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Effect of an Inhibitory Additive on the Formation of Asphaltene-Resin-Paraffin Sediments in Highly Paraffinic Oil

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Abstract

An effect of inhibitory additive on the kinetics of sediment formation in highly paraffinic oil was investigated. It has been demonstrated that the maximum rate of sediment formation occurs within the first minutes of the process. The inhibitory additive promotes greatly decreasing to a considerable extent the rate of sediment formation in the oil due to the retention of solid paraffin hydrocarbons in the bulk. An influence of the inhibitory additive upon the group composition of sediments and the composition of paraffinic hydrocarbons was investigated.

Key words: oil, asphaltene-resin-paraffin sediments, paraffinic hydrocarbons, inhibitory additive

INTRODUCTION

Oil species inherent in many oil fields under development in the territory of Russia are characterized by a high content of paraffinic and resin-asphaltene components. The extraction and transportation of paraffinic and high paraffinic oil species is usually accompanied by precipitation of asphaltene-resin-paraffin sediments (ARPS), which results in appearing certain problems (reducing the workover of boreholes and the efficiency of pumping plants, reducing the operating flow capacity of pipelines, *etc.*) [1, 2].

Owing to the reduction of local oil temperature, in the boundary layer there takes place reducing the dissolving ability with respect to paraffins and the adhesion thereof on the surface of pipelines. The mechanism of ARPS formation and accumulation on the surface of equipment consists in the appearing and growth of the crystals of paraffinic hydrocarbons (PH) immediately under mechanical cohesion with cracks, surface irregularities followed by a subsequent nucleation and growth of crystals on the resin-paraffin film already formed [3].

One of the most efficient ways of combating the paraffin sedimentation consists in adding the chemical reagents those prevent or inhibit the ARPS in the course of oil extraction and transportation [4]. For these purposes, one uses inhibitory additives those exhibit co-crystallizing with PH in the course of lowering the temperature is lowered at the moment of forming a new phase to impair the hydrophilicity to the paraffin crystals by the additive's polar groups to reduce the adhesion of the solid phase on metal surfaces. Inhibitory additives maintain the solid phase to be in a finely dispersed state [5, 6]. Establishing the mechanism of the action of additives represents a rather difficult task, which includes studying the mechanism of the formation of *n*-alkane crystals in a multicomponent medium, the investigation of the PH crystallization kinetics and thermodynamics, the investigation of changing the dielectric and other physical properties, as well as of the intermo-

lecular interactions between the additive and *n*-alkanes, and other oil components, *etc.*

The aim of this work consisted in studying the effect of an inhibitory additive on the kinetics of sedimentation process in highly paraffinic oil species and the ARPS composition.

EXPERIMENTAL

The effect of inhibitory additives based of poly(meth)acrylates on the sediment formation kinetics was studied by the example of oil with the pour point equal to 5 °C and the content of the PH and the resinous-asphaltene components (RAC) equal to 6.6 and 8 %, respectively. The field of the oil under investigation belongs to the Vasyugan suite of the West Siberian oil and gas bearing province, the average depth of occurrence amounting to 3170 m, the reservoir temperature and the temperature at the wellhead being equal to 85 and 20 °C, respectively.

The process of ARPS formation was simulated using a set-up (Fig. 1), based on the technique of cold finger method [7]. Oil temperature ranged within 20–50 °C, the temperature of sediment forming surface was equal to 12 °C. The ARPS sampling was carried out in 5, 10, 20, 40 and 60 min.

The mass fraction of asphaltenes in the oil sediment was determined *via* asphaltene extraction by means of a Holde method, the resinous substances were analyzed using a chromatographic (column adsorption) method [8, 9].

The determination of the molecular mass distribution of *n*-alkanes in paraffin was performed with the use of a Perkin-Elmer SIGMA 2B gas-liquid chromatograph. Electronic-band spectra of the samples were obtained prepared using a UVIKON 943 ultraviolet spectrophotometer.

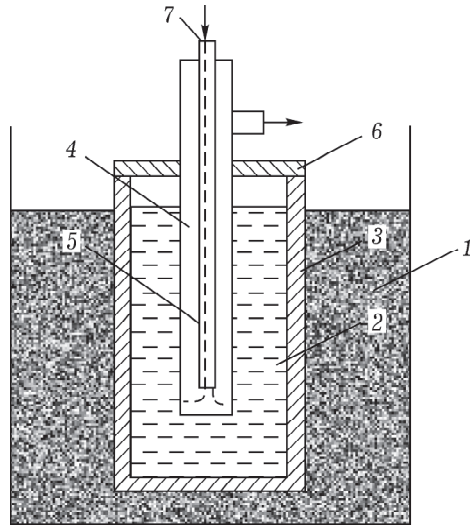


Fig. 1. Schematic diagram of the set-up for determining the amount of oil in the oil sediment using a cold finger method: *1* – heat carrier (H_2O), *2* – oil, *3* – metallic glass, *4* – metallic rod, *5* – metallic tube, *6* – cork, *7* – refrigerant (H_2O).

RESULTS AND DISCUSSION

Table 1 demonstrates experimental data concerning the sediment formation of the original oil and the oil with the inhibitory additive at different temperature values. Sediment formation process in the oil under investigation begins at 50 °C, the maximum amount of ARPS

TABLE 1

Sediment formation in oil at different temperature values

Samples	Sample temperature, °C	Accumulation of sediment (mass %) with time, min				
		5	10	20	40	60
Oil	20	15.3	17.9	22.0	24.5	26.4
Oil + additive		7.6	8.6	9.4	9.6	9.6
Oil	30	10.7	11.3	13.4	15.4	17.5
Oil + additive		8.2	8.8	9.6	10.6	10.8
Oil	40	10.0	10.9	11.8	12.7	13.2
Oil + additive		9.8	10.3	10.8	11.2	11.8
Oil	50	3.8	3.9	3.7	5.3	5.5
Oil + additive		3.0	3.5	3.3	4.0	5.1

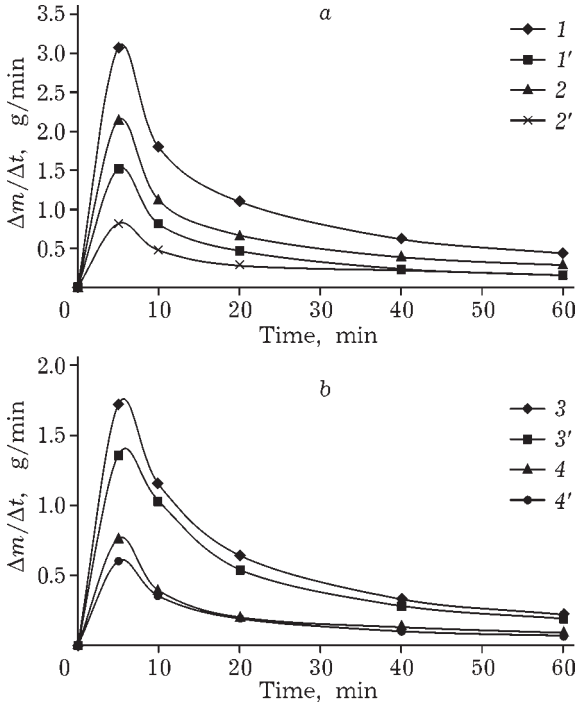


Fig. 2. Rate of ARPS formation in the original oil samples (*1*–*4*) and oil with the additive (*1′*–*4′*) at different temperature values, °C: 20 (*1*, *1′*), 30 (*2*, *2′*), 40 (*3*, *3′*), 50 (*4*, *4′*).

equal to 26 mass % is observed to form at the temperature of 20 °C. After introducing 0.07 mass % of the inhibitory additive we observed almost threefold reducing the amount of ARPS at the given temperature; the inhibitory effect corresponds to 60 %. Increasing the oil temperature up to 40–50 °C is accompanied by the reduction of the additive inhibitory activity down to 7–10 %.

According to the experimental data we calculated the rate of sediment formation in highly paraffinic oil at different temperature values (Fig. 2). The rate of ARPS formation of the is to a considerable extent dependent on the temperature of oil: an increase in the temperature from 20 to 30 °C results in a decrease in the rate of sediment formation in the oil by 1.5 times, whereas increasing the temperature up to 40 °C and up to 50 °C results in 2- and 4-fold decreasing the sediment formation rate, respectively.

Within the entire temperature range under investigation, the maximum rate of sediment formation occurs within the first 5 min of the process. With an increase in the duration of the process the rate demonstrates a 3–5-fold decrease depending on the temperature.

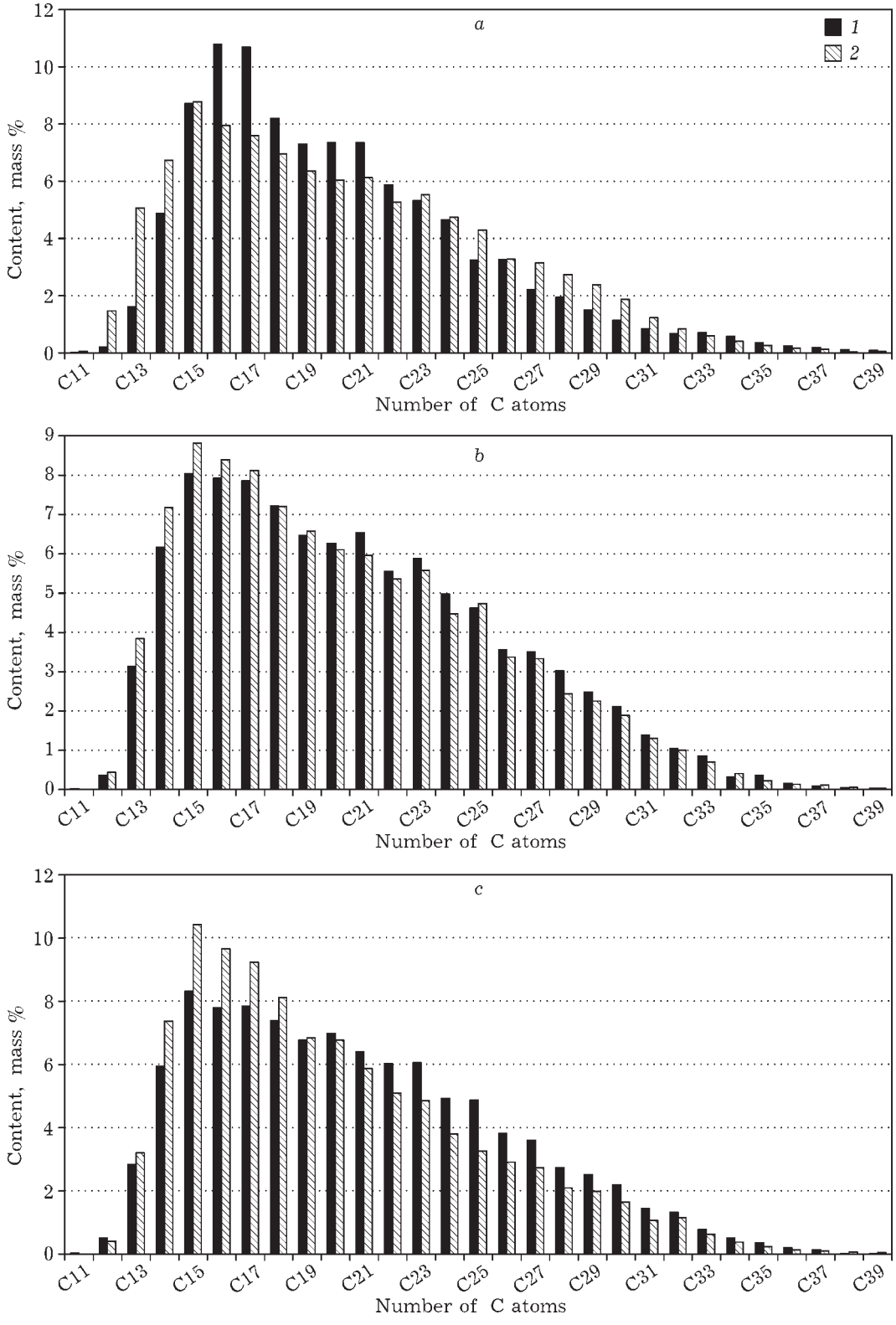
Using the inhibitory additive causes the rate of sediment formation in the oil to decrease. At the temperature ranging within 20–30 °C, this parameter demonstrates a decrease on average by half as compared with the original oil. At the temperature ranging within 40–50 °C the rates of sediment formation of the origi-

TABLE 2

Group composition for original oil sediment and oil with the additive sampled at 40 °C, depending on sediment formation time

Samples of sediments	Time, min	Content, mass %				PH/RAC
		WHF (PH)	BR	ABR	Asph	
Oil		84.5 (6.6)	2.4	4.0	1.6	0.83
Original oil	5	65.67(35.6)	8.3	8.3	17.4	1.10
Oil + additive		67.8 (30.9)	7.7	7.7	16.7	0.96
Original oil	10	67.6 (47.1)	4.4	8.6	18.7	1.50
Oil + additive		67.9 (40.6)	4.7	11.1	15.8	1.33
Original oil	15	72.5 (47.7)	7.7	6.1	12.9	1.78
Oil + additive		68.1 (40.6)	8.8	9.3	10.7	1.41
Original oil	30	74.7 (47.0)	7.3	7.1	10.0	1.76
Oil + additive		68.4 (43.0)	7.2	14.3	9.1	1.41
Original oil	60	70.4 (51.0)	6.9	11.8	10.1	1.77
Oil + additive		73.7 (44.1)	6.4	8.1	11.6	1.71

Note. WHF – wide hydrocarbon fraction; PH – paraffinic hydrocarbons; BS – benzene resins, ABR – alcohol-benzene resins; Asph – asphaltenes; RAC – resin-asphaltene components.


a
1
2
Content, mass %
Number of C atoms
b
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c
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C11
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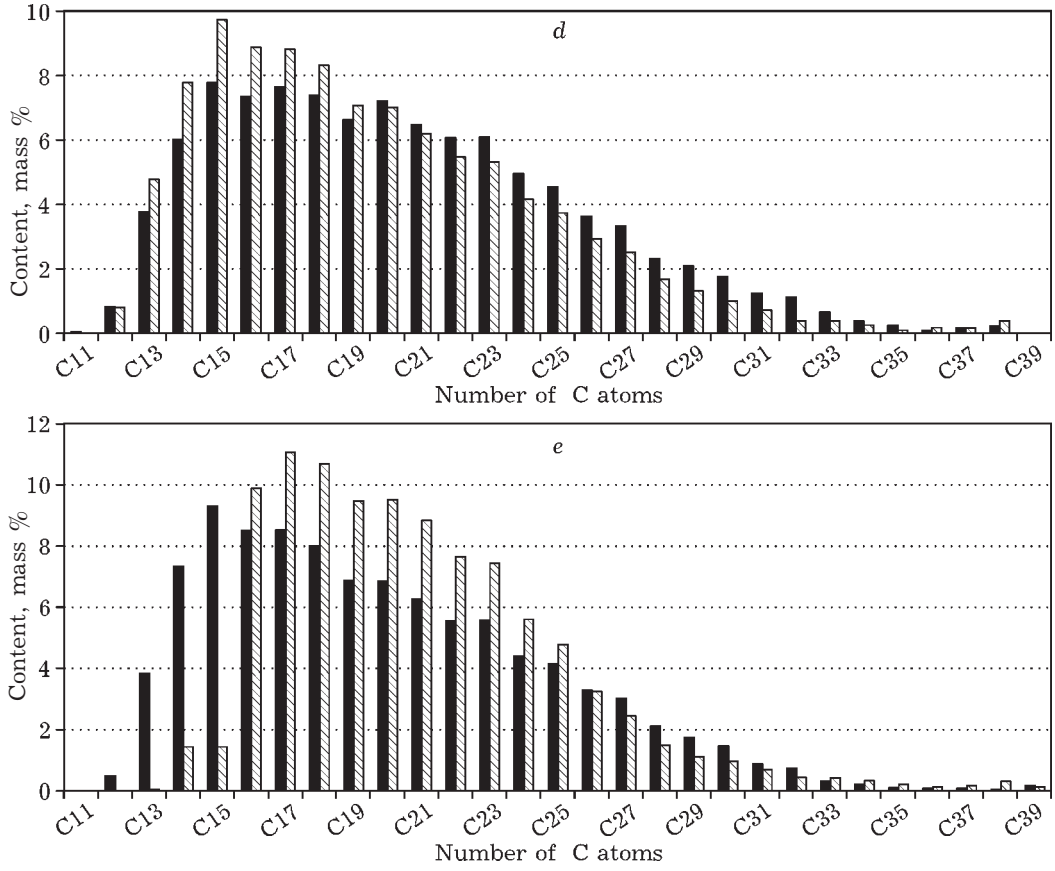

Fig. 3. PH molecular mass distribution in the sediment of the original oil (*1*) and the oil with the additive (*2*) sampled in 5 min (*a*) and 10 (*b*), 15 (*c*), 30 (*d*), and 60 min (*e*).

nal oil and the oil with the additive are comparable with respect to each other, so the use of additives in this case is inappropriate.

In order to choose the most efficient method for preventing and/or combating the ARPS, of importance is not only the information concerning the kinetics of sediment formation, but also information on the group composition of the oil sediment.

The ARPS group composition changes as the sediment accumulates (Table 2). The sediments of the original oil samples within in the first 5–10 min exhibit an abrupt increase in PH content, and further it almost does not change, which is consistent with data concerning the rate of ARPS formation.

In the course of time, the composition of ARPS in the original oil exhibits the PH/RAC ratio to increase from 1.1 to 1.77, which indicates the fact that the there is a paraffinic type of the sediment observed [10, 11] and the major PH contribution to the sediment formation process. The use of the inhibitory additive allowed 4–7 % reducing the amount of PH in ARPS depending on the time of sediment formation as compared to the ARPS in the original oil.

The composition of the sediments inherent in the original oil and in the oil with the additive differs in the molecular mass distribution (MMD) of *n*-alkanes (Fig. 3). The samples of the original oil sediments, taken after 30 min, the PH exhibit almost unchanged MMD, but there is a slight increase in the fraction of low molecular mass *n*-alkanes in the sediment in 60 min after beginning the experiment (Table 3). Basing on the analysis of changing the PH content depending on time, one could assume that the initial increase in ARPS occurs at the expense of solid *n*-alkanes, whereas at the final stage the sediment is enriched with low molecular mass *n*-alkanes. These results are in a good agreement with the data concerning the group composition of ARPS: the sediments sampled in the beginning of the experiment (5–15 min),

TABLE 3

PH composition for sediments from original oil and oil with the additive depending on the sediment formation time

Samples of sediments	Time, min	Content, mass %		
		$\Sigma C_{11}-C_{16}$	$\Sigma C_{17}-C_{39}$	$\Sigma C_{11}-C_{16}/\Sigma C_{17}-C_{39}$
Original oil	5	26.2	73.8	0.36
Oil + additive	5	30.0	69.9	0.43
Original oil	10	25.6	74.4	0.34
Oil + additive	10	30.7	69.3	0.44
Original oil	15	25.4	76.8	0.33
Oil + additive	15	31.0	69.0	0.45
Original oil	30	25.8	74.2	0.35
Oil + additive	30	31.9	68.1	0.47
Original oil	60	29.5	70.5	0.42
Oil + additive	60	12.8	87.2	0.15

are characterized by a high content of asphaltenes those retain solid PH in ARPS (see Table 2). With reducing the concentration of solid hydrocarbons in the composition of sediments (30–60 min), the proportion of asphaltenes is also reduced.

The MMD curves for *n*-alkanes in the sediments extracted from the oil with additive in 5–60 min are of different shape. Within the first 5 min, there is a shift of MMD observed towards lower molecular mass region(see Fig. 3, *a*), then the maximum is observed to undergo gradually shifting towards PH with a higher molecular mass as compared with *n*-alkanes inherent in the sediments of the original oil (see Fig. 3, *c*–*d*).

As one could see from Table 3, adding the additive results in increasing the concentration of low molecular mass *n*-alkanes and decreasing the fraction of solid *n*-alkanes in the ARPS composition sampled within 5–30 min of the experiment, as compared with the original oil sediments. To all appearance, during this time the inhibitory additive retains preferably solid PH in the bulk, therefore the concentration thereof in the sediments is lower as compared to that in the ARPS of the initial paraffin oil [12]. The sediment in the oil with additive sampled within 60

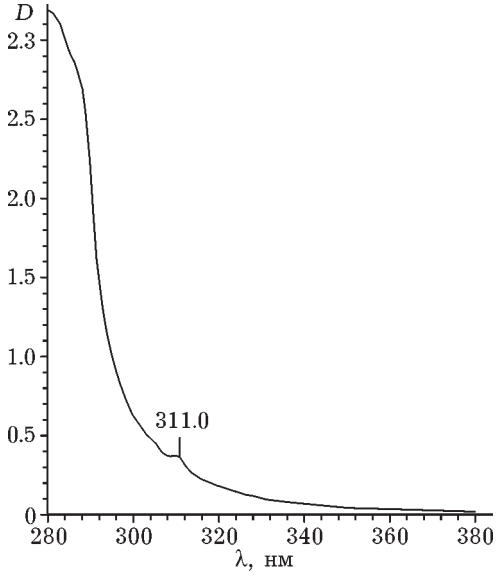

Fig. 4. UV spectrum of the additive.

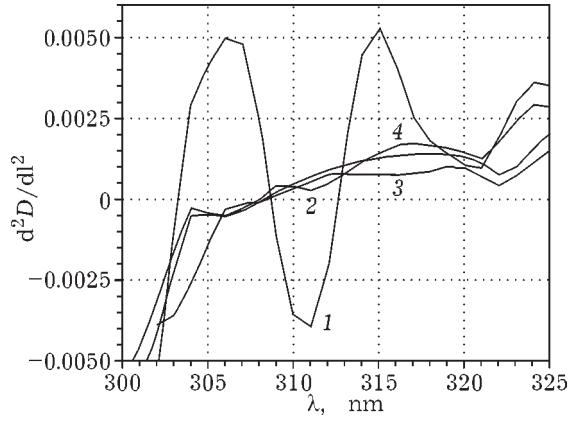

Fig. 5. Second derivatives of the absorption spectra of: *1* – additive; *2* – sediment from oil with additive sampled after 60 min; *3*, *4* – original oil sediments sampled at 30 and 60 min, respectively.

min is characterized by a high content of solid hydrocarbons as compared to the above mentioned samples (5–30 min). This difference in the composition of the sediments could be, to all appearance, connected with reducing the ability of the additive to retain solid PH in the bulk of oil and to form joint sediment.

The presence of additives in the sediment taken in 60 min was registered in the electronic spectra (Fig. 4). The electronic spectrum of the inhibitory additive is characterized by the absorption within the wavelength range 311 nm.

Figure 5 demonstrates the second derivatives of the spectra for the inhibitory additive, as well as for of the original oil and oil with the additive. Using the method of the second derivatives of the spectra one could can obtain information concerning the location of the absorption bands, which information is not available from conventional spectra intractable because of mutual overlapping and ghost absorption [13].

It is seen that the absorption at 311 nm inherent in the additive itself is observed only for the sediment produced in the presence thereof during 60 min. The sediment sampled from the oil with the inhibitory additive after 30 min of the experiment (see Fig. 5, curve *3*) did not exhibited the extremum within the mentioned absorption region, which indicates the absence of the additive in the composition of the sediment.

CONCLUSION

Sediment formation kinetics was investigated for highly paraffinic oil. It has been established that the rate of ARPS formation is to a considerable extent dependent on the oil temperature. Increasing the oil temperature is observed to result in decreasing the sediment formation rate. The maximum rate of ARPS formation is observed within the first few minutes of the process in the entire temperature range investigated. The sediments of the original oil within the first 5–10 min demonstrate an abrupt increase in PH content, further the concentration of PH in the sediment remains almost unchanged. It has been demonstrated that the initial ARPS growth occurs due to solid *n*-alkanes, whereas at the final stage the sediment exhibits enriching with low molecular mass alkanes.

It was revealed that the use of the inhibitory additive allows reducing the rate of sediment formation in the oil due to solid PH retention in the bulk, which results in changing the group composition of the sediment. At the temperature ranging within 20–30 °C, the rate of sediment formation is reduced on the average by half as compared to the original oil. At the temperature of 40–50 °C the rate values for sediment formation inherent in the original oil and oil with the additive are comparable with respect to each other, so the use of the additive is unpractical.

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