

Supramolecular Structures of Oil Systems as the Key to Regulation of Oil Behavior

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Abstract

The paper is devoted to investigation of supramolecular structures formed by high-molecular components of oil – asphaltenes and waxes. Petroleum asphaltenes that are characterized by their ability to self-organization can be considered as a polydisperse system. The aggregation of A1 and A2 asphaltenes both in toluene solution and in diluted heavy oils was studied by dynamic light scattering technique. The stabilizing role of resins was confirmed. Due to the fact that the supramolecular structures in oils can be also formed by high molecular microcrystalline waxes, their influence as well as A1 and A2 asphaltenes on wax crystallization process was evaluated using optical microscopy. The effect of the different molecular structures of asphaltenes (A1 and A2) on the rheological properties of crude oils was also observed. Self-organization of asphaltenes directly in heavy high-viscosity oils with high content of resins was investigated by varying the ratios oil:precipitant. It was shown that extremely stable supramolecular structures in heavy oils had been formed. The influence of ultrasonic action for the destruction of stable supramolecular structures and the reduction of oil viscosity were considered.

Also petroleum asphaltenes can be the indicators of many processes that occur in the reservoir. We have shown the possibility of using the gradient of asphaltenes, as well as their structure, to confirm the influx of deep light hydrocarbons in carbonate reservoirs. Thus, all obtained results of investigation of structure formation processes will let regulate the macroscopic properties of heavy oils in the future and identify the processes occurring in the reservoir.

Keywords: Supramolecular structures; Disperse system; Asphaltenes; Asphaltene aggregation

Introduction

According to the modern concepts, the oil is a complex multi-component disperse system. The theory of oil disperse systems [1-4] supposes that the liquid phase compounds are oriented around the supramolecular structures forming solvation layers. The disperse particles are characterized by a complex structure in this case: the core formed by high-molecular components of oil (asphaltenes, microcrystalline waxes) and the solvation shell surrounding the core and consisting of resins. The disperse media in such model is presented by hydrocarbons of oils. At present, the focused attention is paid to the most high-molecular-mass, polar oil components-asphaltenes [5-30]. Asphaltenes are characterized by their ability to self-organization (or self assembly), and therefore the presence of a hierarchy of structures in oil media: molecules-nanoaggregates-clusters of nanoaggregates [5-9] (Figure 1). That is why asphaltenes can be attributed to the objects of supramolecular chemistry.

Petroleum asphaltenes can be considered as a complex polydisperse system of molecules in which subcomponents with significantly different characteristics can be distinguished as the result of the fractionation procedure [27]. At present, two asphaltene molecule types—"continental" (A1 fraction) and "archipelago" (A2 fraction) are adopted as the basic models (Figure 2) [10-15,26]. It should be noted that in crude oils asphaltene aggregates of both types exist in various proportions. As the asphaltene fractionation procedure is rather time and labor consuming, it is not possible to isolate absolutely pure fractions of asphaltenes but concentrates enriched in asphaltenes of one or another structure [26,27].

The main difference between A1 and A2 asphaltenes is their

structure determining different ability to aggregate. A1 asphaltene molecules even at low concentrations form aggregates, followed by the introduction of A2 asphaltene molecules into these units [13]. Thus, A1 and A2 asphaltene molecules in oils form a disperse phase where the core is presented by stacks of the "continental" type of asphaltenes and the periphery rich in the "archipelago" type of asphaltenes [14,15].

In recent scientific literature, there are many studies on the self-organization of asphaltenes in solutions of solvents [28-30]. However, the study of the asphaltenes behavior directly in the oil system is of a much greater interest, since regularities obtained in solutions do not reflect the nature and completeness of the processes that occur in real oils. Therefore we have studied aggregation of A1 and A2 asphaltenes both in toluene solution and in diluted heavy oils with concentrations that are close to real oils by dynamic light scattering technique. The concentration of solutions is also limited by the sensitivity of instruments. The effect of the different molecular structures of asphaltenes was also shown by measuring rheological properties of crude oils.

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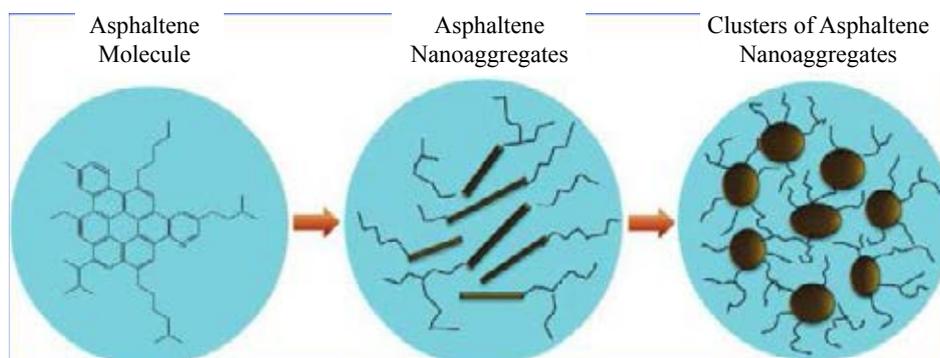


Figure 1: A modified Yen model (or Yen-Mullins model of asphaltenes) [5].

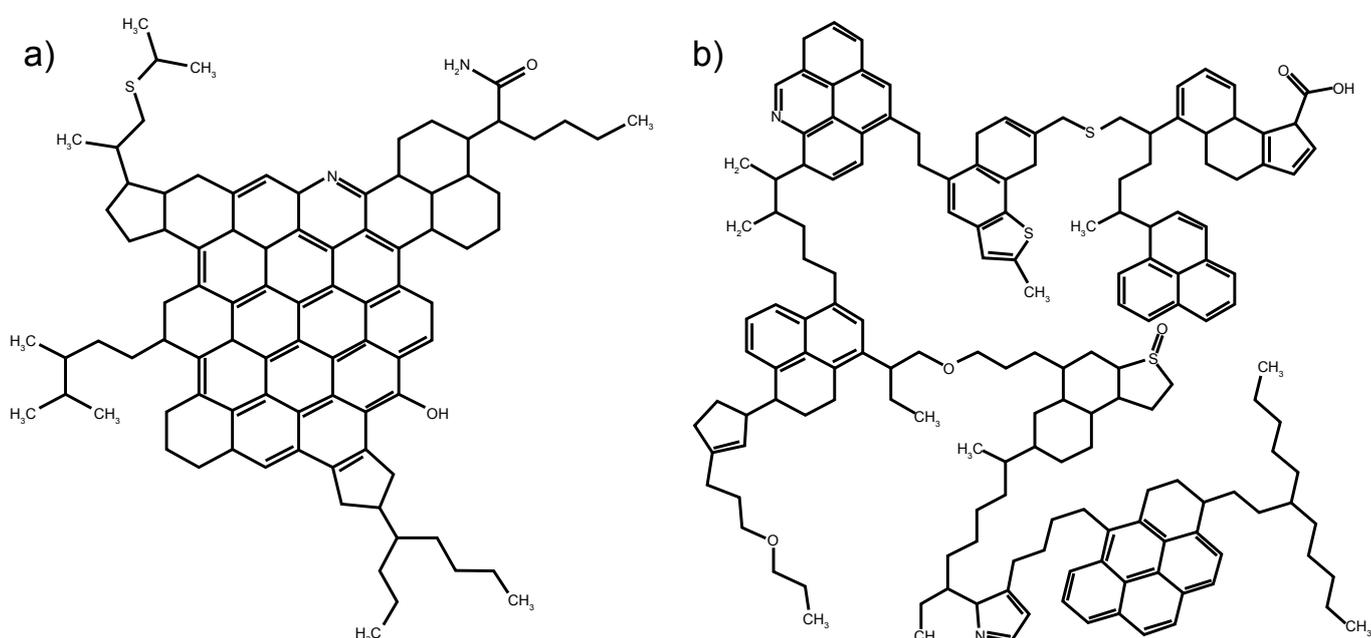


Figure 2: Model of asphaltene molecules: a) the "continental" type, and b) the "archipelago" type [11].

Method

The objects of study were heavy high-viscosity crude oils from carbonates of the Akanskoe field of Tatarstan Republic, Russia. It should be noted that oil samples from one of the wells have been specially selected from the upper (top) and bottom parts of the reservoir [31].

Asphaltenes under investigation were precipitated from the crude oils with a 40-fold excess of nhexane followed by separation into three asphaltene fractions according to their ability to form the aggregates [12]. It is assumed that the first asphaltene fraction that is precipitated under the minimal addition of the precipitant, is a concentrate of A1 asphaltene molecules (the "continental" type), while the third fraction, which remains in solution, presented by A2 asphaltene molecules (the "archipelago" type). The intermediate fraction is a mixture of A1 and A2 asphaltene molecules [12].

The asphaltene aggregation was studied by photon correlation spectroscopy (dynamic light scattering). Toluene-heptane system used is a widely accepted model system for studying the properties of the asphaltenes [32-34].

The photomicrographs of oils and model systems were obtained using Olympus CX41 microscope with a digital photomicroscopy system based on Olympus E420 digital camera and ImageScope M software. Photomicrographs were obtained in transmitted light between crossed polaroids at 100-400 x magnifications.

Thermal analysis (TA) of asphaltenes and their fractions 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°C/min. The chemical composition of asphaltenes was characterized by the mass loss values at different stages of thermal oxidative degradation (20-410°C, 410-530°C and 530-700°C) [35].

The presence of waxes in asphaltenes was fixed by high-temperature gas-liquid chromatography technique (GLC) on a Perkin-Elmer chromatograph with a flame-ionization detector in the mode of temperature programming from 20 to 360°C.

Electron Paramagnetic Resonance (EPR) spectrum of asphaltenes and their fractions were obtained at room temperature with a spectrometer type SE/X-2544. The content of stable free radicals (IR)

was estimated by the amplitude of a single line in the center of the EPR spectrum. Complex viscosity measurements were carried out using Rheotest RN4.1 (MessgeräteMedingen GmbH) over temperature range 20-80°C.

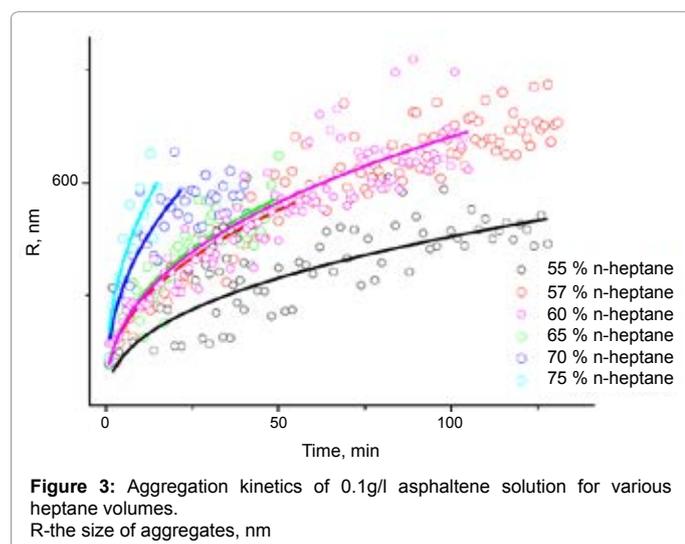
Oil processing by ultrasound was performed using an ultrasonic apparatus “Alena” [36] with the frequency of 22 kHz. The intensity of ultrasound was regulated from 10 to 100 W/cm². Exposure time was from 1.5 to 20 minutes [37].

Results

One of the most promising techniques to monitor in real time the kinetics of asphaltene aggregation and measure a changing size of the aggregates is the dynamic light scattering (DLS) [32-34]. It allows determining the value of the threshold concentration of precipitant that characterizes so called “zero rate of aggregation” -the stability threshold of system. The aggregation of initial asphaltenes and their fractions were studied in toluene solutions, diluted heavy oils and model systems by dynamic light scattering technique. Initial asphaltenes were obtained from the crude oils from the top and bottom parts of the reservoir. In order to identify the role of asphaltene molecules-A1 and A2, the model mixtures from deasphalted oil with different asphaltene fractions were prepared.

The kinetics of asphaltene aggregation in toluene solutions with asphaltene concentration of 0.1 g/l is described by the diffusion-limited mechanism, i.e. aggregation rate is mainly determined by diffusion of particles. The changes in the aggregates sizes are shown in Figure 3. The rate of aggregation increases significantly with increasing of precipitating agent volume. For each volume of precipitant aggregate, size increases with time according to a power law.

The values of the stability threshold were determined for the majority of solutions of asphaltenes and their fractions with a concentration of 0.1 g/l and 5 g/l (Table 1). The solutions with the concentration of asphaltenes 5 g/l in toluene were investigated at installation with the Infrared (IR) laser. The wavelength of IR laser was 980 nm; the wavelength of red laser was 632 nm. In the solutions of A2 asphaltenes with concentration of 0.1 g/l the formation of aggregates was not observed up to a precipitant concentration of 90% (by weight). The aggregation of A2 asphaltenes was fixed only for solutions with a concentration of 5 g/l and to a much lesser extent than in solutions of A1 asphaltenes even with a concentration of 0.1 g/l.



No.	Sample	The threshold concentration of heptane,% wt. (for 0.1g/l asphaltenes/toluenesolutions)	The threshold concentration of heptane,% wt. (for 5g/l asphaltenes/toluene solutions)
1	Initial asphaltenes (top part)	46	40
2	Initial asphaltenes (bottom part)	48	46.5
3	Asphaltenes A1 (top part)	43	25
4	Asphaltenes A1 (bottom part)	28	20.2
5	Asphaltenes A2 (top part)	-	69
6	Asphaltenes A2 (bottom part)	-	55

Table 1: The threshold concentrations of heptane for 0.1g/l and 5g/l solutions of asphaltenes and their fractions in toluene.

In toluene solutions with a low asphaltene concentration the stability threshold of asphaltenes of oils from top and bottom parts of the carbonate reservoir is almost the same despite the different content of A1 and A2 fractions (which differ by their stability) in initial asphaltenes. Initial asphaltenes of oil from the bottom of the reservoir are enriched in A1 asphaltenes (64.6%) and depleted in A2 asphaltenes (8.1%) while asphaltenes from the top of the reservoir contains less A1 asphaltenes (49.4%) and twice the amount of A2 asphaltenes (15.7%) [31]. The rest part of asphaltenes is presented by the intermediate fraction-a mixture of A1 and A2 asphaltenes [12]. This may be stipulated by the fact that asphaltenes in both cases exist only as nanoaggregates in solutions with a low asphaltene concentration.

Further research was devoted to investigation of asphaltene aggregation in diluted heavy oils as well as model systems with the concentration of 125 g/l by weight in toluene. Model systems are the mixtures of deasphalted oils (maltenes) supplemented with 5%(15%) of different asphaltene fractions (A1 or A2). Solutions with the concentration of 500 g/l by weight in toluene were also prepared for crude oils (ratio 1:1 by weight). The threshold stability of oil systems was defined by titration.

Thus, the method of dynamic light scattering showed a greater capacity of asphaltenes enriched in A1 molecules for aggregation in the oil systems. With increasing concentration of A1 asphaltenes from 5 to 15% the threshold stability is not so much reduced as it could be expected, while the viscosity increases from 1020 mPs-s to 7185 mPs-s (the shear rate was 11s⁻¹).

Probably, the increasing concentration of A1 asphaltenes leads to the formation of coagulation structures which impede their further additional aggregation of asphaltenes.

An interesting fact is that the stability threshold of crude oils is only slightly dependent on the volume of added toluene (Table 2). This suggests a slight influence of the solvent proportion (1:1 or 1:4) on the process of asphaltene aggregation, particularly the threshold concentration of heptane, despite the fact that viscosity changes are essential.

It was found that aggregation of asphaltenes and A1 and A2 fractions in toluene solution has a higher rate in comparison with the aggregation in diluted oils and model systems (Table 2), confirming the stabilizing role of components of oil systems. According to the literature [19-22], resins are the stabilization factor of asphaltenes in

No.	Sample	The concentration of solution, g/l	The threshold concentration of n-heptane, % wt.
1	Oil (top part)	500	60.8
2	Oil (bottom part)	500	57.5
3	Oil (top part)	125	61.4
4	Oil (bottom part)	125	59.7
5	Maltenes + A1 asphaltenes (5%) (top part)	125	48.1
6	Maltenes + A1 asphaltenes (15%) top part)	125	43.3
7	Maltenes + A2 asphaltenes (5%) (top part)	125	77.4
8	Maltenes + A1 asphaltenes (5%) (bottom part)	125	44.9
9	Maltenes + A2 asphaltenes (5%) (bottom part)	125	69.5

Table 2: The threshold concentration of heptane for solutions of oils and model systems.

crude oils, due to their peptizing action. However, there is virtually no experimental data quantifying the role of resins.

To study the effect of resins on the stability of the hydrocarbon fluids the kinetics of asphaltene aggregation in toluene-heptane system was investigated during addition of resins with three different concentrations: 0.2 g/l, 0.6 g/l and 1 g/l. The concentration of asphaltenes in all cases was 0.1 g/l. For ease of comparison, the kinetics of growth of aggregates was measured at concentrations of n-heptane equal to 60, 65, 70, 75 and 80 weight percent. In all cases the same power-law dependence of the radius on time as that in the absence of resins was observed, i.e. for solutions with asphaltene concentration of 0.1 g/l the diffusion limited aggregation is observed.

Figure 4 shows the measurement results of the radius of asphaltene aggregates in the solutions containing different amounts of resins at a fixed (70 weight percent) concentration of n-heptane. The results obtained for other n-heptane concentrations (60, 65, 75 and 80 weight percent) are quite similar.

It was shown that an increase in resins concentration leads to the decrease of the rate of aggregates growth as well as their amount. Furthermore, the introduction of resins into the asphaltene solution increases the threshold concentration of n-heptane. In the field of hydrocarbon solutions instability with respect to precipitation of heavy fractions, addition of resins leads to a significant slowdown in the aggregation reaction. Thus, the stabilizing role of resins is substantiated.

Due to the fact that the supramolecular structures in oils can be also formed by high molecular microcrystalline waxes, their influence as well as influence of asphaltene fractions on wax crystallization process was evaluated using optical microscopy. Figure 5 shows photomicrographs of oils and model systems. Observation between crossed polaroids allows to characterize the distribution and size of the wax crystallites in the samples.

Maltenes (deasphalted oil) from the oil of the top part of the reservoir contain wax crystallites that are large enough compared with the original oil (Figure 5). This can be explained by the procedure of maltenes separation resulting in removing gasoline fractions that serve as a solvent of waxes, and asphaltenes inhibiting the wax crystallization process from crude oils. In maltenes from the oil of the bottom of the reservoir the crystal growth is not observed due to the fact that the oil is enriched in microcrystalline waxes with carbon atoms number from 40 to 60 (C40-C60), which are likely to disperse macrocrystalline

waxes (C16-C40) [31]. The content of microcrystalline waxes in the oil from the top of the reservoir is substantially lower but the content of macrocrystalline waxes is higher. The dispersion of the crystalline

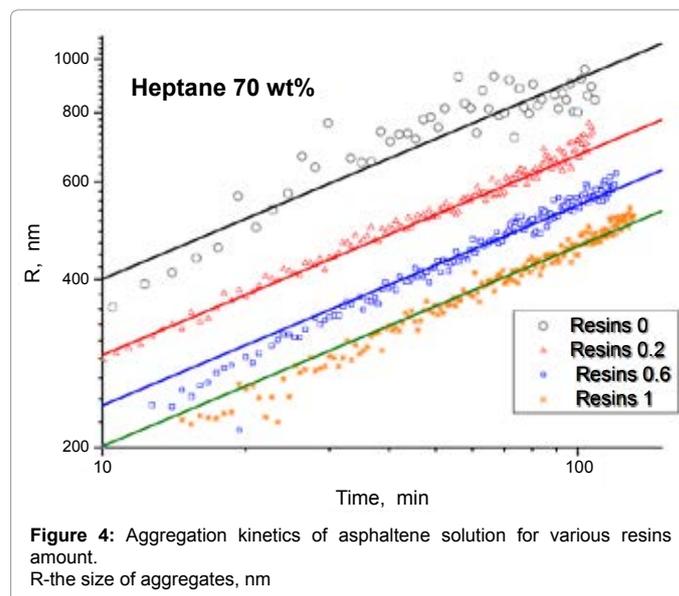


Figure 4: Aggregation kinetics of asphaltene solution for various resins amount. R-the size of aggregates, nm

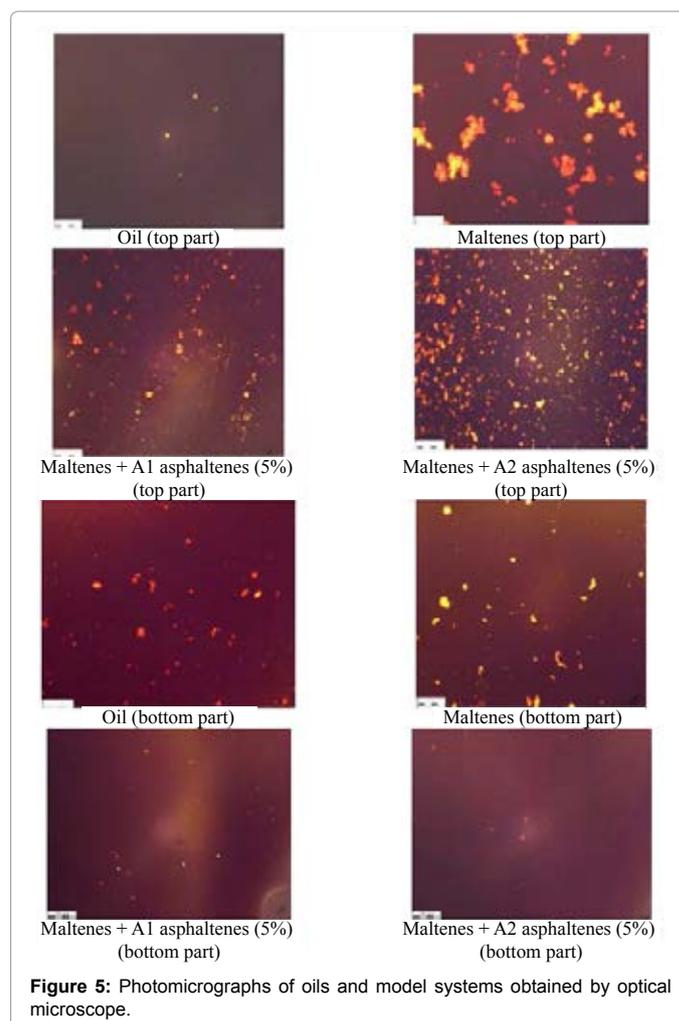


Figure 5: Photomicrographs of oils and model systems obtained by optical microscope.

phase can also be observed when asphaltenes (A1 and A2 fractions) are added to maltenes. This finding confirms the role of asphaltenes as the inhibitors of wax crystallization [23,24]. Moreover, the introduction of A2 asphaltenes in maltenes leads to more intensive dispersion.

Self-organization of asphaltenes directly in heavy high-viscosity oils with high content of resins was investigated by varying the ratios oil:precipitant [38]. It was found that the quantitative content of precipitating asphaltene aggregates in heavy oils from carbonate reservoirs is not dependent on the concentration of the first portion of the precipitant-n-alkane (10, 20, 30%) (Table 3). The thermal analysis data (Δm^3 -mass loss values at very high temperatures-530-700°C) [35] and EPR spectroscopy data (content of stable free radicals) showed that a decrease in the share of the first portion of the precipitant leads to reducing the content of polycondensed 8 aromatic structures in the asphaltene aggregates (Figures 6 and 7) due to co-precipitation of waxes according to GLC data (Figure 8). The purest separation of

asphaltenes is observed during a conventional technique of asphaltene precipitation in a 40-fold excess of n-alkane.

The effective technique to fix the formation/destruction of supramolecular structures in oils is rheology method. The capacity of high-viscosity oils from carbonate reservoirs to structure forming at higher temperatures was shown. In order to identify the effect 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.

The phase transition temperatures were identified (Figure 9). At low temperatures (20-30°C) according to the high values of the activation energy of viscous flow oil systems are characterized by coagulation structure (so called the bound-dispersed state). Since investigated oil systems contain waxes, the phase transition at 30-60°C can be attributed to the process of destruction of the crystalline phase.

Sample	The ratio oil:precipitant upon addition the first portion of the precipitant									
	1:40	1:30			1:20			1:10		
		I fr.,%	II fr.,%	Σ,%	I fr.,%	II fr.,%	Σ,%	I fr.,%	II fr.,%	Σ,%
Crude oil	11.0-12.0	11.9	0.1	12	12	0.2	12.2	11.5	0.5	12

Table 3: The content of asphaltenes obtained from crude oils by two-step precipitation and standard precipitation techniques.

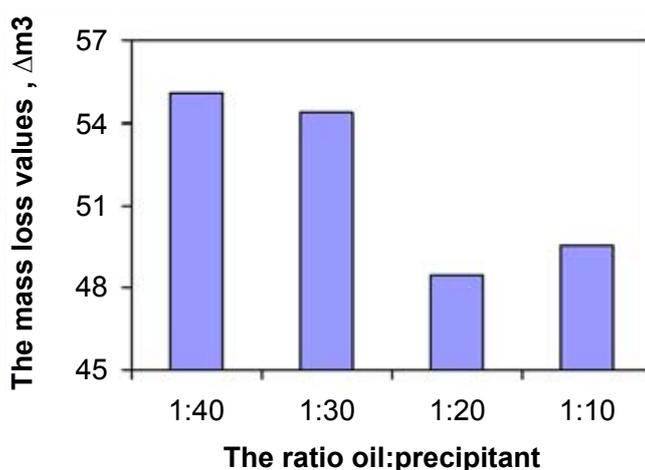


Figure 6: The thermal analysis data of the first asphaltene fractions.

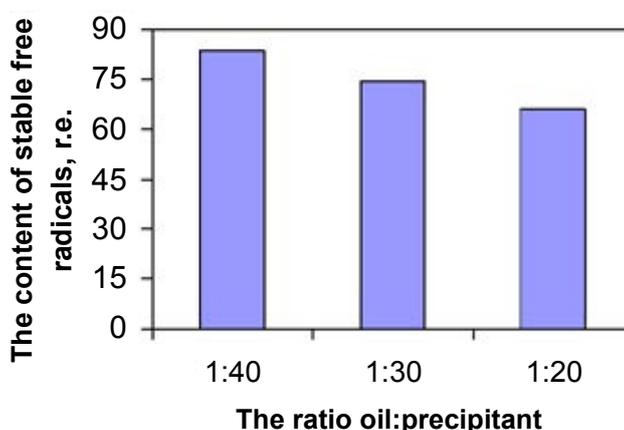
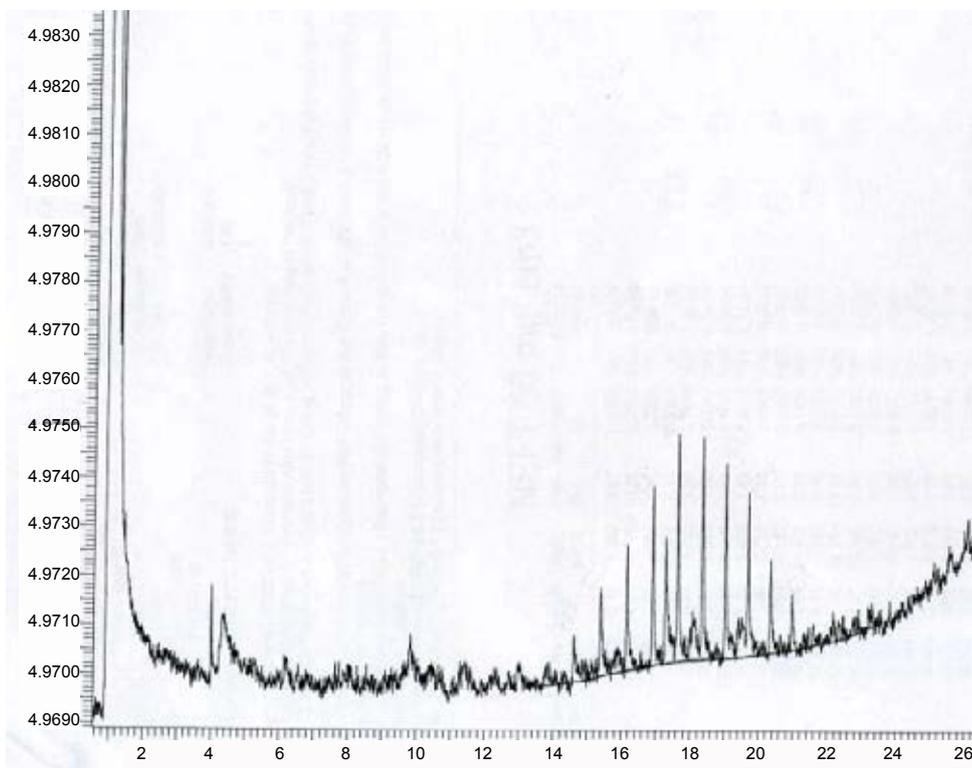
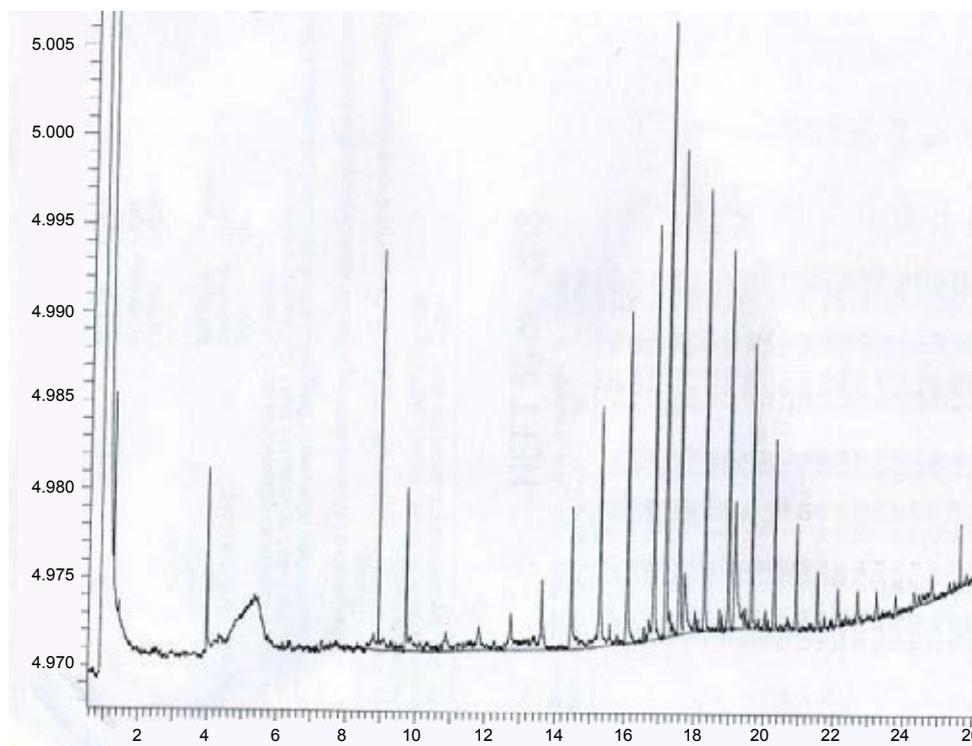


Figure 7: The EPR spectroscopy data of the first asphaltene fractions.



(a)



(b)

Figure 8: Chromatograms of asphaltenes separated varying ratio oil:precipitant: a) 1:10, b) 1:40.

At a temperature of 60°C or higher there is a transition into the freely dispersed state with low values of the activation energy of viscous flow.

It was found that A1 asphaltenes contribute to the formation of the most stable bound-dispersed structure of oils, which greatly increases their viscosity. A2 asphaltenes disperse waxes greater than A1 asphaltenes, preventing the formation of the large crystals (Figure 5). Comparative analysis of the oil residue after distilling of the low-boiling fractions and maltenes with A1 asphaltenes it was shown that the stabilizing effect of resins in the absence of A2 asphaltenes is less pronounced.

Since the stable supramolecular structures are formed in heavy oils, it is necessary to apply technologies that affect directly to the core of the oil dispersed systems in order to reduce their viscosity. One of

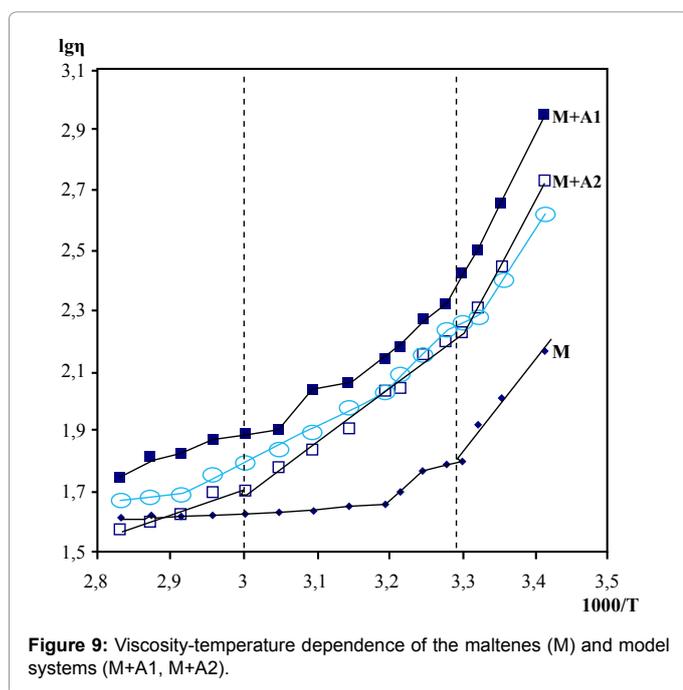


Figure 9: Viscosity-temperature dependence of the maltenes (M) and model systems (M+A1, M+A2).

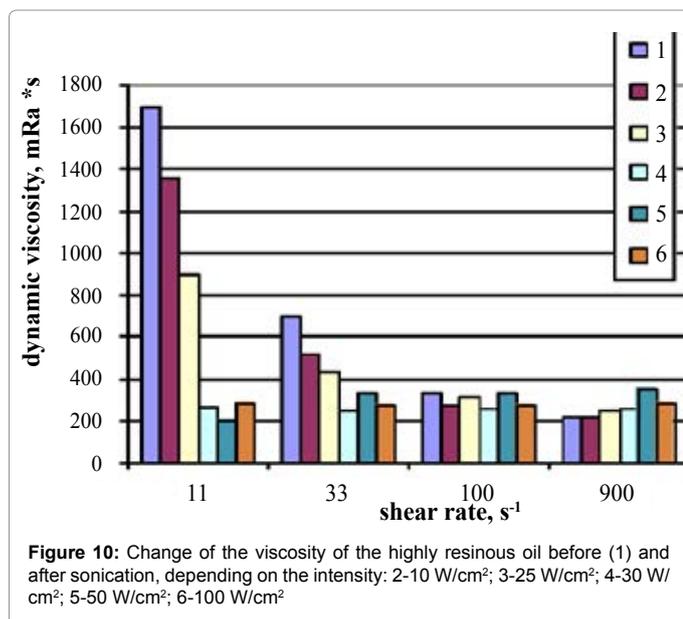


Figure 10: Change of the viscosity of the highly resinous oil before (1) and after sonication, depending on the intensity: 2-10 W/cm²; 3-25 W/cm²; 4-30 W/cm²; 5-50 W/cm²; 6-100 W/cm²

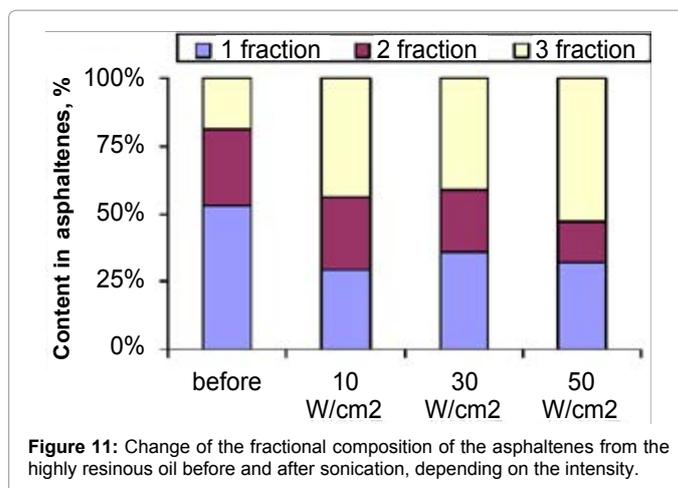


Figure 11: Change of the fractional composition of the asphaltenes from the highly resinous oil before and after sonication, depending on the intensity.

such technologies is the ultrasonic action [39-43]. The regularities of the influence of ultrasonic treatment on the structure of heavy oil with high content of resins were identified. It was found that ultrasound treatment leads to a decrease of oil viscosity (Figure 10), which is associated with changes in their dispersion structure [37].

The destruction of A1 and A2 asphaltene aggregates by sonication is proved by comparative data of asphaltenes fractionation from oil before and after sonication (Figure 11). The high content of A1 asphaltenes before ultrasound treatment can be explained by segregation of stable aggregates of A1 and A2 asphaltenes. After processing it is possible to isolate a more pure fraction of A1 asphaltenes according to EPR data (the content of stable free radicals: before sonication is 80 r.e., after sonication—more than 90 r.e.), the amount of which is markedly reduced. This effectively reduces the oil viscosity.

Asphaltene are the indicators of many processes that occur in the reservoir. Previously [31] we have shown the possibility of using the gradient of asphaltene, as well as their structure, to confirm the influx of deep light hydrocarbons in carbonate reservoirs.

Thus, all obtained results of investigation of structure formation processes will let regulate the macroscopic properties of heavy oils in the future and identify the processes occurring in the reservoir.

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