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DTA AND TG STUDIES OF PALEOCENE BITUMINOUS ROCKS FROM EL IUSR OIL DEPOSIT – EGYPT

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Abstract

The organic and mineral composition of selected samples from boreholes P-24, P-27 and P-26 of the oil deposit El Iusr, in the Suez Channel region, were characterized by DTA and TG supplemented by X-ray and luminescence-bituminous studies.

It was established that the content of bitumens in sandstones is higher than in clays and their compositions changes with the depth of the borehole. A slight vertical and lateral migration of hydrocarbons in the first clay member of the lateral migration of hydrocarbons in the first clay member of the Iusr article was observed. The content of light hydrocarbons rises with the increase of the proportion of clay minerals. It was found that montmorillonite is more effective in retaining light hydrocarbons than kaolinite.

Keywords: clay minerals, DTA analysis, kaolinite, montmorillonite, oil deposit, X-ray studies

Introduction

Thermal methods have been widely applied for characterizing the evaporation capability, coke-forming tendency and thermal stability of various petroleum hydrocarbons [1–3]. The same methods were successfully used in determining the type of bitumens in rocks [4–7].

Using thermovacuum pyrolysis, Tverdova [8] has established that the Lower Jurassic deposits containing humic constituents undergo considerable mass loss up to 200 and 400°C and the presence of light hydrocarbons has been confirmed by GC.

The aim of the present investigation is to characterize the organic material and the mineral matter of samples from the petroliferous area of the El Iusr deposit, Egypt by means of DTA and TG methods.

Materials and methods

Selected samples from boreholes P-24, P-27 and P-26 of the oil deposit El Iusr in the Suez Channel region were studied. The boreholes are located in the central part of the deposit along the line from the north-northwest to the south-southeast.

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Borehole P-24 is situated in the most northern part and P-26 is located in the most southern part of the deposit with a distance of 2200 m between them. The sample areas were at a depth from 1302.5 to 1364 m for borehole P-24, from 1146 to 1227 m for P-27, and from 1140 to 1199 m, for P-26. The interval corresponds to Iusr member, Rudene formation, of Early Miocene age and is petroliferous.

The samples with particle size below 0.25 mm were subjected to DTA and TG analyses on a Derivatograph Q-1500 D, system Paulik-Paulik-Erdey (MOM, Budapest). The experiments were carried out following a predetermined program at a heating rate of 10°C min^{-1}, in platinum crucible and Al_2O_3 was used as an inert substance. The analysis was performed in static air atmosphere which permits evaluation of the thermo-oxidative and destructive properties of hydrocarbons which are constituents of the rock bitumens [4].

Thermal analyses were supplemented by X-ray studies using the powder method on a DRON-2 diffractometer with cobalt-filtering radiation. The particle size was below 0.005 mm. Mineral phases were identified by comparison with JCPDS data.

The luminescence-bituminous analysis was carried out according to the method of Frolovska [9]. For this purpose the sample (2 g) was treated with 5 ml pure non-luminescent chloroform and after 16 h extraction at ambient temperature, the extract was compared with reference samples. This way, the percentage of bitumen in rocks was determined. The standard was a crude oil sample from the same region [10].

Results and discussion

The DTA and TG curves of the samples from the three boreholes were quite different (Fig. 1–A, B, C). The absence of any endothermal effect at 100–110°C in the DTA curves is most probably due to the minimum content of adsorbed water which is also confirmed by the insignificant mass loss exhibited by the TG curves. For boreholes P-24 and P-27 it hardly reaches 0.8% per rock and for P-26 –1.6% per rock. It is known that clays contain very small amounts of adsorbed water. Thus, the thermal effects registered in the DTA curves up to 500°C are due mainly to the organic material filling the mineral matrix. The mass loss up to this temperature is probably related to the presence of light hydrocarbons in bitumens (Tables 1–3).

The appearance of an intense exothermal effect at 330–440°C is characteristic of samples from borehole P-24 except for samples No. 7^2, 10, 11^1 and 12^2. The latter show two exothermal effects in their DTA curves, at 250–360°C and at 400–440°C, respectively (Fig. 1–A). Generally, up to a depth of 1338 m one exothermal peak is observed while at increased depth a second peak also appears. TG data demonstrate that the mass loss of clays in the 100–350°C interval is in the range from 4.0 to 5.6% per rock, and for 350–450°C it is considerably lower (0.4–1.8% per rock) (Table 1). At the same temperatures the sandstones from this borehole undergo a mass loss of 2.6–4.0% per rock and 0.8–2.0% per rock, respectively. The exothermal effects at about 450°C are related to thermo-destructive processes. The first exothermal effect registered at temperatures above 300°C is probably due to ther-

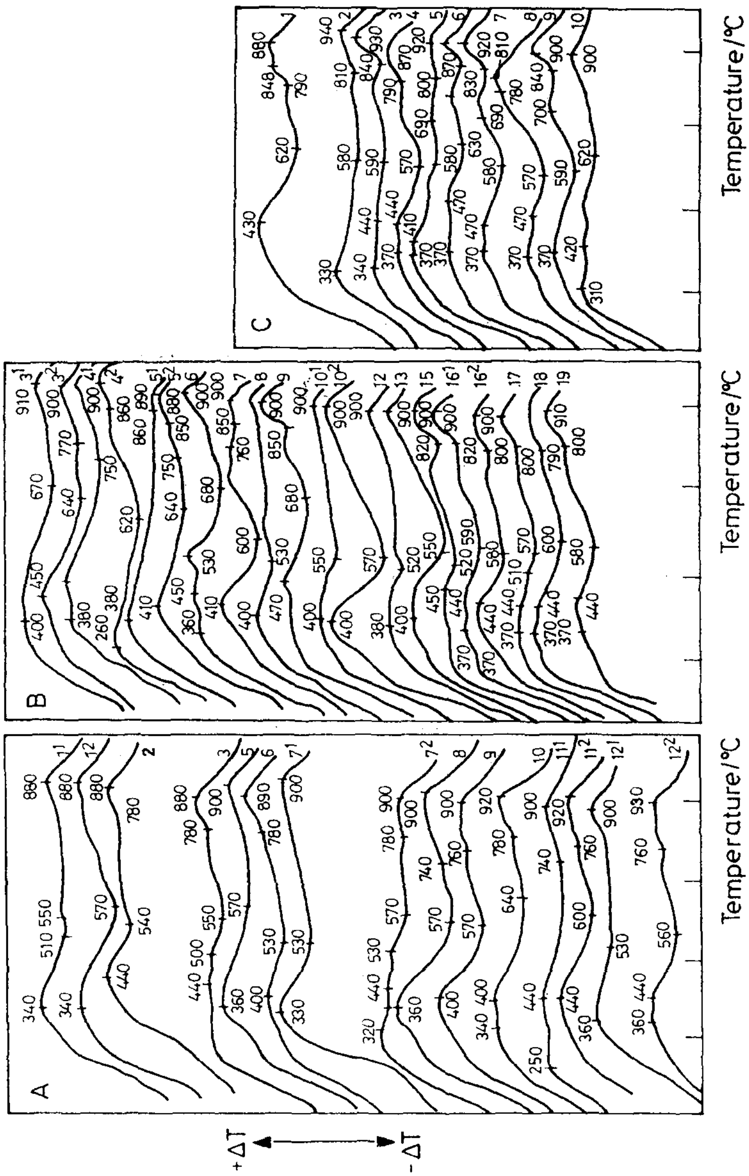

Fig. 1 DTA curves of samples from borehole: A _ P-24; B _ P-27; C _ P-26

mal-oxidative processes which mainly affect long-chain paraffinic and cyclic hydrocarbons. The second exothermal effect with maximum temperature at about 450°C is assumed to be due to a polycondensation process. Consequently, in the clays light hydrocarbons predominante, as opposed to sandstones.

Table 1 Characteristics of the bitumens from borehole P–24

Sample No.	Depth/m	Lithologic type	Chl.b./% [10]	Mass loss/% TG, at T/°C		Luminescence of chl.b.
				100–350	350–450	
1^1	1302.5–1303.5	packed clay	0.04	4.6	1.6	weak milk white
1^2	1303–1308.5	sandstones	2.4	2.0	1.8	beige-dark grey
2	1308.5–1309.5	packed clay	0.02	burns		intensive milk-white
3	1311.5–1317.5	clay sandstones	0.3	1.6	1.8	beige-dark grey
5	1322.5–1328	bituminous sandstones	2.4	2.4	1.6	beige-dark grey
6	1328–1329	packed clay	0.3	5.6	1.2	weak milk white
7^1	1335–1338	clay bituminous sandstone	0.01	4.0	1.6	beige-dark grey
7^2	1338–1339	packed clay	0.04	4.6	0.4	beige-dark grey
8	1339–1344	weak bituminous sandstone	2.4	2.4	2.0	beige-dark grey
9	1344–1347	bituminous sandstone	2.4	2.4	1.6	beige-dark grey
10	1348–1352	clay sandstone	0.08	3.6	0.8	milk white
11^1	1357–1359	clay sandstone	0.6	0.8	0.8	intensive milk white
11^2	1359–1360	clay sandstone	2.4	2.2	1.4	weak milk white
12^1	1361–1363	clay sandstone	2.4	1.0	1.4	beige-dark grey
12^2	1363–1364	packed clay	0.04	4.0	1.8	beige-dark grey

Standard-extraction analysis of the samples shows that the content of bitumens in the clays is 0.02% in sample No. 2, and 0.3% for sample No. 6. In sandstones it is 0.01% for sample No. 7^1 and 2.4% for samples No. 1^2, 5, 8, 9, 11^1 and 12^2. Hence, the percentage of bitumens in sandstones is higher than in clays. Besides this, bitumens from the clay samples luminescence with a milk-white to light yellow colour, which is indicative of the presence of light hydrocarbons and is supporting the data from the DTA and TG analyses. The luminescence of the sandstone extracts is beige-dark grey and is indicative of the presence of large amounts of heavy resins and asphaltenes (Table 1).

The DTA curves of samples No. 3–No. 15 from borehole P-27 show one exothermal effect with maxima in the range from 380 to 470°C (Fig. 1–B), except for samples Nos 4^2 and 6. In the DTA curve of the first one a single exothermal peak appears with a relatively low maximum temperature –260°C, and the DTA curve of the second one displays two exothermal effects at 350 and 450°C. Thus, two exothermal effects of identical maximum temperatures (370 and 440°C) appear with the increase of the depth below 1208.5 m (Fig. 1 –B).

The profile of the TG curves demonstrates that the mass loss of the clay samples from 100 to 350°C is 1.6–5.2% per rock, and from 350 to 450°C it is 0.4–1.8% per rock. In the same temperature intervals sandstones decrease their mass by 0.8–4.6% per rock and 0.8–2.4% per rock, respectively (Table 2). This supports our notion that the clays of this borehole are enriched with light hydrocarbons.

The content of bitumens in the clay samples from borehole P-27 is in the range form 0.005% (Nos 8, 9, 10, 13) to 0.01% per rock (Nos 4^1, 5^1 and 6) (Table 2). In the sandstones it varies from 0.3% per rock (samples No 3^1, 4^2, 15) to 2.4% per rock (samples No. 5^2, 7, 10^2, 16^1, 17, 18 and 19) (Table 2). The sandstones of this borehole, similarly to that in P-24, contain higher percentage of bitumens than the clays. The bitumens of the clays show weak luminescence and more intensely milk-white, and the sandstones from milk-white to beige-dark grey. Thus, we have found that in this borehole (P-27) the light hydrocarbons are concentrated in the clays, while the heavy resins and the asphaltenes are dominating in the sandstones. Regardless of this fact, a decreasing tendency of the bitumen content with the decrease of depth is observed.

In the DTA curves of samples from borehole P-26 up to about 500°C and a depth of 1151.5 m, one exothermal effect was observed at 430°C (sample No. 1) or 330°C (sample No. 2). Below this depth two exothermal peaks appear at 340–370°C and at 410–470°C (Fig. 1–C). However, the DTA curve of sample No. 9 is characterized by only one exothermal effect at 370°C. Similarly to borehole P-27, in the DTA curves of all samples beyond 1151.5 m one exothermal effect was observed at one and the same temperature –370°C, except for sample No. 10 (Fig. 1–C).

The results of TG analysis show that the clays from borehole P-26 decrease their mass by 1.2–4.0% per rock from 100 to 350°C and by 0.8 to 1.6% per rock from 350 to 450°C (Table 3). For the sandstones these losses are 0.8–2.4% per rock and 0.8–1.6% per rock, respectively (Table 3). It can be seen that the percentage of light hydrocarbons in the bitumens increases with the decrease of depth. The amount of bitumens in the clays is 0.04% per rock for sample No. 8. In all cases, the content of bitumens in the sandstones is maximum –2.4% per rock (samples Nos 4–7, Table 3). We have found that the sandstones from this borehole similarly to the sandstones form the other tow boreholes contain larger amounts of bitumens than the clays. While the bitumenes in the clay luminesce from milk-white to light

Table 2 Characteristics of the bitumens from borehole P–27

Sample No.	Depth/m	Lithologic type	Chl.b./% [10]	Mass loss/% TG, at T/°C		Lumines-cence of chl.b.
				100–350	350–450	
3^1	1146–1147	strongly clay sandstones	0.3	2.0	0.8	beige
3^2	1147.5–1151	clay sandstones	1.2	3.2	1.6	beige-dark grey
4^1	1153–1154	clay	0.01	4.4	1.2	intensive milk white
4^2	1154–1155	linseed clay sandstones	0.3	1.6	0.6	beige
5^1	1357–1158	clay	0.01	4.0	0.8	milk white
5^2	1158–1160	strongly clay sandstones	2.4	2.4	1.6	beige-dark grey
6	1160–1162	clay	0.01	5.2	1.2	milk-white
7	1162.5–1163.5	stronly clay sandstones	2.4	2.6	1.8	beige-dark grey
8	1163.5–1168	clay	0.005	4.0	1.4	milk-white
9	1168–1171	clay	0.005	1.6	0.4	intensive milk-white
10^1	1188.5–1189.5	packed clay	0.005	5.0	1.8	intensive milk-white
10^2	1189.5–1190.5	clay bitumenous sandstones	2.4	2.0	2.4	beige-dark grey
12	1192–1197.5	clay sandstones	0.005	4.6	0.8	weak milk white
13	1198–1200.5	clay	0.005	4.0	1.6	milk-white
15	1201.5–1208.5	lins. clay sandstones	0.3	0.8	0.8	milk-yellow grey
16^1	1208.5–1213.5	clay sandstones	2.4	2.0	0.8	beige-dark
16^2	1213.5–1214.5	clay alevrolite	2.4	2.4	1.2	beige-dark grey

Table 2 Continued

Sample No.	Depth/m	Lithologic type	Chl.b./% [10]	Mass loss/% TG, at T/°C		Lumines-cence of chl.b.
				100–350	350–450	
17	1216–1220	alevrolite clay sandstone	2.4	0.8	0.8	beige-dark grey
18	1220.5–1222	clay sandstone	2.4	2.8	0.8	beige-dark grey
19	1222.5–1227	clay sandstone	2.4	1.2	1.6	beige-dark grey

beige colours, the luminescence of the bitumens in the sandstones is beige colours, the luminescence of the bitumens in the sandstones is beige-dark grey. This proves that like the other boreholes, the clays are enriched in light hydrocarbons while in the sandstones the heavier ones are concentrated, i.e. heavy resins and asphaltenes.

Figures 1–A, B, C demonstrate that the analysed samples which are multicomponent mineral mixtures have relatively similar DTA curves. They are characterized by a broad endothermal effect whose maximum temperature for the samples of borehole P-24 is 500–740°C, of P-27 520–750°C and of P-26 570–630°C. Clearly defined exothermal effects at 880–930°C for borehole P-24, at 880–910°C for borehole P-27, and at 880–940°C for borehole P-26 appear in all DTA curves. These effects point to the presence of both quartz and kaolinite. For example, quartz is characterized by an endothermal effect at 570°C which is due to the transformation of α-quartz to β-quartz. The presence of kaolinite is confirmed by the appearance of an endothermal effect at 400–600°C which is related to the release of hydroxyl-bound water resulting in amorphisation of the substance. This mineral is characterized by an exothermal effect at about 900°C which is due to the crystallization of Al_2O_3 and mullite [11]. For some samples – Nos 6, 7^2, 10, 11^2, 12^2 (P-24), Nos 4^2, 5^1, 7, 16^2 (P-27) and Nos 1, 2 (P-26), the sinusoidal character of the DTA curves in the temperature range 570–770°C is indicative of the presence of montmorillonite. The endothermal effects correspond to the release of structural water and to an almost complete destruction of the crystal lattice with starting of partial amorphization [11]. The loss of hydroxyl water which is included in the crystal lattice starts at 450–500°C and ends at 750°C with maximum at 700°C.

There appear also endothermal effects which prove the presence of carbonates. Thus, the endothermal effect appearing at 720–1000°C which is due to the dissociation of $CaCO_3$ indicates the presence of calcite (samples Nos 2, 3, 6, 7^2, 9 – borehole P-24; Nos 3^2, 4^2, 5^1, 5^2, 18 – borehole P-27; Nos 1, 4, 6, 8 – borehole P-26). The appearance of two endothermal effects at 720–870°C and at 870–1000°C which are resulting from the dissociation of $MgCO_3$, or $CaCO_3$ in some of the samples from borehole P-27 (sample No. 5^1) and from P-26 (sample No. 1) points to the presence of dolomite.

The exothermal effects at 500 –530 °C observed for samples Nos 1^1, 3, 7^2 – P-24, for Nos 6, 10^1, 2, 12, 17 – P-27 and for Nos 5, 10 from borehole P-26 are ascribed to the presence of pyrite which is oxidized to haematite at this temperature.

X-ray studies of the selected samples reveal the presence of the following minerals: quartz, kaolinite, montmorillonite, calcite, dolomite, pyrite, chaelite and feldspar in different ratios (Fig. 2–A, B, C). Quartz whose reflectances are too intense and are definitely seen (422 and 333 A) is present in all the samples and its quantity is greater for boreholes P-24 and P-27.

Kaolinite a representative of clay minerals is found in all the samples in amounts decreasing in the following order: P-24 (sample No. 1^1) > P-27 (sample No. 5^1) > P-26 (sample No. 10). Montmorillonite is also found but in lower amount.

The carbonates are present in all the samples, with calcite predominating. Dolomite was found in minimum amounts in boreholes P-24, P-27 and P-26. However, sample No. 9 from borehole P-27 is composed entirely of dolomite. Most of the samples contain pyrite and chaelite.

Table 3 Characteristics of the bitumens from borehole P–26

Sample No.	Depth/m	Lithologic type	Chl.b./% [10]	Mass loss/% TG, at T/°C		Luminescence of chl.b.
				100–350	350–450	
1	1140–1144.5	bituminous clay	0.15	3.2	1.6	beige
2	1144.5–1148.5	clay	0.08	4.0	1.6	milk white
3	1151–1151.5	clay	0.08	1.8	1.6	intensive milk white
4	1161–1164	sandstone	2.4	2.4	1.6	beige-dark grey
5	1169–1174	weak clays sandstones	2.4	2.0	1.6	beige-dark grey
6	1174–1176	strongly clay bitumineous sandstones	2.4	1.6	0.8	beige-dark grey
7	1176–1184	weak clay bitumenous sandstones	2.4	0.8	0.8	beige-dark grey
8	1188–1189	highly packed clay	1.2	0.8	0.4	pale beige
9	1189–1194	clay	0.3	2.0	1.6	pale beige
10	1194–1199	clay	0.04	4.0	0.8	pale milk white

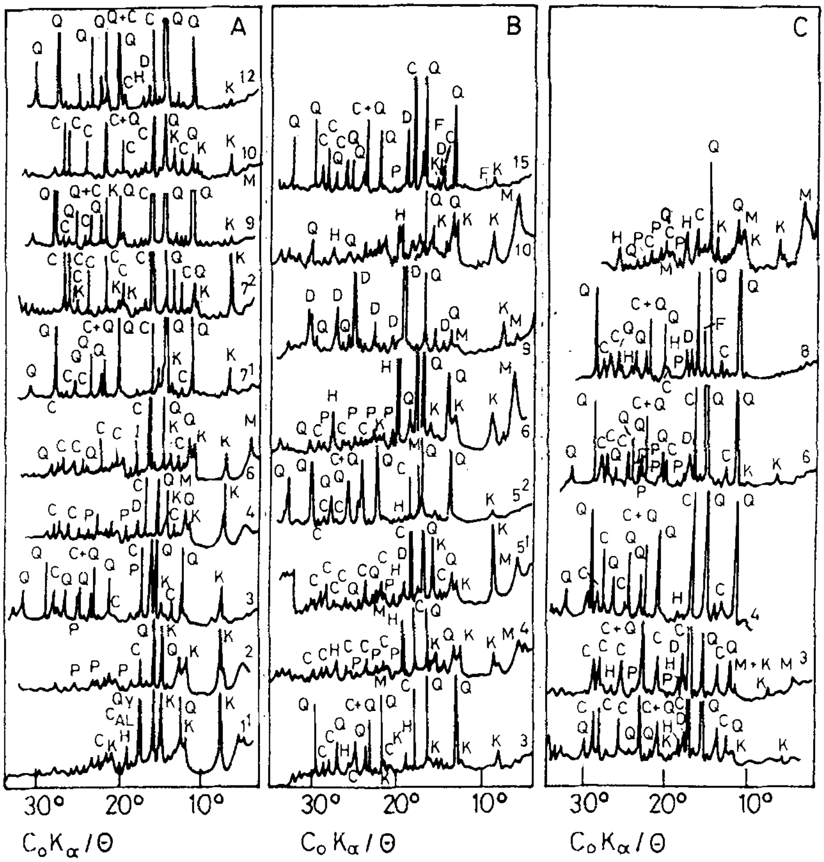

Fig. 2 X-ray diffractograms of samples from borehole: A – P-24; B – P-27; C – P-26

The results obtained from the X-ray analysis coincide, support and supplement the DTA data.

The complex investigations performed in this work prove that the bitumen content is considerably higher in the sandstones than in the clays. Besides this a weak vertical migration of hydrocarbons has been observed. Taking into consideration that the samples containing organic material represent mainly a multicomponent mineral mixture whereby quartz and calcite are accompanied by clay minerals (kaolinite and montmorillonite), one can suppose that the influence of the latter two minerals on the hydrocarbon composition of the bitumens is essential. Generally, with the increase of their amount, the content of light hydrocarbons increases, too (Fig. 3). It has also been found that the effect of montmorillonite on the retention of hydrocarbons is more pronounced than that of kaolinite (Fig. 3).

In the three sand members separated from the article Iusr from the southern part of the basin, where the boreholes P-27 and P-26 have been developed, some regularities were established in the distribution of the mineral and the organic compo-

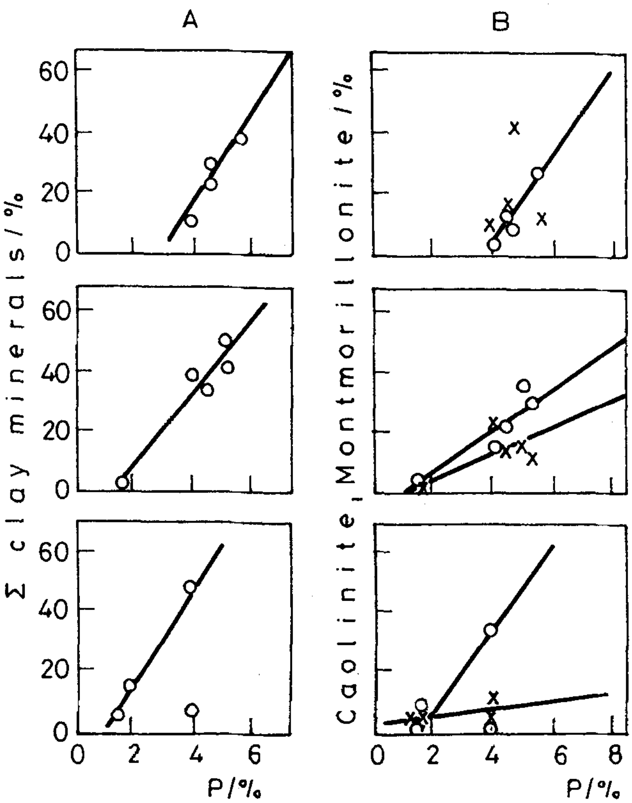

Fig. 3 Dependence between the mass loss of the samples in the temperature range 100–350°C and the content of clay minerals (A), the content of kaolinite and montmorillonite (B), respectively: o – montmorillonite; x – kaolinite

nent. These changes have not been followed for the third member and for the first member of borehole P-26 for lack of samples. In the second sand member from both boreholes a tendency for reduction in the content of kaolinite and montmorillonite from borehole P-27 and P-26 was established. In the same direction the amount of the chloroform extracted bitumen increases and the content of light hydrocarbons decreases.

In the first clay member of the same zone of the basin from borehole P-27 to borehole P-26, the content of kaolinite and montmorillonite increases accompanied by an increase in the quantity of the chloroform extract and the light hydrocarbons contained in it.

Conclusions

Thermoanalytical investigations combined with luminescence-bituminous and X-ray studies suggest the following conclusions:

1. The content of bitumens is higher in the sandstones than in the clays;

2. Variations in the composition of bitumens with the depth of the boreholes were established;

3. A weak vertical migration of the hydrocarbons was observed;

4. With the increase of the amount of clay minerals the content of light hydrocarbons rises;

5. The effect of montmorillonite is considerably higher than that of kaolinite with respect to the retention of light hydrocarbons.

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