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The Effect of Inhibitory Additive on the Structural Parameters of Resins and Asphaltenes in the Deposits of Oil-Water Emulsions with Different Water Content

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Abstract

Changes in the composition and content of paraffin and resin-asphaltene components in the deposits of oil-water emulsions in the presence of inhibiting K-210 additive are investigated. It is shown that the inhibiting ability of the additive is higher in oil-water emulsions than in oil. The additive not only provides a substantial decrease in the amount of oil deposit but also affects the composition of the formed asphalt-resin-paraffin deposits (ARPD) of emulsions. It is established that the use of the additive causes a decrease in the fraction of liquid n-alkanes with the composition $\sum C_{10}-C_{15}$ and an increase in the amount of resins in ARPD. The appearance of the aqueous phase in crude oil causes a significant increase in the proportion of asphaltenes in the composition of deposits, so that an increase in water content in oil leads to a monotonous decrease in the content of asphaltene components in the deposits. Calculation of the structural parameters of the average molecule according to the data of ^{1}H NMR spectroscopy and the data on molecular masses showed that an increase in water content of oil-water emulsions leads to concentrating the most polar components prone to resin and asphaltene aggregation in the deposits, as evidenced by an increase in the concentrations of nitrogen, sulphur, oxygen, and aromaticity factor. With the use of the additive, the composition of emulsion precipitates is characterised by resinous-asphaltene components with lower molecular masses and an increased content of aromatic fragments, while the content of heteroatomic components in the composition of the average molecules of resins and asphaltenes decreases. It is possible that the interaction of the additive and paraffin aggregates in the asphalt-resin-paraffin deposits causes concentrating of less polar resinous-asphaltene components. Resins and asphaltenes with an increased number of heteroatoms remain in the volume of the oil-water system, maintaining its stability.

Keywords: resins, asphaltenes, additive, water-oil emulsion, asphalt, resin and paraffin deposits

INTRODUCTION

With an increase in the number of producing oil deposits with increased content of paraffin hydrocarbons (PH) and high watering, the processes involved in mining and transport of water-oil emulsions become substantially complicated. The reason is increased viscosity and the formation of asphalt-resin-paraffin deposits (ARPD) from emulsions on the surfaces of oil mining equipment [1–3]. Paraffinization is first of all due to a decrease in the temperature of oil-containing systems while they move along pipelines from borehole bottom to well head [4]. The composition of ARPD may include PH, resins, asphaltenes, water, mineral salts and mechanical impurities [5–8]. Resins and asphaltenes that are present in oil may (depending on their structure) not only decelerate or prevent the growth of crystal nuclei but also interact with n-alkanes promoting co-crystallization [9–13]. It was demonstrated in [14–16] that asphaltenes with a smaller number of aliphatic substituents are distinguished by a lower tendency to form paraffin-asphaltene complexes preventing nucleation and the growth of the crystal paraffin network.

The formation of ARPD in emulsions is complicated by the presence of water globules with asphaltenes, resins, PH adsorbed on their surface. Resin-asphaltene components form structured layers on water drops, thus providing high stabilization of emulsions. Emulsion stability depends not only on the nature of emulsifiers but also on their quantitative relation [17, 18].

One of the efficient and widely used methods to inhibit the formation of ARPD in high-paraffin oil is the use of additives. The basis of these additives is the synthetic polymers of different classes [19–24]. The structure of the additive is represented by the polar components (in the form of acrylate, methacrylate, acetate, *etc.*) and a hydrocarbon chain that provides the interaction between the additive and PH; the polar segment is responsible for the change of the morphology of the formed crystals. The efficiency of the existing polymer additives decreases substantially in water-oil emulsions.

The goal of the present work was to study the effect of the additive based on ordered amphiphilic nitrogen-containing polymers on the amount of deposits formed in water-oil emulsions, on the content and composition of natural emulsifiers.

EXPERIMENTAL

The subject of the investigation was high-paraffin oil from the Urmanskoye (H) deposit. Paraffin hydrocarbons content was 6.6 mass %, resins 13.5 mass %, asphaltenes 1.6 mass %.

Artificial emulsions were prepared by mixing oil and distilled water with the help of a mixing device PE–0118 with the power of 150 W, with the frequency of blade rotation 2000 r.p.m. for 10 min at 20 °C. Emulsions with 5 to 20 mass % content of distilled water are stable for 2 weeks and do not get layered when heated to 70 °C.

A quantitative evaluation of sediment formation in initial oil and water-oil emulsions was carried out with the help of a set-up developed on the basis of the cold-finger test. During the experiment, the sample under analysis in a tightly closed glass was thermostated for 1 h at 20 °C. Sediment formation due to temperature gradient proceeded at the steel finger cooled to 10 °C.

To inhibit ARPD in oil and emulsions, K-210 additive (A) based on ordered amphiphilic nitrogen-containing polymer was used. The synthesis procedure and the major characteristics of the K-210 additive are described in [25].

Asphaltene content in the sediments formed in emulsions was determined with the help of the cold Golde procedure, oils and resinous substances were determined with the help of chromatography (the column adsorption method). The elemental composition of resins and asphaltenes isolated from dehydrated sediments was analyzed using a Vario EL Cube CHSN-analyzer (Elementar Analysensysteme GmbH, Germany).

The structural group analysis (SGA) based on the data of ^{1}H NMR spectroscopy, elemental composition and the data on molecular masses allows calculating the average distribution of atoms between the structural elements of the high-molecular compounds in oil [26].

RESULTS AND DISCUSSION

Investigation of the formation of sediments in oil and water-oil emulsions showed that an increase in the watering of the oil disperse system (ODS) causes a substantial increase in the amount of ARPD. The effects of oil watering degree and the additive on the amount of the formed sediment are shown in Fig. 1. The amount of the sediment in emulsions increased by 16–20 g in comparison with the amount of sediment formed in initial oil. The introduction of the additive causes a substantial decrease in the amount of sediment in oil and in water-oil emulsions. The extent of inhibition in oil is 64 %, and in emulsions it is 75–79 %.

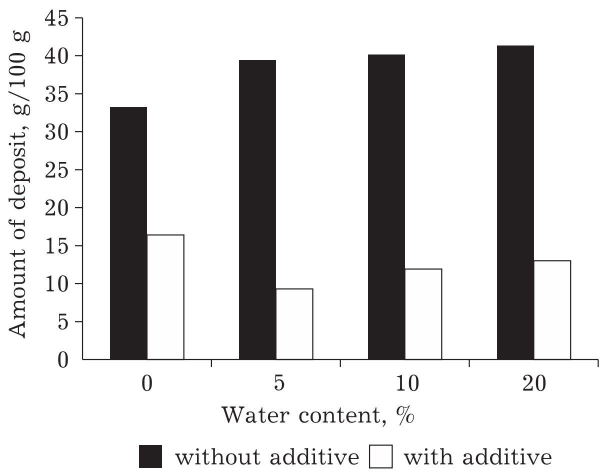

Fig. 1. Effect of the inhibiting additive on the amount of deposit formed in oil and in water-oil emulsions with different water content.

TABLE 1

Content of n-alkanes in ARPD formed in water-oil emulsions based on oil from the Urmanskoye deposit in the presence of the additive (A)

Sample	Content, mass %	
	$\sum C_{10}-C_{15}$	$\sum C_{16}-C_{40}$
Oil	11.9	88.1
Oil sediment	11.3	88.7
The same + A	10.2	89.8
Precipitate in 5 %* emulsion	12.5	87.5
The same + A	9.8	90.2
Precipitate in 20 % emulsion	17.2	82.8
The same + A	8.3	91.7

* Water content in the water-oil emulsion is indicated.

The data on the content of PH, resins and asphaltenes in the ARPD of emulsions are shown in Fig. 2. The content of PH in the sediments of emulsions increases with an increase in water content. After the introduction of the additive, the fraction of PH in the sediments of water-oil emulsions decreases by a factor of 6 as average.

An increase in water content in water-oil emulsions is accompanied by an increase (by 11–24 %) in the fraction of low-molecular n-alkanes with the composition $\sum C_{10}-C_{15}$ (Table 1). Higher-molecular PH with the composition $\sum C_{16}-C_{40}$ may participate in the formation of interfacial shells on water globules, which causes a decrease in their fraction in sediments with an increase in water content in emulsions.

Additives preventing the formation of ARPD interact mainly with PH in ODS, which is accompanied by the redistribution of n-alkanes in the sediments. The application of the additive causes a decrease in the fraction of liquid PH ($\sum C_{10}-C_{15}$) in the formed ARPD.

With an increase in water content in water-oil emulsions, the fraction of resins in the sediments decreases insignificantly (see Fig. 2, *b*). This may be due to the fact that resins, being surfactants, are adsorbed in the interfacial films of water globules. The introduction of the additive into emulsions leads to an increase in the content of resins in the formed sediments.

The content of asphaltenes in ARPD formed in oil with the additive is higher than in the case of the sample without the additive. The amount of asphaltenes in the sediment formed in 5 % emulsion increases by a factor of 3 in comparison with the amount of sediment formed in oil (see Fig. 2, *c*). With further increase in water content in water-oil emulsions, the fraction of asphaltenes in the sediments decreases.

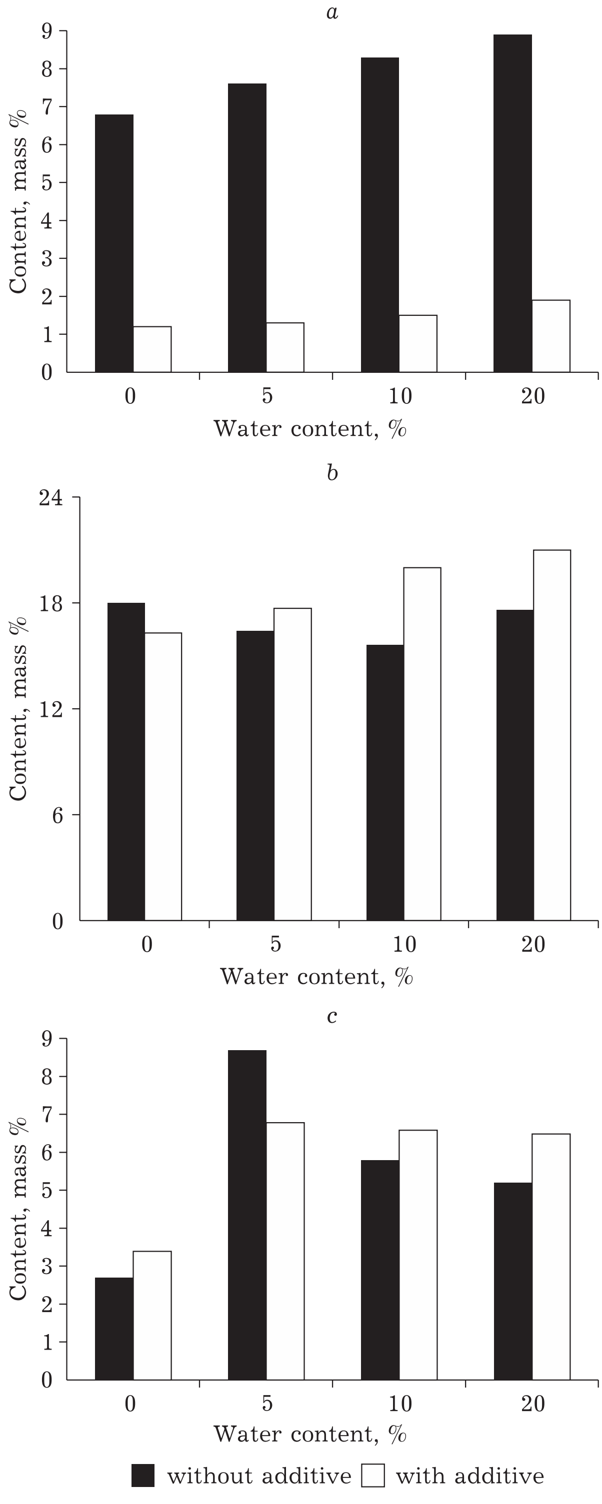

Fig. 2. Effect of inhibiting additive on the content of PH (*a*), resins (*b*) and asphaltenes (*c*) in the deposits of oil and water-oil emulsions with different water content.

The structural group analysis allowed us to determine the changes in the composition of resin-asphaltene components of sediments formed in water-oil emulsions with different water content,

TABLE 2

Effect of inhibiting additive (A) on the structural parameters of resins extracted from oil and sediments formed in water-oil emulsions with different water content

Parameter	Oil	Sediment					
		Oil		Emulsion*			
		without additive	with additive	5 %	5 % + A	20 %	20 % + A
MM, a.m.u..	770	752	760	533	553	696	569
Number of atoms in average molecule:							
C	51.8	52.3	52.3	36.9	38.1	47.9	39.0
H	71.8	76.0	71.3	53.0	55.2	71.2	58.1
N	0.29	0.15	0.16	0.31	0.13	0.44	0.13
S	0.49	0.44	0.49	0.31	0.36	0.40	0.36
O	2.18	2.23	2.33	2.61	1.70	3.15	1.79
Distribution of carbon atoms, %:							
f_a	31.4	32.5	32.7	32.6	30.4	28.9	29.8
f_n	34.7	17.5	26.7	24.3	27.7	22.2	20.8
f_p	33.8	40.9	40.6	43.0	41.9	48.9	49.4
Number of carbon atoms of different kinds:							
C_a	16.3	17.0	17.1	12.0	11.6	13.8	11.6
C_n	18.0	9.2	14.0	9.0	10.5	10.6	8.1
C_p	17.5	26.1	21.2	15.9	15.9	23.4	19.3
C_α	7.2	7.2	6.0	6.7	5.8	6.3	5.5
C_γ	4.0	4.1	4.4	3.9	2.8	4.4	3.0
Proton deficiency	31.8	28.7	33.2	20.7	20.9	24.6	19.9
Z = 2C−H							

Note. Here and in Table 3: f_a, f_p, f_n are the fractions of carbon atoms in aromatic, paraffinic and naphtenic structural fragments, respectively; C_a is aromatic carbon; C_n is carbon in naphthene rings; C_p is carbon in aliphatic (paraffinic) substituents; C_α is carbon in α-positions with respect to the cycle; C_γ is carbon in terminal methyl groups.

* Water content in oil emulsion is indicated.

and to evaluate the efficiency of the inhibiting additive. The effects of the degree of oil watering and the presence of inhibiting additive on the molecular mass (MM) and the elemental composition of resins are shown in Table 2. The presence of the aqueous phase is accompanied by a substantial decrease in the MM of resins in the sediments formed in the samples both with the additive and without it.

Water appearing in an oil system causes an increase in the fraction of the heteroatomic component (oxygen, nitrogen) in the resins of ARPD in water-oil emulsions. It is possible that more polar resins with increased content of heteroatomic components, due to their ability to form strong intermolecular bonds, remain in the interfacial shells of water drops, so the stability of emulsions increases with an increase in water content.

An increase in the concentrations of oxygen and nitrogen in the composition of an average molecule of resins from the deposits of the water-oil emulsion is observed with an increase in water content in the emulsions. The application of the additive leads to resin (less polar and disposed to aggregation) concentrating in the deposit, which is evidenced by a decrease in the fraction of heteroatomic components.

The effect of the additive and water content in the emulsions on the structural parameters of asphaltenes in ARPD under investigation is shown in Table 3.

In an average molecule of the asphaltene components of ARPD from emulsions, insignificant changes in the content of heteroatomic fragments are observed with an increase in water concentration.

The presence of the additive and an increase in water content in the emulsions promote the formation of deposits in which the asphaltenes are characterized by an increased proton deficiency (the percentage of aromatic fragments).

TABLE 3

Effect of inhibiting additive (A) on the structural parameters of asphaltenes isolated from oil and deposits formed in water-oil emulsions with different water content

Parameter	Oil	Deposit					
		Oil		Emulsion*			
		without additive	with additive	5 %	5 % + A	20 %	20 % + A
MM, a.m.u.	946	953	1050	1286	1214	1295	1282
Number of atoms in the average molecule:							
C	63.9	64.2	67.8	83.9	84.6	87.1	82.4
H	54.1	57.2	71.2	87.2	88.7	86.9	81.0
N	0.41	0.35	0.42	0.49	0.50	0.48	0.49
S	0.94	0.57	0.92	0.72	0.80	0.69	0.76
O	3.34	7.05	3.60	7.56	4.78	7.93	4.97
Number of carbon atoms of different kinds in an average molecule:							
C_a	27.6	28.7	27.1	33.6	30.4	36.0	34.0
C_n	33.7	24.2	37.2	40.0	50.2	34.2	40.2
C_p	2.5	11.2	3.4	10.3	4.0	14.6	8.2
C_α	10.3	9.5	9.1	14.3	12.5	12.7	12.8
C_γ	2.5	3.0	3.3	5.7	4.0	6.6	5.5
Proton deficiency $Z = 2C-H$	73.7	71.2	71.2	80.6	80.5	87.3	83.8

Note. For designations, see Table 2.

* Water content in oil emulsion is indicated.

In the asphaltene despots of emulsions, the number of carbon atoms in the paraffin fragments of molecules is 4 times higher than in the molecules of oil asphaltenes.

The introduction of the additive leads to a decrease in the fraction of oxygen and an increase in sulphur concentration in the asphaltenes of the deposits of water-oil emulsions, the nitrogen concentration in an average molecule of asphaltene components remains practically unchanged.

CONCLUSIONS

The following conclusions may be made on the basis of results obtained in the investigation:

1. The introduction of water into an oil system leads to an increase in the inhibiting ability of the K-210 additive.

2. In the presence of inhibiting additive, a decrease in the fraction of paraffin hydrocarbons with respect to the deposits of initial emulsions is observed in the formed deposits.

3. An increase of water content in water-oil emulsions leads to the accumulation of most polar, prone to aggregation resin-asphaltene components in the asphaltene-resin-paraffin deposits, which is evidenced by an increase in the fraction of nitrogen, suphur, oxygen, and aromaticity factor.

4. In the case when K-210 additive is used, resin-asphaltene components in the deposits of emulsions are characterized by lower molecular mass and increased content of aromatic fragments. The content of heteroatomic components in the average molecules of resins and asphaltenes decreases. A possible reason may be the accumulation of less polar resin-asphaltene components (a decrease in the fraction of heteroatomic fragments) in the asphaltene-resin-paraffin despots as a result of the interaction of the additive and paraffin hydrocarbons. Resins and asphaltenes with increased amount of heteroatoms remain within the water-oil system thus maintaining its stability.

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