EFFECT OF SURFACTANTS ON THE STRUCTURE OF DISPERSE SYSTEMS OF HIGH-VISCOSITY OILS

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The results of studies of the effect of group and hydrocarbon composition of oils on their physicochemical properties and capacity to form cross-linked oil disperse systems (ODS) are reported. Pulsed nuclear magnetic resonance (NMR) method was used to determine the molecular mobility of the components of the dispersion medium and the disperse phase and to establish a correlation between the structural-dynamic, physicochemical, and rheological properties of the ODS. The degree of effect of surfactants on the change in mobility of the phases of the ODS and their rheological behavior is determined. It is shown that the processes of breakdown of associates of complex structural units of ODS in the presence of a surfactant occur in all oils and water-oil emulsions and their effect on the mobility of ODS increases with increase of initial degree of cross-linking of the ODS. The mechanism of the action of polyalkylbenzene resin (PABR) in the oil medium stems from the peculiarities of its structure, and addition of PABR enhances molecular mobility of the ODS components and alters their solvation, structural-mechanical, and adsorptive properties.
Keywords: heavy oil, oil disperse systems, rheological properties of oil, NMR.

The key to solving the problems of enhancing oil recovery, and preparation and transportation of heavy high-viscosity oils is a complex effect on the structural and mechanical properties of the oil disperse system (ODS) in conjunction with the processes occurring at the phase boundary interface. High viscosity of

oils, high adsorption capacity of group components, and complexity of the generated ODS require finding effective technological solutions that could be applied in a complex for all field development stages. Such an approach should be based on the study of mechanisms of action of chemical reagents on colloid-chemical properties and structure of the oil disperse systems formed by highly viscous heavy oils.

The colloid-chemical approach to the structure of oil systems, considering oil as a disperse system, allows one to determine its basic components that play a crucial role in the processes of dispersion, phase formation, and cross-linking. For high-viscosity oils with a high content of resin-asphaltene compounds (RAC) the formation of cross-linked systems is particularly characteristic, the core of which are asphaltenes, while the resins form the solvation shell [1-3]. The presence of associated structures of asphaltenes and resins has a significant impact on production and transportation of high-viscosity oils.

To determine the effect of the group and hydrocarbon composition of oils on their physicochemical properties and the ability to form cross-linked ODS, heavy oils were investigated from wells of different fields with a high content of resin-asphaltene compounds, and the ratios characterizing the stability of the disperse structure were determined (Table 1).

It is expected that the smaller the value of the ratios O/RAC and HC/RAC, the more resistant to degradation is the disperse oil system. While for the majority of the investigated objects the content ratio of light fractions to resin-asphaltene compounds is approximately the same and is close to unity, for oil from well No. 655 of the Stepnozerskoye oil field the O/RAC ratio is minimal, which suggests a high content of resin-asphaltene compounds and asphaltenes within its composition. This leads to the conclusion that the asphaltene core of a structural unit of this oil contains the thinnest solvation shell made of resins.

The composition and structure of petroleum systems were studied by pulsed NMR [4], which allows one to study the oil system without disturbing its colloidal structure, examine the parameters of molecular motion, structural ordering, and phase transitions. The present study was conducted based on the theory and methodology described in [4].

The main parameters for the study of the ODS are the spin-spin T_2 and the spin-lattice T_1 relaxation times characterizing the translational and rotational diffusion of the system components.

Temperature dependences of the spin-spin relaxation times of the investigated oils (Fig. 1) indicate the presence in the ODS of at least two phases with different molecular mobility of components. The first phase, characterized by the longest spin-spin relaxation time, can be attributed to the molecules of the dispersion medium. The second phase with a shorter relaxation time corresponds to the disperse phase. The change in temperature affects the molecular mobility of the oil system components: the sharpest increase in relaxation time is observed for the dispersion medium – Phase A, which includes light and medium crude oil hydrocarbons and oil components characterized by translational and rotational diffusion. The disperse phase formed by the heavy oils and resins is less mobile.

Comparison of the pulsed NMR data and structural-group analysis lead to the following conclusion: an increase in the content of resins and asphaltenes reduces the molecular mobility of the ODS components resulting in a sharp decrease in T_2 relaxation times. The decisive role in the formation of the structural skeleton of oil belongs to asphaltene particles [5, 6], which form the core of a complex structural unit, and to components of alcohol-benzene resins, which comprise the boundary layer. The disperse phase determines the strength of the spatial structure and affects the rheological behavior of oils at low shear rates, and the composition of the dispersion medium determines the viscosity properties in general. Thus, the spin-spin relaxation time is an important rheological parameter – Fig. 2 shows that the dynamic viscosities of oils from different fields decrease with increasing relaxation time.

Table 1

Indices	Oil				
	Stepnoozerskaya, well No. 655	Stepnoozerskaya, well No.636	Zyuzeevskaya, well No. 962	Bureykinskaya, well No 4121	Demkinskaya, well No. 962
Density, g/cm^3	0.933	0.925	0.924	0.924	0.921
Dynamic viscosity at 20 °C, mPa·s	765	130	389	312	216
Water content, wt. %	0.14	0.31	0.18	trace	0.09
Pour point, °C	**-10.0**	-24.2	-17.2	-17.0	-6.4
Content, wt. %:					
IBP–200 °C	14.86	19.21	13.65	26.76	16.53
oils (O)	39.14	42.80	43.85	36.46	40.43
benzene resins	27.17	22.41	29.81	23.02	27.25
alcohol-benzene resins (R_{al-b})	11.60	7.07	8.49	7.61	10.63
asphaltenes (A)	7.22	8.52	4.21	6.14	5.15
Total sulfur, wt. %	4.63	4.02	4.00	3.83	3.83
O/RAC	0.85	1.13	1.03	0.99	0.94
HC/RAC	1.17	1.63	1.35	1.72	1.32
O/R_{al-b}	3.37	6.05	5.16	4.79	3.80
HC/R_{al-b}	4.66	8.77	6.76	8.31	5.36
A/RAC	0.16	0.22	0.10	0.17	0.12
R/A	5.37	3.46	9.12	4.99	7.36

Note.   HC – total fraction of low-boiling – 200 °C hydrocarbons and oils, R – total fraction of resins.

The tendency to cross-linking and formation of highly concentrated disperse systems affects the efficiency of production, transportation, and processing of high-viscosity oils [7, 8]. Their structural and mechanical properties may be manipulated through destruction of complex structural units of the ODS or changes in the nature and strength of intermolecular interactions. Surfactants, having high adsorption properties, play an important role in these processes. The introduction of surfactant allows one to change phase interactions on different interfacial surfaces and to have a real impact on the processes of structure formation of oils.

Effect of surfactants on the formation of spatial structures of heavy high-viscosity oils and their interaction with each other through dispersion medium layers and the solvation layer were studied by pulsed NMR (Fig. 3). Introduction of the surfactant into the oil system changes intermolecular interactions of both the disperse phase (phase B) and the dispersion medium (Phase A). Polyalkylbenzene resin (PABR) played the most significant role in changing phase mobility of all the studied oils.

It can be assumed that PABR due to its aromatic nucleus penetrates the solvate sheath consisting mainly of resins, and then due to high mobility is incorporated into the structure of complex structural unit cores, but it does not stabilize it, in contrast to asphalt-resinous compounds, but destroys it since the presence
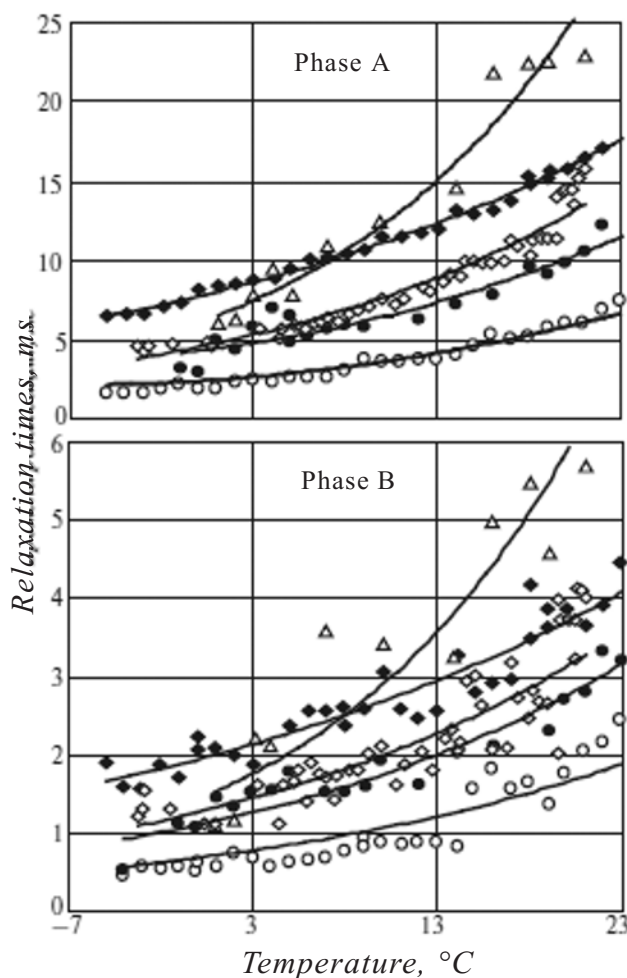

Fig. 1. Spin-spin relaxation times of the ODS as a function of temperature: ○, ♦ – Stepnoozerskaya oil, wells Nos. 655 and 636, respectively; △ – Bureykinskaya oil; ● – Zyuzeevskaya oil; ◊ – Demkinskaya oil.
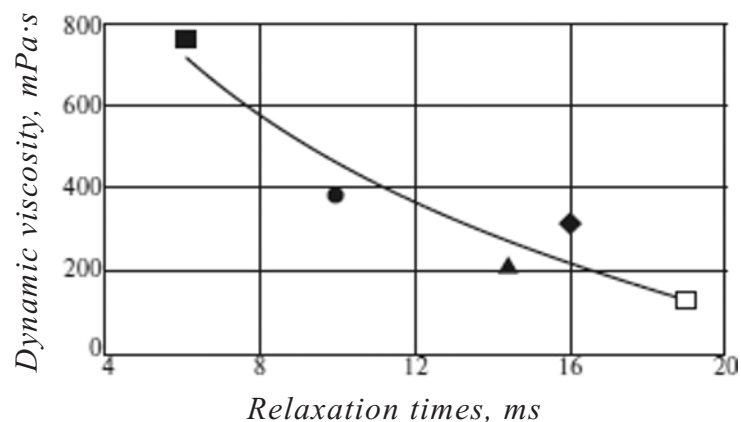
Fig. 2. Dynamic viscosity of oils as a function of relaxation time: ■,□ – Stepnoozerskaya oil, wells Nos. 655 and 636, respectively; ● – Bureykinskaya oil; ◆ – Zyuzeevskaya oil; ▲ – Demkinskaya oil.

of two or more mobile alkyl radicals gives the molecule a so-called "virtual" dipole moment, which, as if spinning the molecule, destroys the plane-parallel formation of the associate. This is evidenced by a stronger increase in molecular mobility of group components of oils in the presence of PABR.

Introduction into the oil system of surfactants (R-4V, ALM-10) contributes to a change in the ratio of "mobile" and "associated" molecules, whereby there is a change in intermolecular interactions, the composition and size of a structural unit, resulting in increasing proton relaxation times. Surfactants penetrate into the structural framework of the disperse oil system destroying it and preventing its restoration [9]. Due to the formation of a new solvate sheath on the surface of macromolecular components of the oil, the latter loses its ability to form associates, which leads to a decrease in structural and mechanical strength of the ODS and the ability to form stable water-oil emulsions. This prevents deposits on pore channel surfaces and oilfield equipment.

The introduction of surfactants also has a significant impact on reducing the viscosity of water-oil emulsions. On the example of oils from the Zyuzeevskoye field it has been shown that the greater the water content in the emulsion, the greater the effect achieved in reducing the viscosity of the system (Fig. 4). For oil from well No. 2365 with a 14.3% water content by weight the decrease in viscosity was 200-250 mPa·s, while for water-free oil from well No. 935 there was a decrease of only 100 mPa·s.

Despite the fact that PABR has no distinct surfactant properties, its role in the mechanism of destruction of the emulsion is based on the change of intermolecular interactions and a change of structural-mechanical properties of high-viscosity oils. The contribution of PABR to the destruction of the associative structure of high-viscosity oils consists in that there is a loosening of the adsorption layer and a reduction of its mechanical strength so that upon collision water globules are capable of coalescence. Therefore, the presence of this component is preferred in composite formulations for breaking oil-water emulsions and reducing oil viscosity [10, 11].

Conclusions:

• High content in oils of asphaltenes, alcohol-benzene and benzene resins, which are the main structure-forming components, leads to the formation of a spatial frame having high mechanical strength, and as a result viscosity of such oils increases significantly.
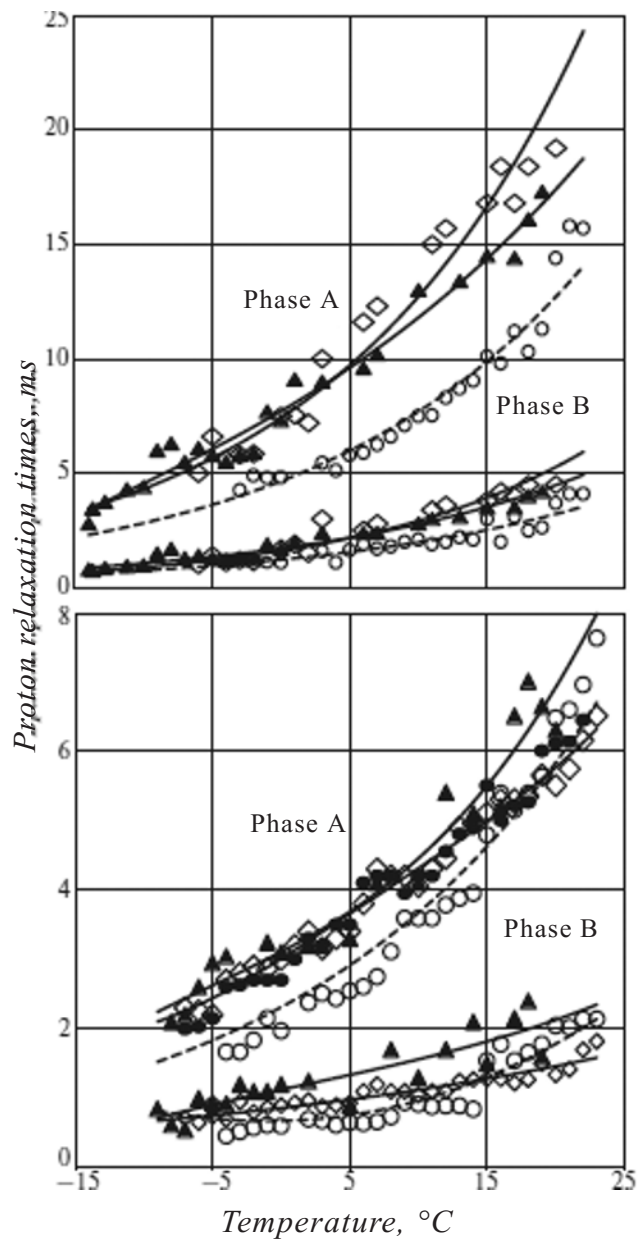
Fig. 3. Changes in the proton relaxation time as a function of temperature under the influence of various reagents: $\circ$ – no reagent; $\lozenge$ – PABR; $\blacktriangle$ – reapon R-4V; $\bullet$ – SYNTANOL ALM-10

• Using NMR and rheological studies it was shown that a collection of surface and bulk properties of surfactants plays a major role in changing the structure of adsorption layers at the interface of the phases in the bulk of the oil. The introduction of surfactants changes the structure of the oil disperse system, its rheological properties, and allows one to set such conditions of the petroleum system in which its transportation and further processing are considerably facilitated.
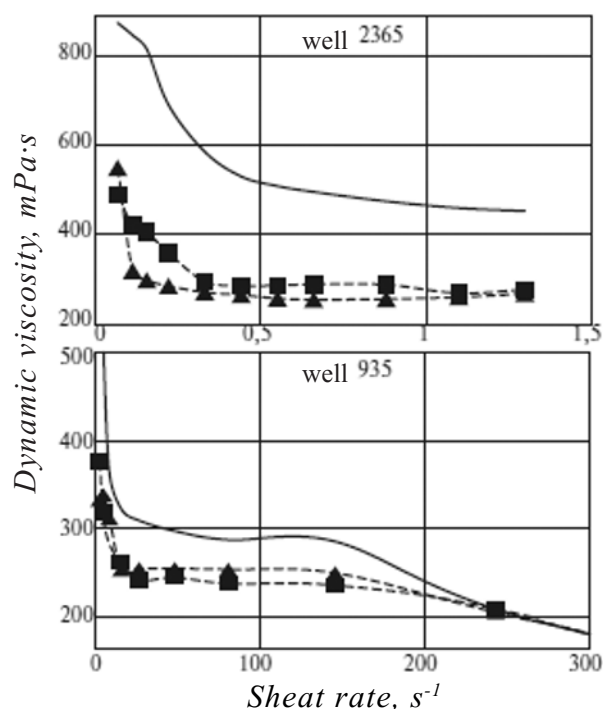
Fig. 4. Dynamic viscosity of Zyuzeevskoye oils as a function of shear rate under the influence of various reagents: solid line – no reagent; ▲– PABR; ■ – SYNTANOL ALM-10 .

• In order to effectively reduce the viscosity of crude oils with a high content of resin-asphaltene substances it is necessary to use solvating action reagents (e.g. polyalkylbenzene resin) that can reduce the strength of the structural frame formed by asphaltenes and components of resins.

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