

## Features of Hydrocarbon Distribution in the Viscous Oil–Aqueous Phase System during Testing of Oil Displacement Fluids

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**Abstract**—The chemical composition of high-viscosity Mongolian oil and the influence of surfactant-based, composite oil displacement agents on the distribution of hydrocarbons (HCs) during thermostating of the crude oil–agent (oil–water) system under laboratory conditions have been studied. It has been shown that the presence of the agent in the system leads to redistribution of hydrocarbons, a change in the HC composition of the oil phase, and an increase in the concentration of petroleum components in the aqueous phase. The increase is especially noticeable when a surfactant is used: the proportion of light C<sub>10</sub>–C<sub>15</sub> alkanes increases in the oil and C<sub>16</sub>–C<sub>25</sub> alkanes and cyclohexanes dominate in the aqueous phase.

**Keywords:** viscous oil, composite oil displacement agent, surfactant, hydrocarbons

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The balance of hydrocarbons produced currently in the world is dominated by high-viscosity oils, with their share tending to increase, a situation that greatly complicates the oil production technology. Petroleum engineering, especially, concerning the production of high-viscosity, paraffinic, and high-resin oils requires a special approach. Crude oil occurring in hydrophilic rocks together with saline water is a complex mixture of substances that include natural water- and oil-soluble surfactants as well. Oil adsorption on the rock causes its lyophilization. To facilitate access to oil, a chemisorbing surfactant solution is injected into a well after drilling; the surfactant hydrophobizes hydrophilic areas of the rock and facilitates the inflow of oil to the well through cracks and capillaries. Subsequently, for the completeness of oil recovery (as low as 30–40% is often recovered), edge flooding is used: water, surfactant solutions, and micelle-forming solutions that improve selective wetting with water and displace the oil to the producing well are injected into a number of auxiliary wells [1].

The results of pioneering experimental and field studies on the use of surfactants as an additive in waterflooding of oil reservoirs were reported in the United States in 1940s–1950s. In Russia, the problem has been studied for more than 40 years [2–4]. During this time, mainly physicochemical and engineering principles of the method were developed, approximate criteria for the applicability of surfactants were proposed, and the method was tested in various geological and field conditions [5]. However, many aspects of this

problem are still not fully understood and require clarification and further research. The mechanism of oil recovery by the action of aqueous surfactant solutions on residual and produced oils is complex and multifaceted, thus calling for further experimental and field studies on the modern scientific basis.

During the process of oil displacement by a surfactant, the following interrelated factors have an effect: interfacial tension at the oil/water, water/rock, and oil/rock interfaces, which is due to their adsorption on these interfaces. In addition, the surfactant effect is manifested in a change of the selective wetting of the rock surface with water and oil, oil film fracturing and washing off the rock surface, stabilization of oil dispersion in water, an increase in the efficiency of oil displacement by the aqueous phase in both the displacement and capillary imbibition, and enhancement of relative permeability of porous media [6, 7].

In this work, we studied the characteristic features of the joint effect of the compositions of crude oil and oil-displacing fluids on the distribution of individual groups of petroleum hydrocarbons in model water–oil systems using a high-viscosity, paraffinic Mongolian oil as an example.

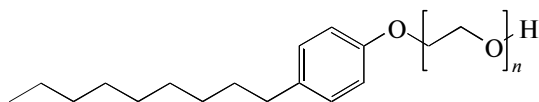
### EXPERIMENTAL

The object of study was crude oil with a paraffin content of 10.5 wt % from the main producing formation of the Zuunbayan oilfield in Mongolia. The phys-

icochemical characteristics and the component composition of the oil [8] are presented in Table 1.

It is seen that Zuunbayan oil contains a relatively high amount of resins and asphaltenes (23.6 wt %) and the amount of light fractions (IBP–200°C) does not exceed 8.5 wt %.

As an oil displacement fluid, we used the NINKA® composition, which has been designed at the Institute of Petroleum Chemistry, Siberian Branch and is based on an aqueous solution of urea, ammonium nitrate, and surfactants of different types [4–6]. To study the effect of various surfactants on the composition and properties of crude oil, the nonionic surfactants ethoxylated alkylphenols with varying degrees of ethoxylation of the general formula  $R\text{ArO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$  was used, where Ar is the benzene ring, R is a long hydrocarbon radical (usually  $\text{C}_9\text{--}\text{C}_{18}$ ), and  $n$  is the average number of ethoxy groups in the surfactant molecule nonionic (degree of ethoxylation). The surfactant structural formula is given below:



In particular, we used the domestic nonionic surfactant Neonol AF 9-12, which is ethoxylated isononylphenol with a degree of ethoxylation of 9–12 as derived from propylene trimers, and the nonionic surfactant Neonol NP-50 manufactured in China, which is ethoxylated isononylphenol with a degree of ethoxylation of 50. Neftenol VVD of the winter grade (partially sulfonated Neonol AF 9-12), a composite surfactant comprising a mixture of nonionic surfactant Neonol AF 9-12 and its sulfoethoxylate as an anionic surfactant (29–35%) with ethylene glycol (25–30%), was also used.

The oil was thermostated at 125°C for 32 h in the presence of distilled water or the oil displacement fluid under laboratory conditions simulating the reservoir conditions [9–11]. After completion of thermostating and cooling the autoclave to 20°C, the aqueous phase was separated from the oil and analyzed. Using triply repeated extraction with chloroform followed by solvent removal, petroleum (organic) compounds—chloroform-extractable aqua bitumenoid (CAB)—were isolated from the aqueous phase.

Infrared spectra of oil and CAB samples were recorded on a Nicolet 5700 Fourier-transform IR spectrometer (resolution, 4  $\text{cm}^{-1}$ ; number of scans, 64) in the range of 1800–600  $\text{cm}^{-1}$  in a thin film between KBr plates. Spectral coefficients, defined as the ratios of optical densities ( $D$ ) of characteristic absorption bands due to different types of bonds in organic molecules [12, 13], were calculated from the IR spectra.

Individual and group compositions of saturated and aromatic hydrocarbons present in the oil phase and CAB were determined by GC and gas chromatog-

**Table 1.** Physicochemical characteristics of crude from the Zuunbayan oilfield, Mongolia

Parameter	Value
Sampling depth, m	700–800
Average reservoir temperature, °C	45
Density at 20°C, $\text{kg/m}^3$	889.4
Dynamic viscosity at 20°C, mPa s	1996
Content, wt %:	
hydrocarbons	76.4
resins	22.8
asphaltenes	0.8

raphy–mass spectrometry (GC–MS) using a Thermo Scientific DFS magnetic sector mass spectrometer (Germany) [14, 15].

Control samples were (1) the original crude oil for studying the effect of the oil displacement fluids on the composition of the oil phase during thermostating (control 1) and (2) the oil phase and CAB isolated after thermostating of the oil–(distilled) water system in the absence of surfactant (controls 2 and 3, respectively).

## RESULTS AND DISCUSSION

The test oil is a highly viscous, heavy, waxy, high-resin oil in its physicochemical characteristics (Table 1) as defined in [15]; it is classified with hard-to-recover hydrocarbon reserves and requires the use of different methods of enhanced oil recovery, including the application of oil displacement fluids.

As a result of thermostating of the oil–fluid (oil–water) systems, the organic components were redistributed between the oil and aqueous phases. Analysis of the GC–MS data for the isolated oil phase showed that the composition of petroleum hydrocarbons had undergone changes, of which the most substantial alteration was in the case of the fluid comprising Neftenol VVD as a surfactant (Table 2).

The concentration of alkanes decreased by 2.2 rel. %; that of tetraarenes decreased by 0.3 rel. %; and the relative amount of alkylcyclohexanes, tri-, tetra-, and pentacyclanes, and mono- and biaromatic compounds increased. The samples of oil contacted with the Neonol AF 9-12 and Neonol NP-50 based fluids were found to have less noticeable changes in the distribution of saturated (alkanes and naphthenes) and aromatic hydrocarbons.

As a result of thermostating of the oil–fluid (oil–water) system, the oil components were partially transferred to the aqueous phase, with the most significant amount passing in the presence of the surfactant-containing fluid (Fig. 1). It is known that surfactants reduce interfacial tension between phases and promote the transfer of hydrocarbons to the aqueous phase [16].

**Table 2.** Amount of hydrocarbons in the oil and the oil phase isolated after thermostating the oil–water and oil–fluid system

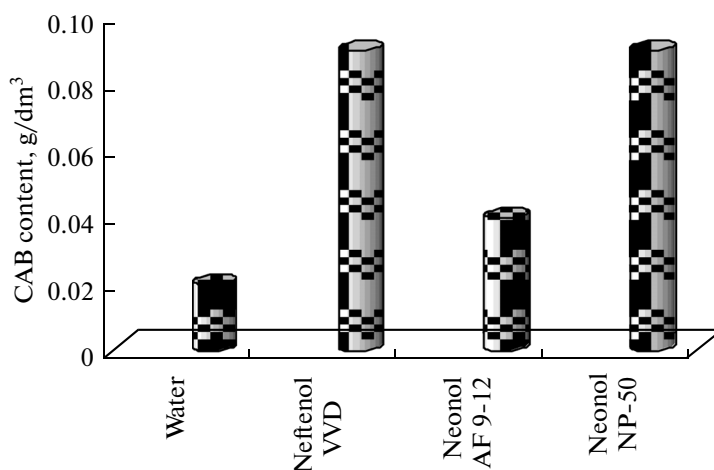
Hydrocarbons	Control 1	Control 2	Surfactant in fluid		
			neftenol VVD	neonol AF 9-12	neonol NP-50
	amount of hydrocarbons, rel. %				
Alkanes	86.80	85.36	84.61	86.13	85.63
Monocyclanes (alkylcyclohexanes)	6.75	7.92	8.25	7.27	7.51
Bicyclanes (sesquiterpanes)	0.50	0.56	0.49	0.42	0.52
Tricyclanes (tricyclic terpanes)	0.02	0.07	0.10	0.11	0.09
Tetracyclanes (steranes, secohopanes)	1.42	1.37	1.47	1.31	1.32
Pentacyclanes (hopanes)	1.76	1.79	1.98	1.86	1.75
Monoarenes (alkylbenzenes)	0.41	0.47	0.58	0.42	0.48
Biarenes (naphthalenes, biphenyls)	1.45	1.57	1.67	1.43	1.77
Triarenes (phenanthrenes)	0.77	0.82	0.76	0.90	0.81
Tetraarenes (benzanthracenes, pyrenes, chrysenes, fluoranthenes)	0.12	0.4	0.09	0.15	0.12

The maximal amount of CAB ( $0.09 \text{ g/dm}^3$ ) in the aqueous phase was found after oil thermostating with the Neftenol VVD-containing fluid, being five times that in the control experiment. It is known that non-ionic surfactants, such as Neonols NP-50 and AF 9-12, are well compatible with high-salinity water and exhibit a solubilizing activity (surfactant micelles dissolve substances that are insoluble in the dispersing medium) [7]. Neftenol VVD is a mixture of nonionic and anionic surfactants. The latter are known to have a higher solubilizing power compared with nonionic surfactants, thus enhancing the transfer of organic components from the oil to the aqueous phase [16].

The composition of organic compounds in the oil and aqueous phases was determined according to the IR spectral coefficients, which conventionally reflect the concentrations of various structures (Table 3).

Aromaticity factor  $C_1$  determining the ratio of aromatic to aliphatic compounds is maximal for CAB isolated after thermostating the oil with the Neonol NP-50-based fluid, whereas its minimum value is observed in the experiment with Neonol AF 9-12. The higher aromatics content in the aqueous phase containing the surfactant in comparison with the oil phase may be due to the presence and the amount of ethoxy (hydrophilic polar) groups, which are readily soluble in water and promote the transfer of aromatic compounds to it from the oil phase, in the molecule of the surfactant used. For example, the degree of ethoxylation in Neonol NP-50 is 50, which is almost four times that in Neonol AF 9-12 (degree of ethoxylation 12).

The amount of branched structures (coefficient  $C_2$ ) in CAB is practically the same for both the control

**Fig. 1.** Amount of chloroform-extractable aqua bitumenoid (CAB) in the aqueous phase after oil thermostating with water and surfactant-based fluids.

**Table 3.** Spectral characteristics of organic compounds of the oil and water phases

Surfactant in fluid	Spectral coefficients				
	$C_1 = D_{1610}/D_{720}$	$C_2 = D_{1380}/D_{1465}$	$C_3 = D_{818}/D_{1610}$	$C_4 = D_{1710}/D_{1465}$	$C_5 = D_{1670}/D_{1465}$
Oil phase					
Control 2	0.50	0.53	0.79	0.05	0.06
Neftenol VVD	0.52	0.47	0.81	0.03	0.04
Neonol AF 9-12	0.52	0.50	0.82	0.04	0.05
Neonol NP-50	0.47	0.50	0.80	0.03	0.05
Aqueous phase					
Control 3	1.36	0.56	0.00	1.04	0.00
Neftenol VVD	1.11	0.54	0.94	0.12	0.17
Neonol AF 9-12	0.97	1.51	1.95	0.12	0.39
Neonol NP-50	2.55	0.75	0.30	0.03	0.45

experiment and the experiments with Neftenol VVD and Neonol NP-50; the maximal value is observed in the case of Neonol AF 9-12. A slight decrease in the proportion of branched structures was found for the oil phase.

The maximum amount of polysubstituted aromatic structures (coefficient  $C_3$ ) for both the aqueous and oil phases was observed in the experiments with Neonol AF 9-12, whereas the control samples showed their presence in a minimal amount.

The amount of carbonyl compounds (coefficient  $C_4$ ) in the aqueous phases was higher than in the oil in all the experiments. It has been established that the maximum value of  $C_4$  is in CAB of the control sample and a minimum value, in CAB isolated in the experiment with the Neonol NP-50 composition. Being polar, oxygen-containing compounds are knowingly well soluble in aqueous phase, a fact that explains their lower content in oil.

Carboxylic acid amides (coefficient  $C_5$ ) formed in the reaction of petroleum carboxylic acids with ammonia, released during the decomposition of the urea present in the fluid, were detected in the oil phases and CAB.

The results of determination of the group composition of saturated and aromatic hydrocarbons identified in aqua bitumenoids are shown in Table 4.

Analysis of the data showed that alkanes are present in maximal amounts in all of the CAB samples. In addition, monocyclanes (alkylcyclohexanes) and mono-, bi-, and triarenes (alkylbenzenes, naphthalenes, phenanthrenes, fluorenes) were detected in smaller amounts in CAB, as well as traces of tetraarenes (pyrene, chrysene, fluoranthene, benzanthracene). The molecular weight distribution of *n*-alkanes present in the oil and aqueous phases (Fig. 2) showed that  $C_{16}$ – $C_{25}$  alkanes dominate in all of the test samples.

The thermostating of the oil with the oil displacement agents (Fig. 2a) resulted in an increase in the relative amount of lighter,  $C_{10}$ – $C_{15}$  alkanes and a slight

decrease in the proportion of the  $C_{16}$ – $C_{25}$  homologues in the oil phases as compared with the control experiment. Changes in the concentration of higher,  $C_{26}$ – $C_{34}$  alkanes turned insignificant.

In the aqua bitumenoids obtained after thermostating the oil with the fluids (Fig. 2b), an increase in the concentration of  $C_{26}$ – $C_{34}$  alkanes and a decrease in the proportion of their  $C_{10}$ – $C_{15}$  homologues to trace amounts were observed. These changes can be due to the increased solubility of the higher hydrocarbons in aqueous systems at a high temperature and to the presence of surfactants [14, 16, 17]. A similar distribution pattern was observed for the other identified hydrocarbons, for example, alkylcyclohexanes. The composition of alkylcyclohexanes (CH) in aqua bitumenoids after the thermostating of both the oil–water and the oil–fluid systems turned to be narrower than that in the initial oil. In the crude oil, alkylcyclohexanes are represented by  $C_{12}$ – $C_{32}$  homologues with a maximum at  $C_{23}$ .

It was found that the aqueous phase does not contain the low-molecular-weight portion and the mixture of alkylcyclohexanes includes only  $C_{18}$ – $C_{28}$  homologues, of which  $C_{21}$  prevails. Among the polycyclic compounds identified in the highest concentrations in crude oil, there are hopanes, steranes, and aromatic hydrocarbons (bi- and triarenes), all of these compounds are transferable to the aqueous phase, although in smaller quantities. The compounds transferred in maximum amounts to the aqueous phase were hopanes and steranes in the presence of Neftenol VVD and bi- and triarenes in the presence of Neonol NP-50.

In addition to the aforementioned influence of the oil displacement fluids containing various types of surfactants, the distribution of hydrocarbons in the oil–aqueous phase system is also determined by the properties and composition of the test oil. Chuikina et al. [14] studied the effect of composite oil displacement agents on the hydrocarbon distribution by thermostating the oil–aqueous phase system using Maiskoe

**Table 4.** Amount of hydrocarbons in aqua bitumenoid after oil thermostating with water and oil displacement fluids

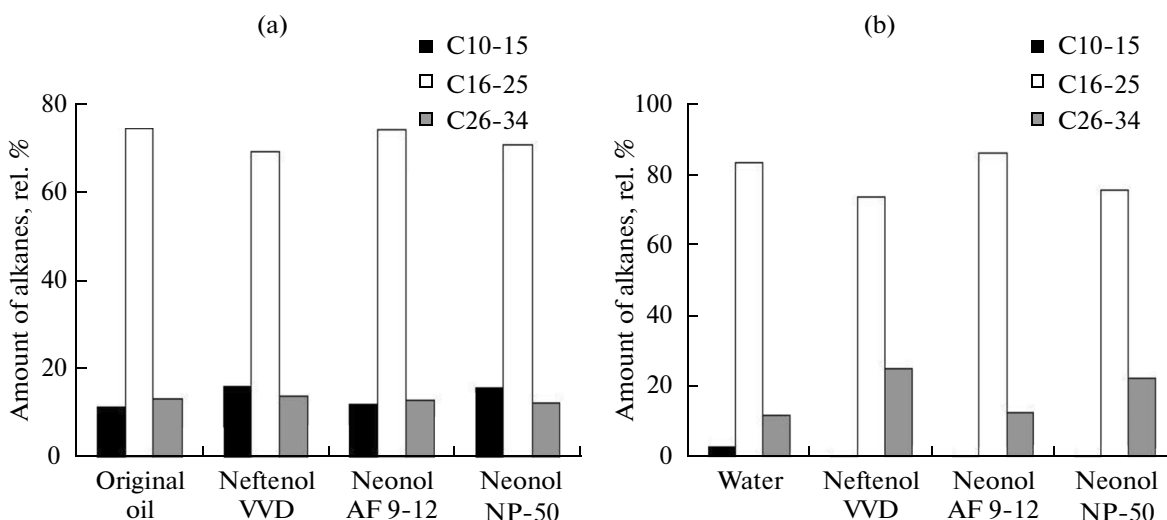
Hydrocarbons	Control 3	Surfactant in fluid		
		Neftenol VVD	Neonol AF 9-12	Neonol NP-50
	amount of hydrocarbons, rel. %			
Alkanes	93.92	91.44	91.99	91.50
Monocyclanes (alkylcyclohexanes)	3.79	5.35	4.30	4.04
Tetracyclanes (steranes)	0.05	0.62	0.15	0.17
Pentacyclanes (hopanes)	0.44	1.08	0.32	0.40
Monoarenes (alkylbenzenes)	0.55	0.56	0.83	1.27
Biarenes (naphthalenes, biphenyls)	Traces	0.03	0.05	0.06
Triarenes (phenanthrenes, retene, fluorenes)	0.95	2.31	2.47	3.08
Tetraarenes (pyrenes, chrysenes, fluoranthenes, benzantracenes)	0.01	0.00	0.02	0.23

crude oil (Western Siberia), which is a high-paraffin, low-resin oil and has a lower density and lower viscosity compared with Zuunbayan oil (Mongolia). Unlike the Mongolian oil, oil from the Maiskoe field was characterized by reduction in the alkylcyclohexane content in the oil phase and an increase in the proportion of alkanes, of which the  $C_{10}$ – $C_{15}$  and  $C_{16}$ – $C_{25}$  homologues prevailed in almost identical amounts. As in the case of Mongolian oil, changes in the concentration of higher  $C_{26}$ – $C_{34}$  alkanes were negligible for the Maiskoe oil and the amounts of naphthenic and aromatic hydrocarbons, which make up a small fraction of all identified compounds, also changed insignificantly.

It was found that the concentration of naphthenic and aromatic hydrocarbons in the aqueous phases contacted with the Maiskoe oil increased and the pro-

portion of alkanes, of which the  $C_{16}$ – $C_{25}$  homologues significantly prevailed, decreased as in the case of Mongolian oil. In contrast to the Mongolian oil, the presence of the agents in the aqueous phase contacting with the high-paraffin, lighter, low-resin Maiskoe oil promotes the increase in the concentration of lower  $C_{10}$ – $C_{15}$  alkanes and the reduction in the proportion of the  $C_{26}$ – $C_{34}$  homologues.

Thus, the analysis of the products of thermostating of the oil–fluid (oil–water) system under laboratory conditions simulating the reservoir conditions showed that changes in the hydrocarbon composition of the oil and aqueous phases depend on both the type of the surfactant used in the fluid and the type of oil. The interaction of both high-viscosity paraffinic oils and light low-resin oils with oil-displacement fluids alters the pattern of partition of hydrocarbons between the

**Fig. 2.** Distribution of normal alkanes in (a) the oil phase and (b) the water phase after oil thermostating with water and surfactant-containing fluids.

oil and aqueous phases. In the oil phase, the concentration of alkylcyclohexanes; tri-, tetra-, and pentacyclanes; and mono and biaromatic compounds slightly increased, especially when the composite surfactant Neftenol VVD was used. The amount of petroleum components transferred from the oil to the aqueous phase in the presence of the fluids is greater than in the control experiments, with the most profound effect being in the case of the Neftenol VVD composition. The alkanes and cyclohexanes in the aqueous phase, as in the oil, are dominated by the  $C_{16}$ – $C_{25}$  homologues, however, the presence of the fluids in the reaction medium causes a decrease in the proportion of the lower homologues  $C_{10}$ – $C_{15}$  and an increase in the amounts of the higher,  $C_{26}$ – $C_{34}$  alkanes, in contrast to the oil phase. The maximum concentration of hopanes and steranes in the aqueous phase was found in the presence of Neftenol VVD, and the concentration of bi- and triarenes was high in the presence of Neonol NP-50.

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