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Effect of Mineralization of Aqueous Phase and Watering on the Composition of the Interphase Layer of Water-Oil Emulsions

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Abstract

Effect of water and salt content in water-oil emulsions on the group composition of their interphase layer was studied. It was demonstrated that an increase in water and salt content is accompanied by an increase in the fraction of heteroatomic components, an increase in the degree of cyclicism and aromaticity in pyrobitumen extracted from the interphase layers of emulsions in comparison with the pyrobitumen species of oil.

Key words: water-oil emulsions, interphase layer, natural oil emulsifiers, pyrobitumen

INTRODUCTION

At present, the most widespread method of oil production is waterflooding of oil-bearing layers with salt solutions, which causes the formation of stable water-oil emulsions [1]. The occurrence of water-oil systems promotes intense corrosion wear of pumping equipment and a decrease in the capacity of oil pipelines. The stability of these systems is due to the formation of strong adsorption layers with natural emulsifiers at the interface [2]. Many works dealing with the studies of the methods of destroying water-oil emulsions have been published; a qualified choice of a proper method is mainly dependent on the composition and properties of oil [3–6]. In addition to natural oil emulsifying agents, stabilization of water-oil emulsions is also affected by mineralization of the stratal water extracted together with oil. However, there are almost no literature data on the effect of salt and water content on changes of the amount and structure of natural oil emulsifiers, such as gum-pyrobitumen components and paraffin hydrocarbons.

The goal of the present work was to study the features of the formation of interphase oil emulsion layer with different water content.

EXPERIMENTAL

Model reverse water-oil emulsions based on gumming paraffinic oil (Table 1) with the mass concentration of gum 19.7, pyrobitumen 0.1 %, paraffin hydrocarbons (PH) 3.6 % were studied in the work. The interphase emulsion layer formed between oil and water was isolated using the procedure described in [2, 7–10]. In order to isolate interphase layers, we prepared stable water-oil emulsions using the mixing device PE-0118 with the capacity of 150 W; the frequency of paddle rotation 1200 min^{-1} for 10 min. After preparation, water-oil emulsions were transferred quantitatively to the separating funnel and settled at room temperature for 24 h. After the formation of the in-

TABLE 1

Group composition of oil and interphase layers of water-oil emulsions, mass %

Water concentration	Hydrocarbons			Gum		Pyrobitumen	GBC*/PH
	Paraffin	Naphthene	Aromatic	Bebzene	Alcohol-benzene		
0	3.6	68.6	8.0	11.5	8.2	0.1	–
			Fresh water				
10	2.6	70.2	7.9	10.9	7.6	0.8	7.4
50	2.8	69.9	7.1	10.7	7.0	2.5	7.2
70	3.1	67.7	6.9	9.0	5.7	7.6	7.2
			Mineralized water				
10	2.5	69.1	7.5	10.1	7.0	3.8	8.4
50	1.3	48.1	4.6	5.0	6.0	35.0	35.4
70	2.7	53.6	8.5	6.2	6.5	22.5	22.5

*GBC stands for gum and bitumen components.

terphase layer, the emulsions were layered with the fivefold amount of distilled water. After separation from oil and water in the separating funnel, the interphase layer was centrifuged in order to separate the organic part (natural oil stabilizers) and the inorganic one (with water content more than 80 %). After the separation of the organic part, its group composition was determined. The group composition of oil and interphase layers was determined according to State Standard GOST 11851–85.

In this work, we studied the interphase layers of emulsions with different water content in the oil phase: 10, 50 (the ratio of oil and water phases 1 : 1) and 70 % (high water content). Fresh water with total salt content 150 mg/dm^3 and mineralized water with the density of 1286.0 kg/m^3 and total salt content 485 g/dm^3 was used as the aqueous phase to prepare emulsions.

The microstructure of pyrobitumen agglomerates was studied with a MBI-15U microscope with a digital video camera at the magnification of 480. The structural and group analysis of pyrobitumen was carried out according to the procedure based on the results of the complex investigation (determination of molecular mass, elemental composition and the data of ^{1}H PMR spectroscopy [11]. The IR spectra of pyrobitumen extracted from oil and from the interphase layer of water-oil emulsions were recorded in the thin layer with a Nicolet-5700 FT-IR spectrometer in the region 400–4000 cm^{-1}. The fractions of oil components were deposited as a film onto the glasses made of KBr. For the determination of the optical density of bands, the straight line between the transmission maxima at 650 and 1800 cm^{-1} was used as the baseline. Then the optical density of the bands was normalized for the optical density of the band at 1465 cm^{-1}. The assignment of the bands according to the presence of definite structural fragments in the objects under investigation was carried out on the basis of the data reported in [12].

RESULTS AND DISCUSSION

The stability of emulsion systems is determined by the presence of high-molecular surface-active substances (so-called stabilizers or natural emulsifiers) in oil. Stabilization of water-oil emulsions is provided due to the formation of strong adsorption layers by natural emulsifiers at the interface. It is known that the main stabilizers of water-oil emulsions are gum, pyrobitumen and paraffin hydrocarbons (PH) [13–16].

It was established that an increase in the water and salt content in water-oil emulsions causes substantial changes in the group composition of interphase layers. In comparison with the initial oil, the interphase layers for emulsions with fresh water exhibit PH content decreased by 14–30 %, and with mineralized water – almost by a factor of 3 (see Table 1). With an increase in the volume fraction of mineralized water in the emulsion to 50 and 70 %, the concentration of naphthene hydrocarbons (NH) decreases by 30 % in comparison with their concentration in the initial oil. The concentration of aromatic hydrocarbons (AH) remains almost unchanged.

With an increase in the water phase content, the fraction of gum in the interphase layers of all the emulsions under investigation decreases substantially, while the fraction of pyrobitumen (P) increases. In comparison with initial oil, in the interphase layers of emulsions the fraction of pyrobitumen increases by a factor of 8–80 with an increase in fresh water content from 10 to 70 %. Changes of the composition of interphase layers of emulsions with mineralized water are similar to those for the emulsions with fresh water (see Table 1). However, with an increase in water content in the emulsions with mineralized water, the fraction of pyrobitumen increases substantially in comparison with the emulsions with fresh water. The fraction of pyrobitumen in the emulsions with mineralized water content 10, 50 and 70 % increases in comparison with the emulsions with fresh water by a factor of 5, 14 and 3, respectively. So, with an increase in mineralized water content and salt concentration, the fraction of pyrobitumen in the interphase layers of these emulsions increases substantially.

Investigation of the group composition of the interphase layer allows us to determine the type of emulsion stabilizer depending on surface-active substances forming a strong shell around the particles of water dispersed in oil. With respect to the ratio of gum and pyrobitumen components (GBC) to PH, stabilizers are divided into the following types: pyrobitumen-gum ($GBC/PH \geq 1.0$), paraffin ($GBC/PH \leq 1$), mixed ($GBC/PH \sim (0.8-1.2)$. The data presented in Table 1 provide evidence of the clearly exhibited pyrobitumen type of the stabilizer for the interphase layers of emulsions with fresh and mineralized water. With an increase in the content of mineralized water in the emulsion up to 50–70 %, the GBC/PH ratio increases by a factor of 2–4. So, the type of emulsion stabilizer for oil under investigation is determined mainly by the concentration of GBC.

According to the data of structural group analysis, the composition of pyrobitumen species extracted from oil and interphase layers

TABLE 2

Structural group analysis of pyrobitumen species extracted from oil and emulsions (fresh and mineralized water content: 50 %)

Parameter	Initial oil	50 % emulsion	
		with fresh water	with mineralized water
Molecular mass, a.m.u.	1050	1320	2036
Number of atoms in an average molecule:			
C	72.5	89.6	135.9
H	122.2	146.3	222.2
N	0.4	0.7	1.2
S	0.3	0.4	0.6
O	2.6	4.4	9.5
Hydrogen deficiency (z)	22.8	32.9	49.6
Number of carbon atoms in paraffin fragments (C_p)	48.3	62.7	95.0
Number of aromatic carbon atoms in an average molecule (C_a)	11.7	26.9	40.9
Aromaticity factor (f_a)	16.2	30.0	30.1
Number of aromatic nuclei (m_a)	1.4	5.0	5.2
Number of different protons in an average molecule:			
H_a	3.8	13.0	16.0
H_{sat}	118.4	133.3	206.2

TABLE 3

Data on the spectral coefficients for pyrobitumen compounds extracted from oil and interphase layers of water-oil emulsions (fresh and mineralized water content: 50 %)

Parameters	Initial oil	50 % emulsion	
		with fresh water	with mineralized water
Relative concentration of condensed aromatics (D_{750}/D_{720})	0.78	0.95	1.16
Relative concentration of C=O (D_{1710}/D_{1465})	0.14	0.21	0.42
Oil oxidability (D_{1740}/D_{1465})	0.11	0.25	0.46

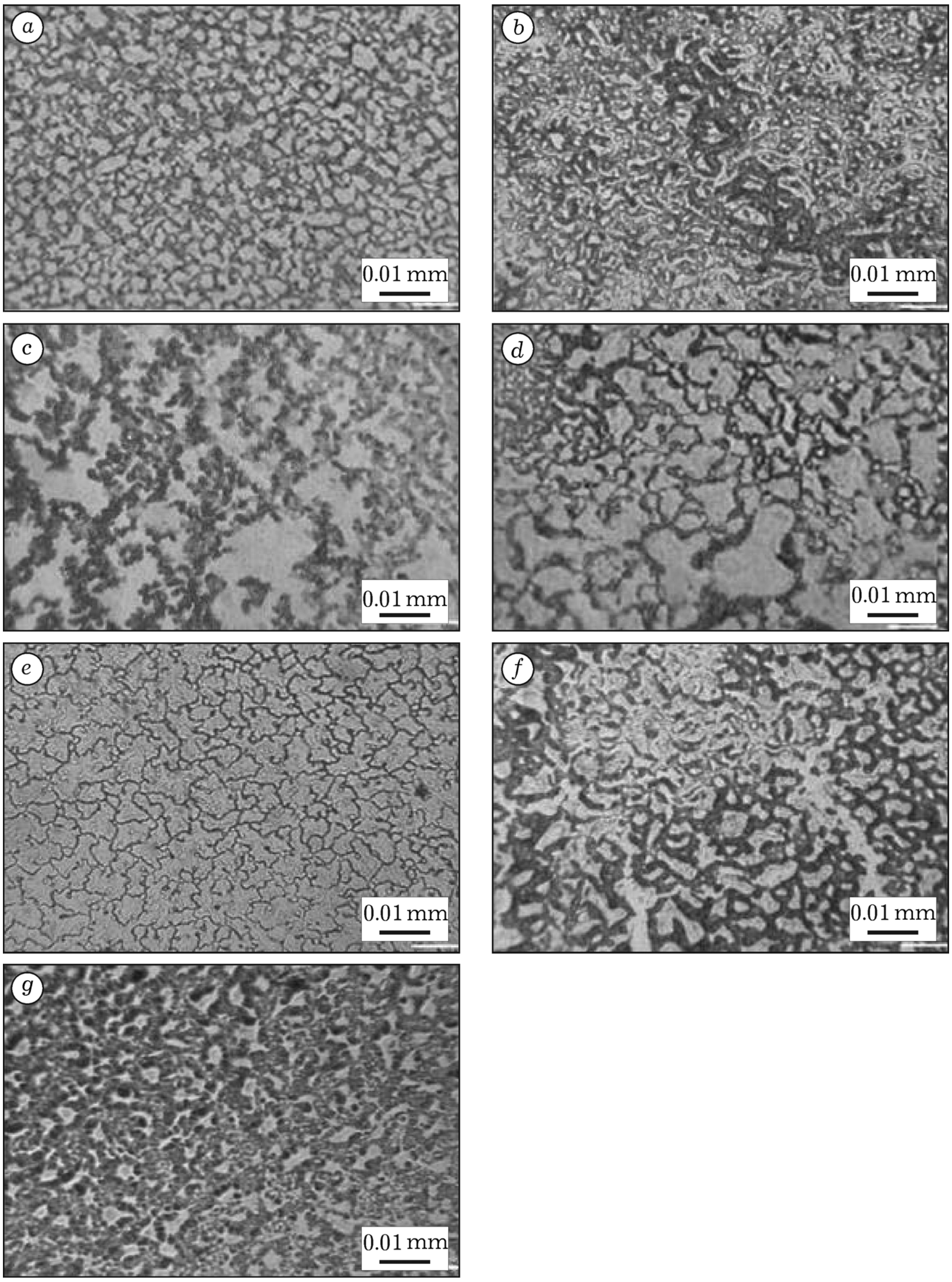

Fig. 1. Micrographs of pyrobitumen extracted from the interphase layers of emulsions with fresh (*a*, *c*, *e*) and mineralized (*b*, *d*, *f*) water and from oil (*g*). Water content, %: 10 (*a*, *b*), 50 (*c*, *d*), 70 (*e*, *f*). Magnification: 480.

of emulsions varies depending on the concentration of water and its mineralization (Table 2). The most substantial changes are observed in the composition of pyrobitumen species extracted from the emulsions with mineralized water. In comparison with the molecular mass of pyrobitumen species of initial oil, the molecular mass of pyrobitumen species extracted from interphase layers of emulsions with fresh and mineralized water increases in the former case by 26 % and almost by a factor of two in the latter case. An increase in the number of heteroatoms is also characteristic of these pyrobitumen species: the number of nitrogen atoms per average molecule increases by a factor of 2–3, sulphur – 3, oxygen – almost 4 times. In comparison with pyrobitumen of initial oil, the degree of hydrogen deficiency in pyrobitumen extracted from the interphase layers of emulsions with mineralized water increases by a factor of 2. The number of aromatic carbon atoms and carbon atoms in paraffin substituents in an average molecule increases by a factor of 2–3. The aromaticity factor increases by a factor of 2; the number of aromatic nuclei increases by a factor of 4. An increase in the fraction of polycondensed aromatic fragments and the fraction of oxygen-containing structures is confirmed by IR spectroscopic data (Table 3). In comparison with pyrobitumen species of initial oil, the spectra coefficients characterizing the fraction of oxygenated structures and the fraction of polycondensed aromatic fragments for pyrobitumen extracted from the interphase layers in 50 % emulsions increase 2.3–4 and 1.3–1.5 times, respectively.

So, an increase in the concentration of water and salts in water-oil emulsions leads to substantial changes in the composition of pyrobitumen species, namely, to the formation of more complicated aggregations and increase in their size in comparison with the pyrobitumen species of initial oil.

Micrographs of pyrobitumen extracted from oil and interphase layers of emulsions are shown in Fig. 1. One can see that the structure of oil pyrobitumen is a homogeneous matrix with separate flake-like particles dispersed in it. For pyrobitumen of the interphase layers of 10 % emulsions with fresh and mineralized water, fine-grained disperse structure with flake-like particles is characteristic. Pyrobitumen from 50 % emulsions are represented by aggregations with clear boundaries, while pyrobitumen from 70 % emulsions are represented by flake-like aggregates with more uniform, fine and ordered structure.

The formation of emulsions with fresh water promotes pyrobitumen concentrating in interphase layers. A substantial increase in the fraction of pyrobitumen in the interphase layers of emulsions with mineralized water may be due to structural rearrangements of the agglomerates of pyrobitumen with gum species activated by the high concentration of slats in water [17, 18]. The formation of agglomerates promotes an increase in the fraction of pyrobitumen components in the interphase layers of water-oil emulsions.

CONCLUSION

It was demonstrated as a result of investigation that an increase in the concentration of water and the degree of its mineralization in the interphase layers of emulsions causes an increase in the fraction of pyrobitumen components. According to the data of structural group analysis and IR spectroscopy, the composition of pyrobitumen species changes with an increase in water content of emulsion. Pyrobitumen species extracted from emulsions differ from those of initial oil by the higher concentration of polycondensed aromatic fragments and oxygen-containing structures.

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