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A Study on the Mechanisms of Oil Formation in Carbonates

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Summary

New data about the mechanisms of formation of oil in carbonate reservoirs according to revealed characteristics of the composition and physico-chemical properties of the fluid of moving part (the extracted oil), and the stationary part that remains in the pore space of carbonate reservoirs. It is shown that the inflow of light oil in the reservoir of Bashkirian deposits of Tatarstan Republic takes place. High-viscous oils from carbonate reservoirs are shown to be capable to structure forming at higher temperatures. The phase transition temperatures are determined. The prevailing role of the A1 asphaltene fraction is defined. The results can be used to improve the hydrocarbon reserves of Bashkirian deposits in carbonate reservoirs of the Middle Carboniferous sediments, as well as the search for new industrial clusters in the underlay petroleum deposits.

Introduction

Nowadays oil production is aimed at developing effective methods for heavy oils recovery. A huge amount of heavy oils is concentrated in carbonate reservoirs [1, 2]. Most carbonate rocks tend to be oil-wet, having low permeability, geological heterogeneity, multitype structure of the pore space [3-5]. All these factors have an ambiguous effect on the anomalies in the fluid characteristics (in the properties of produced crude oil). It is impossible to develop the scientific basis for enhanced oil recovery techniques in the fields without a clear idea about the structuring of oils in porous carbonate media and their composition and properties. In connection with this, we investigated the composition and physicochemical characteristics of samples of oils and oil-bearing rocks from the Akanskoe oilfield, located in Tatarstan Republic of Russian Federation.

Theory and/or Method

The objects of study were oil samples from Vereiskian and Bashkirian (from the upper and bottom parts of formation) deposits and oil-bearing rock samples from Vereiskian and Bashkirian deposits of the Akanskoe field. Crude oil extracts were obtained by successive extraction with chloroform and an alcohol–benzene solvent blend, followed by solvent evaporation.

Thermal analysis (TA) of specimens of crude oils, oil-bearing rocks, oil extracts and asphaltenes was performed with a MOM Q-1500D differential thermal analyzer (Hungary) over the temperature range of 20–1000°C at an oven heating rate of 10^{o}C/min. The amount of organic matter (OM) in the rock was determined. The chemical composition of OM was characterized by the fractional composition index F_{OM} defined as the ratio of the total amount of light and middle fractions (Δm_1 at T = 20–400°C) to that of heavy fractions (Δm_2 at T = 400–600°C).

The component composition of crude oils was determined according to the standard procedure.

The hydrocarbon type composition was studied by high-temperature gas-liquid chromatography (GLC) on a Perkin-Elmer chromatograph with a flame-ionization detector in the mode of temperature programming from 20 to 360°C.

Complex viscosity measurements were carried out using Rheotest RN4.1 (Messgeräte Medingen GmbH) over temperature range 20-80 °C.

The core material from Vereiskian and Bashkirian deposits of the Akanskoe field was investigated by the complex thermal analysis technique to characterize the chemical composition of crude oil directly in the porous medium of reservoir rock [6]. It should be emphasized that it is an in-depth study of the organic matter which allows to get valuable information on the formation mechanisms of the modern oil fields in the Bashkirian deposits.

In the study of core material in the Bashkirian deposits, depth intervals with the samples containing an abnormally high amount of light and middle fractions were found. This result is explained by the assumption of additional inflow in a reservoir of light oil [7].

Table 1: Thermal analysis data for oil-bearing rocks of Akanskoe wells

Sample no.	Coring interval, m	Mass loss in the temperature range of		OM= $\Delta m_1+\Delta m_2$, %	F_{OM}= $\Delta m_1/\Delta m_2$	Extract yield, %
		Δm_1, 150-400oC	Δm_2, 400-600oC			
Vereiskian deposits						
1	1276.3	1.2	0.8	2.0	1.5	2.3
2	1277.5	1.8	1.3	3.1	1.4	2.8
3	1278.9	1.9	1.2	3.1	1.6	4.1
4	1279.7	2.2	1.2	3.4	1.8	2.5
5	1282.5	1.2	0.9	2.1	1.3	0.8
6	1283.3	1.8	1.0	2.8	1.8	1.6
7	1286.7	0.9	0.8	1.7	1.1	1.0
8	1290.9	3.0	2.4	5.4	1.3	6.0
9	1291.9	3.6	3.1	6.7	1.2	2.0
10	1271.7	2.0	1.8	3.8	1.1	3.2
Bashkirian deposits						
11	1252.9	2.0	0.7	2.7	2.9	2.4
12	1253.3	1.4	0.9	2.3	1.6	0.8
13	1253.9	1.1	0.4	1.5	2.8	0.6
14	1254.3	1.4	0.7	2.1	2.0	1.1
15	1254.9	0.8	0.3	1.1	2.7	0.9
16	1262.9	1.6	0.8	2.4	2.0	2.0
17	1263.3	0.8	1.0	1.8	0.8	0.7
18	1264.9	2.2	1.3	3.5	1.7	4.4
19	1265.5	1.8	1.0	2.8	1.8	2.7
20	1266.5	0.7	0.6	1.3	1.2	1.7

21	1267.9	2.0	0.8	2.8	2.5	2.0
22	1269.3	1.8	1.1	2.9	1.6	2.1
23	1270.5	2.5	1.1	3.6	2.3	3.1
24	1272.3	2.4	1.1	3.5	2.2	2.3
25	1275.7	2.0	1.3	3.3	1.5	3.1
26	1277.3	0.8	0.3	1.1	2.7	0.5

To confirm the mechanism of multiphase reservoir filling in the Bashkirian deposits, it is necessary to run a comparative study of crude oils recovered from wells to the surface. We studied Vereiskian (well 27**) and Bashkirian crude oils produced by wells 22**, 20** (upper layer), and 20** (bottom layer).

Crude oils from the Bashkirian deposits are heavier and more viscous. By total sulfur content, Bashkirian and Vereiskian crude oils can be categorized as extremely high-sulfur and high-sulfur oils, respectively.

The data on the component composition show a higher concentration of asphaltenes and alcohol–benzene resins in oils from the Bashkirian deposits. Their high concentration in combination with a high gasoline content and a low amount of lube stock and paraffin wax explains the low colloidal stability of the oil from the bottom compared to that from the top of the reservoir. The crude oil from the Vereiskian deposits is distinguished by a high paraffin content and a 1.5–2 times lower asphaltene content.

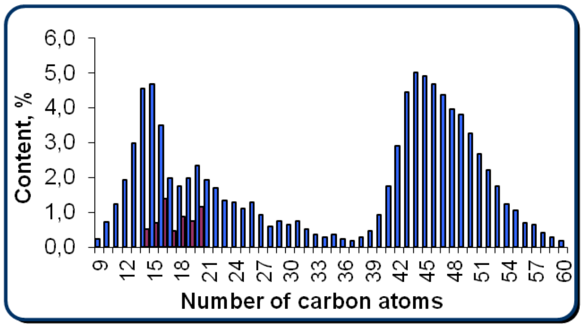
Table 2: Characterization of properties and composition of crude oils from the Akanskoe field

Parameter	Oil from Vereiskian deposits (well 27**)	Oils from Bashkirian deposits		
		well 22**	bottom (well 20**)	top (well 20**)
Physicochemical properties				
Density at 20°C, g/cm^3 according to GOST 3900-85	0.921	0.942	0.938	0.926
Kinematic viscosity, mm$_2$/s according to GOST 33-82	250	862	505	247
Sulfur content, wt %	2.19	4.21	4.15	4.07
Component composition				
Content, wt %:				
- gasoline fraction IBP–200°C	11.97	7.52	13.17	11.43
– lube oil	46.17	47.00	43.26	46.55
– paraffin wax	2.99	1.07	1.86	2.11
– benzene resins	21.46	22.31	21.45	23.35
– alcohol–benzene resins	12.10	11.15	11.10	9.73
– asphaltenes	5.31	10.95	9.16	6.83

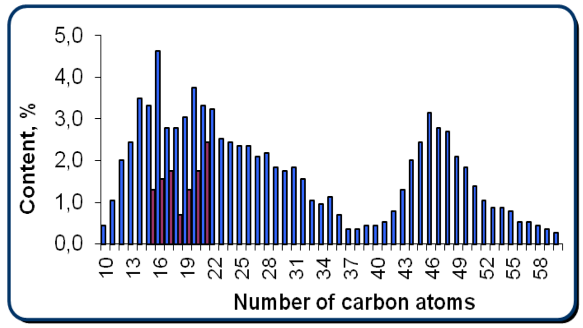
The hydrocarbon composition of the crude oils was studied by gas-liquid chromatography. The comparative analysis of the molecular mass distribution (MMD) of alkanes shows that the composition of crudes from the Bashkirian deposits is significantly enriched in C_{40}–C_{60} higher n-alkanes.

The mechanism of multiphase reservoir filling in the Bashkirian sediments is indicated by a high concentration of C_9–C_{20} light hydrocarbons in these oils as compared with the hydrocarbon composition of oil from the Vereiskian reservoir.

According to Ostroukhov and Bochkarev [8], a decrease in the amount of C_8–C_{13} alkanes in crude oil indicates the inflow of a lighter oil to the formed deposit and the presence of two bands on chromatograms, the one below C_{16}–C_{17} and the other above C_{17}, suggests that the fluid is a mixture of two natural components. It should be noted that this picture is not observed for the Vereiskian oil.



a)



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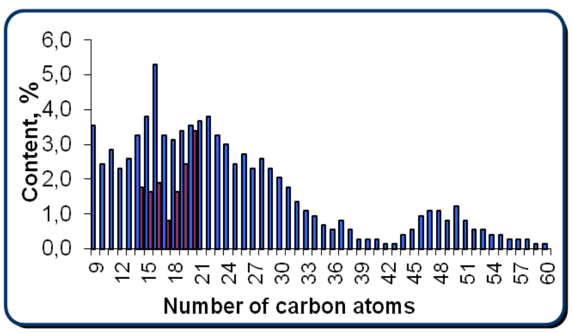

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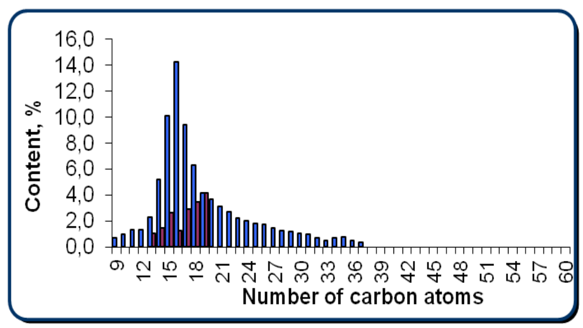

d)

Fig. 1: Molecular-mass distribution of alkanes in crude oils
from wells (a) 22**, (b) 20** (bottom), (c) 20** (top), and (d) 27** of the Akanskoe field

For an in-depth study of petroleum asphaltenes, the test crude oils were separated into three fractions according to their molecular mass [9]. The fractional composition of asphaltenes indicates an enrichment of the Bashkirian oils in components with the highest molecular mass (A1 asphaltene fraction), a finding that also confirms the multiphase reservoir filling mechanism and precipitation of asphaltenes at the bottom of the reservoir as a consequence of inflow of the lighter oil. At the top of the reservoir, asphaltenes are enriched in low-molecular-mass components (A2 asphaltene fraction) and depleted in the components with the highest molecular mass. Another fractional distribution was found for asphaltenes from the Vereiskian oil. The highest amount of the middle- and low-molecular-mass fractions ensures the high stability of the oil toward asphaltene precipitation.

Table 3: Fractional composition of asphaltenes

Sample	Content, %		
	high-molecular-mass	middle fraction	low-molecular-mass

	fraction (A1 asphaltenes)		fraction (A2 asphaltenes)
Well 22**	64.52	25.23	10.25
Well 20** (bottom)	64.58	27.33	8.09
Well 20** (top)	49.42	34.94	15.64
Well 27**	31.52	45.45	23.03

Analyzed asphaltene fractions were studied by thermal analysis (TA). The proportion of peripheral substituents in condensed aromatic structures is defined. According to the lower values of the mass loss of up to 400 ° C (Δm_1), A1 asphaltene fraction is more dense and exhibits a lower propensity for occlusion of low-molecular mass compounds, as compared with the A2 asphaltene fraction. The greater (by factor of 2) P indicator values for A2 asphaltene fraction compared with A1 asphaltene fraction confirm the hypothesis of a greater proportion of lateral substituents in the molecules of A2 fraction.

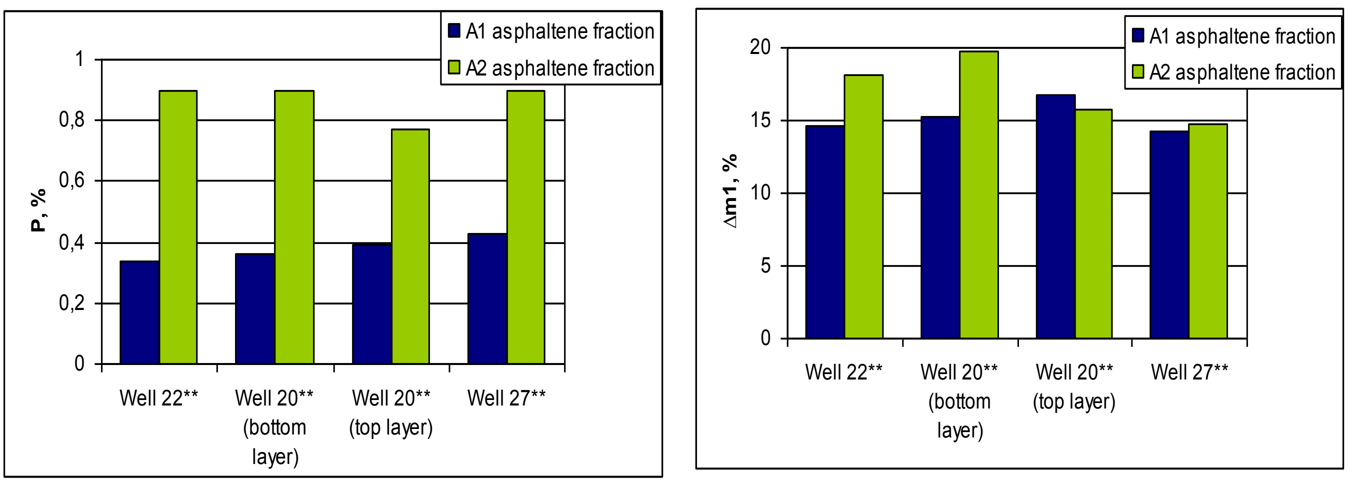

Figure 2: Thermal analysis data on asphaltene fractions

Rheological measurements provide an opportunity to assess the strength of the intermolecular interactions and the nature of the permolecular structures directly in the flow of oil systems. Transformation of the oil systems structure is characterized by the change of the activation energy of viscous flow in the studied temperature range for the field of structural viscosity.

Oils from the Bashkirian deposits are the most viscous and characterized by the highest shear strength. Analysis of changes in the activation energy of viscous flow showed that there are two areas of change in the oil structure: at 30-35 °C and at 60-70 °C. At low temperatures the destruction of structural formations - energy grid formed by the oil asphaltenes from the Bashkirian deposits, takes place. In the area of 60-70 °C structure is destroyed due to melting or destruction of associates of high-molecular wax with resin-asphaltene components. This assumption is confirmed by a sharp change in the activation energy of viscous flow for structured flow field.· Polyextremity of temperature dependence of the activation energy of viscous flow of oil from the Bashkirian formation indicates the low stability of the structure of these oils. This fact supports the argument that the fluid is a mixture of two natural components. The lowest viscosity is fixed for the oil sample from the Vereiskian reservoir. The structure of this oil is stable over the entire temperature range, as shown by virtually non-changing activation energy of viscous flow.

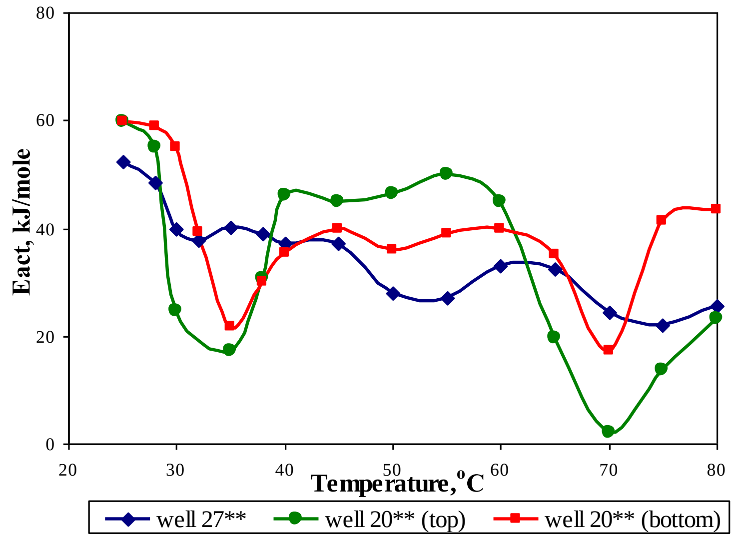

Figure 3: Temperature dependences of the activation energy of viscous flow for crude oils

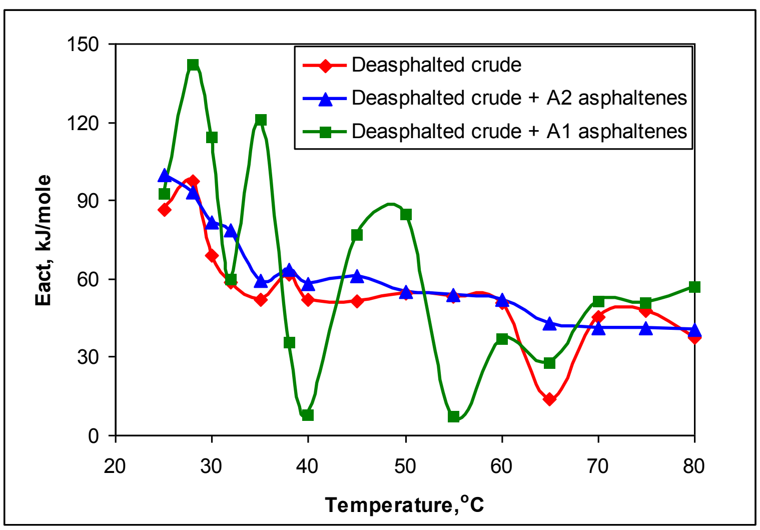

Figure 4: Temperature dependences of the activation energy of viscous flow for model mixtures from deasphalted oil with different asphaltene fractions

In order to identify the role of asphaltene molecules - propagators (A1) and terminators (A2) of aggregation on the oil structure, the study of model mixtures from deasphalted oil with different asphaltene fractions was carried out. Comparative analysis of the temperature dependence of the activation energy of viscous flow shows that the introduction of A1 type asphaltenes into deasphalted crude from Bashkirian deposits results in a significant destabilization of the system (multimodal rate of the curve). On the contrary, the introduction of A2 type asphaltenes leads to a smoothing the effects observed (extreme increase and decrease of the activation energy for structure conversion curve - at both low (25-30 ºC) and high (60-70 ºC) temperatures) due to inhibition of structuring.

Conclusions

A comparative study of the composition of crude oils for Bashkirian and Vereiskian carbonate reservoirs of the Akanskoe field in the Republic of Tatarstan has revealed differences, which are evidently due to differences in the mechanism of filling these reservoirs. The study of the core material of the Bashkirian deposits has revealed the occurrence depth intervals in which abnormally high levels of light and middle oil fractions has been found in the relevant samples. The assumption about the additional influx of a lighter oil from the depth to the reservoir is confirmed by the results of comparative study of surface crude oils produced from Bashkirian and Vereiskian pay formations. It has been shown that the ratio of light and heavy alkane homologues of both normal and isometric structure is higher for heavier and more viscous Bashkirian oils. The MMD of C9–C20 alkanes is bimodal in character for the Bashkirian oils and unimodal for the Vereiskian oil. It is also noteworthy that C40–C60 n-alkanes are present in the hydrocarbon fraction of the Bashkirian oils (especially in the bottom part). The oil in the bottom part of the Bashkirian reservoir is enriched in high-molecular-mass asphaltenes, probably, as a result of their precipitation during the inflow of the lighter oil. Transformation of the oil systems structure is characterized by the change of the activation energy of viscous flow. The capacity of high-viscous oils from carbonate reservoirs to structure forming at higher temperatures is shown. The phase transition temperatures are determined. Also the prevailing role of the A1 asphaltene fraction is defined: introduction of A1 type asphaltenes into deasphalted crude from Bashkirian deposits results in a significant destabilization of the system.

Acknowledgements

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