-alkanes (composed of C_{10}-C_{13}, C_{15}-C_{20}) and 11 carboxylic acids (composed of C_6-C_{12}, C_{14}-C_{16}) were identified and measured. Concentrations of individual alkanes and carboxylic acids in bottom sediments of the various samples varied between 0.001 ÷ 0.88 µg/g and 0.001 ÷ 1.94 µg/g, respectively. Mass spectra, in particular the M+ molecular ion peak and the most intense peaks of fragment ions, are given. The present study illustrates the stability of molecular ions to electronic ionisation and the main fragment ions to the total ion current and shows that the initial fragmentation of alkanes implies radical cleavage of C_2H_5 rather than CH_3. All aliphatic monocarboxylic acids studied were characterised by McLafferty rearrangement leading to the formation of F_4 cation-radical with m/z 60 and F_3 cation-radical with m/z 88 in the case of ethylhexanoic acid. The formation of oxonium ions presents another important aspect of acid fragmentation. Using mass numbers of oxonium ions and rearrangement ions allows determination of the substitution character in α- and β- C atoms. The essence of our approach is to estimate the infiltration of hydrocarbon fluids from the enclosing formation into sea water, comprising an analysis of derivatives of organic compounds in bottom sediments. Thus, concentrations of derived organic molecules can serve as a basis for estimates of the depth at which hydrocarbon fluids leak, i.e., to serve as an auxiliary technique in the search for hydrocarbon deposits and to repair well leaks.

Key words: Gas chromatography–mass spectrometry, carbocations, oxonium ions

1. Introduction

There is ample evidence that shows that hydrocarbon micro-leaks from host layers are apparently caused by the buoyancy of colloid "microbubbles" of light hydrocarbons (mostly methane–butanes (alkanes)) that rise relatively quickly through a network of water-filled fractures, sutures and sed-
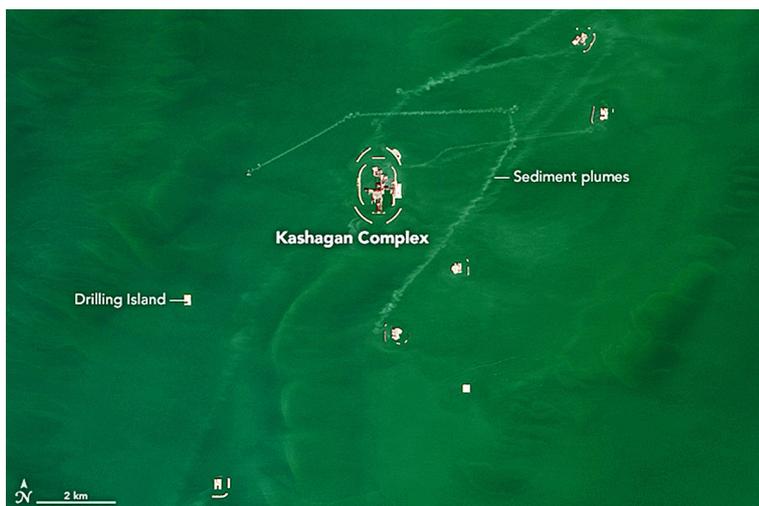
Fig. 1. The Kashagan complex with sediment plumes, indicating water pollution during drilling (NASA aerial photography; http://earthobservatory.nasa.gov/).

imentary rocks. Bacterial consumption of these hydrocarbons generates carbon dioxide and hydrogen sulphide, while bacterial-assisted catalytic oxidation can produce carboxylic acids that can modify sediments by causing detectable changes in the geochemical properties of sedimentary rocks and sea shelf water. For the present study we sampled bottom sediments and analysed them in a laboratory to determine the concentration of hydrocarbons (alkanes and carboxylic acids). These methods of surface control do not document depth, size or quality of reservoirs (i.e., the host rocks), even if extractable hydrocarbons are discovered.

Thus, despite the fact that the proposed method could be used in pay horizon exploration, its main area of application, in our opinion, is environmental monitoring. Figure 1 illustrates bottom sediments that have been elevated through water by drilling near the artificial island in the Kashagan oil field, which again confirms the danger of pollution from petroleum extraction.

The possibility of conducting a quantitative assessment of hydrocarbon leaks from drilling rigs near the surface and distinguishing them from leaks out of reservoirs (host rocks) by grading organic compounds is crucial for the successful reclamation of soil and water that has been polluted due to deterioration and depletion of petroleum wells.

All oil-bearing host rocks demonstrate a certain type of geochemical signal (detection of certain specific hydrocarbon fractions in near-surface layers); however, superrficial geochemical leaks are not always detectable via conventional methods. We used a mass spectrometry method to analyse bottom sediment samples, which is the most sensitive method of chemical analysis to date. The presence of hydrocarbons that seeped into bottom sediments or the sea surface proves the presence of the three

main elements of the petroleum system: the source (host rocks rich in hydrocarbons; rich rocks capable of generating a hydrocarbon flow); the maturing (host rocks having reached physical conditions (temperature, pressure, etc.) required to generate and release hydrocarbons) and migration (hydrocarbons migrating from source host rocks to potential traps and subsequently leaking or migrating to near-surface sediments). The geochemical signal can be absent if these three conditions are not met; however, it is obvious that oil-bearing rocks of industrial importance with hydrocarbon deposits sufficientlt large for extraction will always demonstrate the above-mentioned geochemical signal, especially following the development of hydrocarbons, i.e., a network of fractured rocks is created around the borehole, which facilitates hydrocarbon leakage.

Near-surface exploration methods have been used with mixed success in petroleum exploration, which has led to discussions about the complex nature of hydrocarbon leakage in marine conditions. Numerous thematic studies have demonstrated the effectiveness of near-surface geochemical exploration methods (Villinski et al., 2000; Khoroshko et al., 2004; Gay et al., 2011; Kallmeyer et al., 2012; Mirza et al., 2012; Aeppli et al., 2014). However, additional studies are required to specify conditions of applicability of geochemical methods and to understand when these methods work, what effect the choice of equipment and analytical procedures has, what best suits a specific parameter of the marine system, and, most importantly, how to interpret the results properly. The combination of all these peculiarities is crucial to any successful geochemical exploration of the sea bed.

The purpose of the present study is to provide materials of a situational investigation of a specific oil field on a shallow-marine shelf in the northern

Caspian Sea and to register the concentration of hydrocarbons detected in the near-surface deposits near the developed oil-bearing formation at the start of industrial development, more specifically, at the time of exploration drilling. The aim of the present paper was to study and identify n-alkanes and carboxylic acids contained in bottom sediment samples in the area of the artificial island "D", sampled prior to the experimental oil production at Kashagan field by GC-MS.

2. Study area

Since 1960, oil and gas production in Kazakhstan has acquired new dimensions in view of intensive development of giant and unique fields, including those located in the Caspian Sea. A set of onshore fields, such as Tengiz, Royal (Atyrau area), Zhanazhol (Aktobe area) and Karachaganak in the West Kazakhstan region as well as Kashagan, Kayran and Aktoty deposits occur on the shelf of the Kazakhstan sector of the Caspian Sea. Table 1 provides oil and gas characteristics in above-mentioned offshore.

The Kashagan field area covers an area of > 5,500 square kilometres and consists of five separate fields, producing formations from the Precaspian Basin. These fields are Kashagan, Kalamkas A, Kashagan Southwest, Aktote and Kairan. Kashagan is a carbonate platform of Late Devonian to mid-Carboniferous age. The "reef" is about 75 kilometres long and 35 kilometres across with a narrow neck joining two broader platforms (Kashagan East and Kashagan West). The top of the reservoir is about 4,500 metres below sea level and the oil column extends for over 1,000 metres. The field is in very shallow water, 3 to 9 metres deep. The seal consists of Middle Permian shale and Upper Permian salt. The reservoir comprises limestones with low porosities and permeabilities. The oil is a light oil with 45 API gravity with a high gas-oil ratio and hydrogen sulphide (H_2S) content of 19%. The field is heavily overpressurised, which presents a signif-

Table 1. Characteristics of subsalt oil and gas fields on the Kazakhstan sector of Caspian Sea.

	Kashagan	Kayran	Aktoty
Depth of burial [m]	4000–5500	3200–5500	3600–5000
Layer pressure [MPa]	80–110	70–100	80–100
Layer temperature [°C]	110–130	110–130	110–130
H_2S content [%]	19–22	16–20	22

icant drilling challenge. The figures for oil in place range between 30 and 50 billion barrels (4.8 and 7.9 billion cubic metres) with a common publicly quoted figure of 38 billion barrels (6.0×10^9 m³). The recovery factor is relatively low (15–25%) due to reservoir complexity, with between 4 and 13 billion barrels (640 and 2,070 million cubic metres) being the estimated ultimate recoverable resource. Three of the other fields in the contract area, Kashagan SW, Kairan and Aktote, are also Carboniferous carbonate platforms. Kalamkas offshore has a Jurassic sandstone reservoir (Ronchi et al., 2010). Samples taken during the present study were bottom sediments, sand-clay-detritus in varying combinations, which are typical bottom sediments for the area under consideration (Ogar et al., 2014).

Geological exploration and exploratory drilling on the continental shelf or in the deep sea and ocean are very expensive. Therefore, much attention is paid to the development and improvement of various methods of forecast. In addition to traditional geophysical research and construction of regional and local geological models, there are widespread methods based on geochemical studies of compositions of water mass and bottom sediments. The Caspian Sea and adjacent sedimentary basins are characterised by increased volcanic activity, which is manifested in the form of numerous mud volcanoes. Emissions of mud volcanoes are often associated with hydrocarbon migration from deep water to the surface. Therefore, the study of volcanic activity in the Caspian Sea through geochemical studies of water mass and bottom sediments is very important. It is necessary to emphasise the importance of geochemical studies of water mass and the composition of bottom sediments with a view of verifying the content of hydrocarbon compounds after disasters in the Gulf of Mexico and in the Persian Gulf, related to the uncontrolled petroleum spills. There are many research works on organic compounds in bottom sediments detected on a global scale, as well as recurrence and local transfer intensity of hydrocarbons between the surface areas of bodies of water (Kaiser and Benner, 2009; Kallmeyer et al., 2012). These kinds of works usually combine the results of studies carried out previously in different water areas. Therefore, the results obtained provide the possibility of estimating the relationship between elemental composition and climatic conditions as well as between the identified carbon-containing compounds and cyclic intensity of upwelling.

The study of oil-and-gas source rocks is one of the most important directions in modern petroleum geology. In this regard, geochemical studies of bot-

tom sediments from modern seas and oceans have been actively carried out in order to obtain a deeper understanding of how the organic-rich kerogen rocks in palaeo-sedimentary environments could have formed. One of the key areas implies the study of conditions of sedimentation in various aquatic areas, contributing to the preservation of organic compounds (Hedges and Keil, 1995; Middelburg and Meysman, 2007; Zonneveld et al., 2010).

For example, a number of studies have considered the geochemistry of bottom sediments of the Black Sea. There is a boundary depth in the deep-water part of the Black Sea, below which the concentration of hydrogen sulphide in the water masses precludes the existence of 99% of living organisms. This fact contributes to the preservation of organic compounds in bottom sediments, which in turn forms the future oil-and-gas source rock (Sweeney and Kaplan, 1980; Muramoto et al., 1991; Lyons and Berner, 1992; Lyons, 1997; Neretin et al., 1998; Wijsman et al., 2001).

Much attention has been given to the study of mud volcanoes onshore and offshore in the Caspian region. Different researchers have studied the sediments within the areas adjacent to active mud volcanoes in order to restore the geochemical evolution of volcanoes and to asssess the composition of the substances spewed by them. Particular attention is paid to the study of hydrocarbon compounds. The spewed hydrocarbons directly indicate depth migration and present indirect signs of commercial oil-and-gas potential (Planke et al., 2003; Etiope et al., 2004; Feyzullayev, 2012; Bonini et al., 2013; Feyzullayev et al., 2015).

Similar reasons determine complex multi-vector geochemical investigations of bottom sediments and mud volcanoes on the shelf and on the deep-ocean floor of Taiwan, Brunei and Malaysia (Chen et al., 2014). Similar studies of deep-sea sediments and their inherent organic compounds as prerequisites for oil-and-gas subsurface potential have been conducted in the Gulf of Finland for a long time (Khoroshko et al., 2004).

Many studies are regularly done on the shelf and in deep waters of the Gulf of Mexico (Gay et al., 2011; Aeppli et al., 2014), the Persian Gulf (Mirza et al., 2012; Monazami Tehrani et al., 2013), on the continental shelf and in the deep waters of Thailand (Boonyatumanond et al., 2006), along the western edge of the Bay of Bengal (Fernandes et al., 2014), the Bering Sea (Oguri et al., 2012; Moore et al., 2014) and in bottom sediments of the Chesapeake Bay in Virginia, USA (Kan et al., 2005). Other researchers have studied carbon-containing compounds in bottom sediments of the Ross Sea near the Antarc-

tic coast (Villinski et al., 2000), in the Weddell Sea (Antarctica) (Rau et al., 1991), in the water mass and bottom sediments in the Atlantic and Pacific oceans (Kaiser and Benner, 2009) and in the Sargasso Sea (Sowell et al., 2009).

Studies and identification of organic compounds contained in the sediments and water masses have been carried outby various methods; gas chromatography–mass spectrometry (GC-MS) is widely used (Nesvizhskii et al., 2003; Waldhier et al., 2010).

Samples of bottom sediments have been investigated by mass spectrometry, isotope analysis and a wide range of laboratory tests in order to determine their composition (identifying features of the relationship between elemental and blend composition), to correlate the data obtained with geological processes and, as a result, to identify prerequisites of oil-and-gas potential of subsurface or to clarify their geological structure.

Previously, we have carried out a mass-spectrometric analysis of some sulphur-containing organic compounds in sediments of the northern Caspian Sea (i.e., the area of the artificial island "D"), where intensive oil exploration and oil production works were performed (Zhumagaliev et al., 2013, 2014).

3. Methods

The sampling took place in the Kashagan, Kayran and Aktoty fields (Fig. 2). Bottom sediment at all sites under investigation is light silt. The samples of bottom sediments were taken by Petersen dredge, and were placed in special glass dishes. To analyse the organic compounds contained in the bottom sediments, nine samples were taken. Further, prior to the analysis, they were kept in a freezer at –8°C. Preforms (5–10 g) of bottom sediment samples, preliminarily dried at room temperature and passed through a sieve, were extracted in an ultrasonic bath with 20 ml dichloromethane three times for 10 min. The extracts were combined, and concentrated to 0.5 ml; after that internal standards were added. The perdeuterated naphthalene and phenanthrene were used as standards. The study of "semi-volatile" organic compounds in selected samples was carried out by using GC-MS Pegasus 4D (LECO). The electron ionisation energy was 70 eV, silicone capillary column RTX-5MS (30 m), temperature: 50°C (2 min) – 20°C / min – 300°C (10 min), interval of scanned mass – 29–500 Da. Concentrations of individual n-alkanes and aliphatic carboxylic acids were determined in µg/g. Their retention times (R.T) on silicone capillary column are given in seconds. The m/z molecular ion peak

Fig. 2. Kashagan, Kalamkas A, Kashagan Southwest, Aktote and Kairan – individual oil fields of the Kashagan field. Diamonds – sampling sites; red one – control point.

(MI) M⁺, and ten most intense peaks of fragment ions were determined for the mass spectrum of each compound. The quantitative characteristic of the molecular ion stability to the electron ionisation (EI) was expressed through the molecule stability to EI:

$$W_{MI} = \frac{I_{MI}}{\Sigma I} \times 100\% \qquad (1),$$

where I_{MI} – intensity of the molecular ion, ΣI – total intensity of all ions. This value is expressed as a proportion of molecular ions in the full ion current expressed as a percentage. In order to identify n-alkanes and carboxylic acids contained in the sediment samples, we used a firmware of Pegasus 4D, as well as NIST data base libraries (Stein et al., 2002).

4. Results

Generally, the present study has identified 10 normal alkanes and 11 aliphatic monocarboxylic acids. The GC-MS analysis showed that the concentrations of individual alkanes and carboxylic acids in the different samples of sediments varied between $0.001 \div 0.88$ µg/g and $0.001 \div 1.94$ µg/g, respectively. The maximum detected concentration differs from the minimum one by 2–7 times. The concentration range is much wider for n-heptadecanes.

The difference between the detected maximum and minimum concentration makes 165 times.

The peak of molecular ion (MI) allows determining the gross formula of alkanes (C_nH_{2n+2}), despite the low intensity of these peaks. Full mass spectra of n-alkanes (I–X) (Stein et al., 2002) are characterised by minor peaks of homologous carbocations composed of C_nH_{2n+1}, $CnH2n$ and C_nH_{2n-1} that appear in the following series:
– I (m/z 113, 112, 99, 98, 84, 70, 69, 56, 55, 42, 28);
– II (m/z: 127, hereafter similarly to I);
– III (m/z: 141, hereafter similarly to I, II);
– IV (m/z: 155, hereafter similarly to I – III);
– V (m/z: 183,169, hereafter similarly to I – IV);
– VI (m/z: 197, hereafter similarly to I – V);
– VII (m/z: 211, hereafter similarly to I – VI);
– VIII (m/z: 225, hereafter similarly to I – VII);
– IX (m/z: 239, hereafter similarly to I – VIII);
– X (m/z: 253, hereafter similarly to I – IX).

The mass spectra of the aliphatic monobasic carboxylic acids studied have prominent peaks of molecular ions. Typically, aliphatic carboxylic acids are characterised by low stability under mass-spectrometry due to the highly polar carboxyl group, reducing their volatility and thermal stability (Kemp, 1991). Therefore, in the overlap mass spectrometer system, they are inclined to thermal decarboxylation. Consequently, they have often been analysed as methyl ethers. One should also note that all of the above acid mass spectra (XI–XXI) contain minor peaks of ions [COOH]⁺ (m/z 45).

Individual acid concentrations also vary from sample to sample, the detected concentration range, except for compound XII, is rather wide. The difference between the maximum and minimum concentration of individual components varies from 20 to 200.

5. Discussion

Alkanes (paraffin hydrocarbons) and aliphatic carboxylic acids (alkanoic acids) have been sufficiently studied through mass-spectrometry (Kovats, 1958; McLafferty, 1963; Kemp, 1991; de Hoffmann and Stroobant, 2007). Research results obtained in the present paper correspond to published data. The specific feature of the mass spectra of normal paraffin hydrocarbons implies the presence of intense peaks of homologous ions composed of $[C_nH_{2n+1}]$ which are distributed by intensity in the following row:
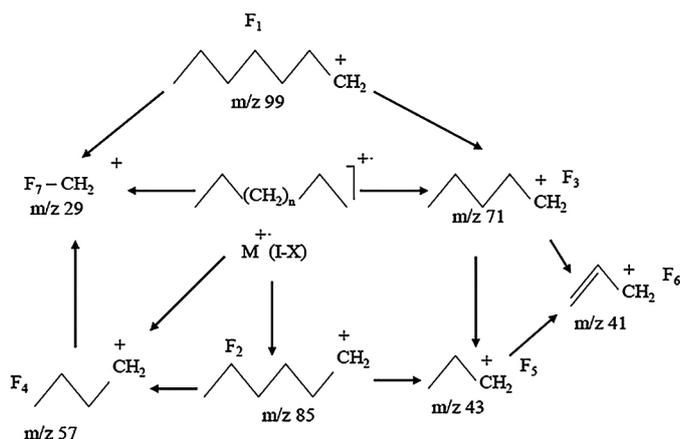
$$[C_4H_9]^+ \ (m/z\ 57) > [C_5H_{11}]^+ \ (m/z\ 71) > [C_6H_{13}]^+$$
$$(m/z\ 85) > [C_7H_{15}]^+ \ (m/z\ 99) \qquad (2).$$
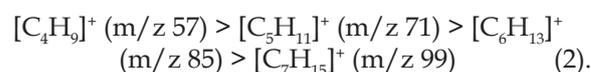
Fig. 3. Fragmentation of n-alkanes (1-X).

Total peak intensity of these ions was used before to determine the paraffin group composition in the paraffin oil fractions [48a]. The mass spectra of n-alkanes (I–X) obtained revealed a large number of ion peaks composed of $[C_n H_{2n+1}]$ + with m/z: 43, 57, 71, 85, etc. Their intensity increases monotonically during transition from the large to smaller mass numbers. The general pattern of the mass spectra is typical of paraffin hydrocarbons.

In total mass spectra of n-alkanes (I–X) the heaviest of the fragment ions corresponds to the ion $[M-C_2H_5]$ + (I –, m/z 113; II – m/z 127; III – m/z 141; IV – m/z 155; V – m/z 183; VI – m/z 197; VII – m / z 211; VIII – m/z 225; IX – m/z 239; X – m/z 253). These peaks are characterised by low intensity. This fact presents the possibility to confirm that the initial act of alkane fragmentation implies removal of the terminal C_2H_5 (ethyl) group with m/z 29, rather than CH_3, from MI (see Fig. 3).

Unlike the homologues (II–A), the ion peak F_5 (m/z 43) has a maximum amplitude in the mass spectrum of n-decane (I). This demonstrates easy

formation of carbocation $[C_3H_7]$ + as a stable MI fragment.

For all aliphatic monocarboxylic acids (XI–XXI) studied, McLafferty rearrangement [49a] is the main characteristic process with formation of a radical cation F_4 with m/z 60, and in the case of compound III – F_3 with m/z 88 in the case of compound III.

Another important aspect of acid fragmentation is the formation of oxonium ions (m/z 73, 87 etc.). Using the mass numbers of oxonium ions (F_1, F_2 and F_3) and rearrangement of ions (F_4) allows determination of the substitution character in α- and β- C atoms.

Fragmentation of aliphatic carboxylic acids (XI–XXI) studied can be represented by the following scheme (Fig. 4). The main process of MI fragmentation is McLafferty's (1959) rearrangement with migration of hydrogen atom from γ position. This process leads to the formation of the most intense peak in the mass spectrum corresponding to the ion-radical F_4 with m/z 60 (Fig. 4).
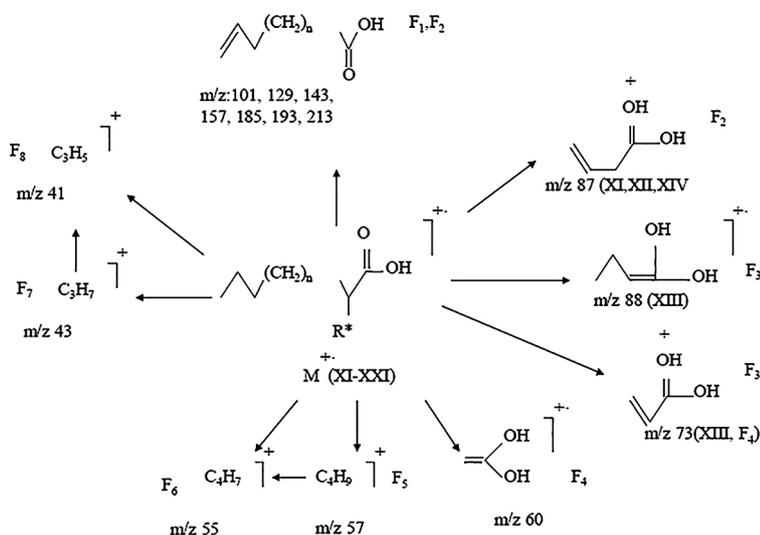

Fig. 4. Fragmentation of aliphatic monocarboxylic acids (XI–XXI).

In the case of 2-ethylhexanoic acid (XIII), this rearrangement leads to the ion-radical F with m/z 88, which peak is the most intense in the mass spectrum. For characteristics along with ions (m/z: 60, 88) the most important factors in the mass spectra of aliphatic carboxylic acid (XI–XXI) are the peaks (the second most intense) of oxonium ions F3 with migration of H-atom from the β- position.

In the mass spectrum of 2-ethylhexanoic acid (XIII), one can observe the intense peak of F1 ion with m/z 116 corresponding to the release of C_2H_4 from MI, with the formation of F1 cation radical. Obviously, this ion F_1 is formed through cleavage of C2H4 from the ethyl radical since the peak of similar ion the mass spectra of other acids studied (XI, XII, XIV–XXI) is not observed.

Prominent peaks of other oxonium ions are important for diagnostic tasks in the mass spectra of acids (XI–XXI): $[M-C_2H_5]^+$ (XI – F_2, m/z 87; XII – F_1, m/z 101; XIII–XIV – m/z 115; XV – F_1, m/z 129; XVI – F_1, m/z 143); $[M-C_3H_7]$ (XII – F_2, m/z 87; XIII – F_2, m/z 101; XIV – F_1, m/z 101; XV – F_2, m/z 115; XVI – F_2, m/z 129; XVI – F_1, m/z 143; XVIII – F_1, m/z 157; XIX – F_1, m/z 185; XX, XXI – F_1, m/z 199). These ions are formed by a similar mechanism, inclusive of migration of H atoms from more distant locations.

The lack of exogenetic water displacement in the Pleistocene aquifer system of the northern Caspian Sea is the most important and unique feature of the sedimentary northern Caspian Basin. The aggravating mineralisation of interstitial and ground water is the result of transformations during diagenesis. Within the context of exogenetic water preservation in geological history, hydromica clays are a powerful source of material, which aggravates the process of interstitial and ground water mineralisation. The most important feature of the Caspian Basin is that its northern part (the northern Caspian Sea and Caspian Depression) is characterised by exceptionally small ground slope and underwater gradient, by the shallowness of the sea and horizontal layer position (see Fig. 5). This is a very important circumstance that determines the specific features of sediment genesis in this part of the basin – the role of horizontal transportation here is reduced to a minimum. The groundwater chemical composition has changed towards increased concentrations of components that can be found in interstitial water of Pleistocene basins in other regions than the Caspian Sea. This is measured by the interaction (physical, chemical and biological) between the water, rocks, fluid and organic matter. Exogenetic water preservation in that part of sedimentary basin that we are considering helps to concentrate chemical elements in groundwater, excluding the horizon-
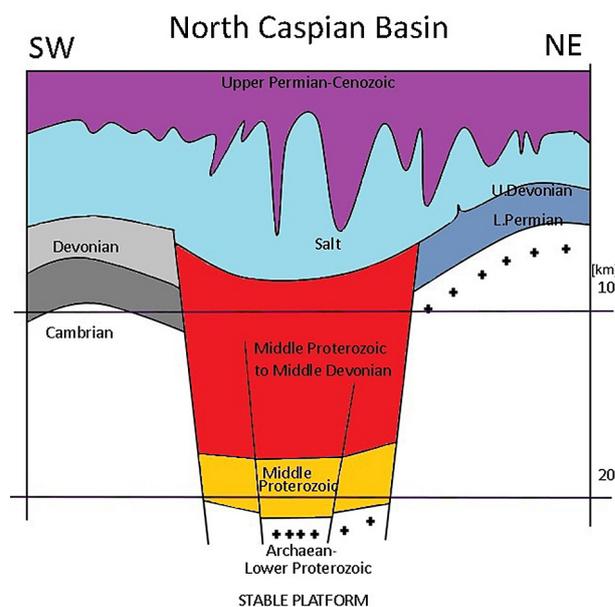

Fig. 5. Cross section through the Caspian Basin, showing the extensive Permian salt diapirs in the stable northern Caspian Basin (after Kroonenberg et al., 2005).

tal migration of water, gases and other chemical elements from other intervals of the cross section. Under such circumstances, one can expect that the matter will migrate mainly in vertical directions under the influence of pressure gradients, etc. Within the context of zero exogenetic water displacement, the hydrogeochemical pattern is determined mainly by the composition of enclosing and underlying rocks, and by features of finely dispersed fraction pattern. Thus, it is obvious that substances are much more likely to migrate in porous, coarse-dispersed media and to accumulate in finely dispersed media. The density and moisture capacity of bottom sediments determining the ability of rocks to accumulate substances depend on granulometric composition. Our studies have shown that organic matter accumulates in bottom sediments with a high content of small (clay and aleuric) fractions. In other words, the highest intensity of organic matter accumulation is typical of finely dispersed soils with a larger active surface area and, accordingly, a better ability to absorb organic compounds. According to our studies with regard to the granulometric composition of the bottom sediments of the northern Caspian Sea, differently sized sand particles are the main type of bottom sediments in the western part of the northern Caspian Sea. A silty sand area is located in the eastern part. Throughout most of the study area, mechanical composition of the bottom sediments is supplemented by shelly material, which content varies from trace amounts to 95% (the central part of the Mangyshlak Thresh-

old). The sand fraction is very often represented by shell detritus. Egg stones can be found in the east of the border with the Middle Caspian Sea and on the Kulalinsky Ridge.

In the Kashagan oil field, bottom sediments are clayey mud while the small sand fraction is represented by shell detritus. One can note an interesting feature that is typical of the bottom sediments of the northeastern Caspian Sea region: they are represented mainly by two phases: large silts and clayey mud. Large silts predominate throughout most of the northeastern Caspian Sea region while clayey mud predominates in the Kashagan oil field (its abundance boundaries can be related to boundaries of the Ural Furrow). The highest concentration of hydrocarbon compounds was recorded in samples of bottom sediments taken from the Kashagan oil field. Although these records are largely conditioned by the presence of oil-bearing rocks beneath the bottom surface (as evidenced by exploratory drilling and experience in putting on stream of oil-bearing horizons), a high concentration of organic matter can also be associated with its greater accumulation in the finely dispersed soils typical of this location. This feature can be used in the following recommendation: hydrocarbon concentration measurements should be renormalised based on the granulometric composition of bottom sediments, so that the local maximum concentration associated with the local predominance of finely dispersed phase was not treated erroneously as a sign of oil-bearing horizons located in the area.

6. Conclusions

An important feature of the Caspian Basin is that its northern part (the northern Caspian Sea and Caspian Depression) is characterised by exceptionally small ground slope and underwater gradient, by the shallowness of the sea and horizontal layer position. That circumstance determines the specific features of sediment genesis in this part of the basin: the role of horizontal transportation is here reduced to a minimum. The groundwater chemical composition has changed towards an increase in the concentration of components that can be found in the interstitial water of Pleistocene basins in other regions of the Caspian Sea. This is measured by the interaction (physical, chemical and biological) between water, rocks, fluid and organic matter. Exogenetic water preservation in that part of a sedimentary basin that we are considering helps to concentrate chemical elements in groundwater, excluding the horizontal migration of water, gases

and other chemical elements from other intervals of the cross section. Under such circumstances, one can expect that the matter will migrate mainly in vertical directions under the influence of pressure gradients, etc. In the context of zero exogenetic water displacement, the hydrogeochemical pattern is determined mainly by the composition of enclosing and underlying rocks, and by features of finely dispersed fraction pattern.

The present study has shown that concentrations of the individual alkanes and carboxylic acids in the sediments range from 0.001 to 0.88 µg/g and 0.001–1.94 µg/g, respectively. In the full mass spectra of n-alkanes (1-X) the heaviest of the fragmented ions corresponds to the ion $[M-C_2H_5]$. This fact indicates that the initial fragmentation of alkanes implies cleavage of the radical C_2H_5, rather than CH_3. Unlike the homologues (II-A), the F_5 ion peak (m/z 43) has a maximum intensity in the mass spectrum of n-decane (I). This demonstrates easy formation of carbocation $[C_3H_7]^+$ as a stable MI fragment. The mass spectra of the higher aliphatic monobasic carboxylic acids studies are characterised by significant MI peaks. In addition, all mass spectra of acids considered (XI –XXI) have minor peaks of ions [COOH]+ (m/z 45). All aliphatic monocarboxylic acids (XI–XXI) studied were characterised by McLafferty's (1963) rearrangement with formation of F_4 cation-radical with m/z 60 and F_3 with m/z 88 in the case of compound XIII. Another important aspect of acid fragmentation is the formation of oxonium ions (m/z 73, 87, etc.). Using the mass numbers of oxonium ions (F_1, F_2 and F_3) and rearrangement ions (F_4) provides the possibility to determine the substitution character in α- and β- C atoms. The presence of F_1 intense ion peak with m/z 116 in the mass spectrum of 2- ethylhexanoic acid (XIII) is a consequence of C_2H_4 release from MI with subsequent formation of F_1 cation radical. The F_1 ion is formed by cleavage of C_2H_4 from the ethyl radical since a similar ion peak was not observed in the mass spectra of other acids (XI, XII, XIV–XXI) studied.

We believe that these data could be of use during full-scale industrial development of the Kashagar oil field for conducting environmental monitoring and early prevention of possible leaks, especially during the pumping of wells and withdrawal of the region from active development, with a view to drafting and implementing a soil and water reclamation strategy and returning the region to its original environmental state.

Acknowledgements

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