Structural and Mechanical Properties of Water Oil Emulsions of Highly Viscous Oils

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Abstract. The results of the study of the process of formation of emulsions in high viscosity oils are presented. The effect of the oil composition and the content of the aqueous phase on the microstructure, rheological properties, and activation energy of the viscous flow of oil-water emulsions are shown. Based on the analysis of the group composition of oils and the intermediate layer formed during the separation of emulsions, an increase in the mass fraction of benzene, alcohol-benzene resins, and asphaltenes in the intermediate layer is established.

1. Introduction
High-viscosity oils form emulsions that are difficult to break. The stability of oil-water emulsions is determined by the amount and composition of surfactants called emulsifiers [1, 2]. These include asphaltenes, resins, salts of naphthenic acids and heavy metals, mechanical impurities, paraffin microcrystals. These substances, adsorbed at the phase boundary, form adsorption membranes with high structural viscosity on the droplets of the dispersed phase. The adsorption sheaths prevent coalescence [3-5]. Significant differences in the quantitative and qualitative composition of the main emulsifying components in oils are reflected in the process of emulsion formation, its stability and structural and mechanical properties [6, 7].

It is known that physicochemical and structural-rheological properties of disperse oil systems are determined by the structure, size and composition of complex structural units resulted from the association of resin-asphaltene components [8-11]. To date, the nature of the processes of structure formation and their relationship with the rheological properties of oils have not yet been fully elucidated, and this explains the lack of sufficient clarity regarding the regulation of the rheological properties of high-viscosity oils and water-oil emulsions under conditions of production, transportation, and storage.

The separation of oil-water emulsions of heavy oils forming highly stable intermediate layers is one of the urgent problems in the preparation of high-viscosity oils. The introduction of new technologies for the breakdown of stable oil-water emulsions requires the development of a science-based approach based on in-depth knowledge of the formation of the structure of the intermediate layer depending on the content and composition of the oil phase.

The purpose of the work was to study the structural and mechanical properties of water-oil emulsions of 3 high-viscosity oil wells of the Usinskoye oilfield, depending on the water content and natural oil emulsifiers.
2. Experimental section

Model water/oil emulsions were prepared using a PE-00118 150-W agitator at a blade rotation speed of 1500 rpm for 10 min. As the dispersed phase for the emulsions, produced water (pH 6.8-7.0, mineralization 86.5 mg/L) was used.

The separation of the intermediate layer (i/l) from the water and oil phases was carried out using a separatory funnel. The intermediate layer was centrifuged to isolate the organic component.

Isolation of asphaltenes was carried out by the ‘cold’ Golde method. The content of saturated (SHs) and aromatic hydrocarbons (АHs), benzene (BR) and alcohol-benzene (ABR) resins in oil and in the intermediate layer was determined by column liquid adsorption chromatography. The mass fraction of paraffin hydrocarbons was determined by the method of urea complexation.

The dispersion of oil-water emulsions was evaluated by optical microscopy. Microphotographs of the samples were taken using an Axio Lab A1 biological microscope (Carl Zeiss) equipped with an Axiocam ERc 5s digital camera.

The rheological parameters of initial oils and emulsions were analyzed using a Brookfield LVDV-III Ultra rotational viscometer. The Arrhenius-Frenkel-Eyring equation was used to determine the activation energy of a viscous flow

\[ \eta = A \cdot \exp \left( \frac{E}{RT} \right), \]

where \( \eta \) is the effective viscosity; \( A \) is the preexponential coefficient, including in a latent form the dependence of viscosity on other parameters of the structure, in particular molecular weight; \( E \) is the activation energy of the viscous flow process, representing the energy barrier of the fluctuation transition process; \( R \) is the universal gas constant; and \( T \) is the absolute temperature. The activation energy of the viscous flow \( E_{act} \) was determined as the angular coefficient of the linear dependence of the effective viscosity on temperature in the coordinates \( \ln(\eta) = f(T) \), and that for nonlinear dependences was determined by the slope of the selected linear sections or tangent to the curve.

3. Results and Discussion

The oil from the Usinskoye oilfield is heavy oil. In Table 1 are presented the physico-chemical characteristics of the oil sampled from different wells of the Usinskoye oilfield. The highest viscosity and density is exhibited by the oil from well No. 3

| Sample from the well No. | Density, kg/m³ | Viscosity, mPa·s | T_r, °C |
|--------------------------|----------------|------------------|--------|
|                          |                | 20 °C            |        |
| 1                        | 959            | 4800             | - 17.0 |
| 2                        | 932            | 5850             | - 20.0 |
| 3                        | 972            | 8840             | - 14.5 |

Emulsions formed on the basis of oil from the Usinskoye oilfield are characterized by high stability. Hence, they do not broken for a long time after formation. The main factors determining the stability of oil-water emulsions are dispersion, viscosity, electrical properties, concentration, and type of natural emulsifiers [1].

In figure 1 there are microphotographs of 10% and 50% emulsions of oil sample from the well No. 1. The average sizes of water globules (d_v) and dispersion (D) of all emulsions under study were calculated from microphotographs.
Figure 1. Microphotographs of 10% (a) and 50% (b) emulsions of the oil from the well No. 1

In Table 2 we gave the average sizes of water globules in emulsions with different water contents. Globules of the lowest diameter and a higher degree of dispersion are formed in the 10% emulsion of oil sampled from the well No. 3. With an increase in the percentage of the aqueous phase up to 50%, an increase in the average droplet diameter by 2.5 times and, accordingly, a decrease in dispersion (D) are observed in the composition of emulsion.

Table 2. Average diameter of water droplets and dispersability of water-oil emulsions

| Sample from the well No. | 10% emulsion | 50% emulsion |
|-------------------------|--------------|--------------|
|                         | $D_{av}$, μm | $D$, μm$^{-1}$ | $D_{av}$, μm | $D$, μm$^{-1}$ |
| 1                       | 6.5          | 0.15         | 16           | 0.06          |
| 2                       | 5.0          | 0.20         | 13           | 0.08          |
| 3                       | 2.0          | 0.50         | 11           | 0.09          |

The features of the formation of supramolecular structures in oils and the strength of bonds in associative complexes were evaluated from viscosity-temperature dependences. It is shown in figure 2 that the viscosity of oil sampled from the well No. 3, which is characterized by the maximum viscosity values among the objects under study and the viscosity of 10% emulsion decreases monotonically in the temperature range from +20 to +50 °C. This is determined by the size of associative structural units. With a decrease in temperature to +10 °C, the viscosity of the objects under study increased by 3 times.

Figure 2. Temperature-viscosity curves for oil from the well No. 3 and emulsions at a shear rate of 9 s$^{-1}$: 1 – oil; 2 – 10% emulsion; 3 – 50% emulsion
In the case of a 50% content of the aqueous phase, the viscosity of the emulsions increases 4-5 times within the range of shear rates and temperatures compared to dry crude oil. The heating of oil and emulsions to 40-50 °C has a significant effect on viscosity, the values of which in this temperature range are reduced and become little dependent on shear load.

Based on the results of rheological measurements, the energies of activation of the viscous flow (Eact) were calculated. In Table 3 are given the values of effective viscosity at a shear rate 9 s\(^{-1}\) and the activation energy of a viscous flow for oils and emulsions. The increase in the viscosity of emulsions formed by the oil from the well No. 3 is the most critical. The droplets of emulsions formed on the basis of this oil are of a smaller diameter in comparison with the emulsions based on oil from other wells.

The graphical dependence of \(\ln(\eta)\) on \(1/T\) in the temperature range from +10 to \(+50\) °C for high resin oils and emulsions is presented as a linear function, which suggests the constancy of structural parameters of the oil system and the absence of phase transitions in the above mentioned temperature range. The bond strength in associative complexes in each structural state corresponding to a certain temperature is characterized by the heat of activation of the viscous flow Eact. The values of Eact for 3 oil wells of the Usinskoye oilfield are 41.4 - 68.5 kJ/mol (Table 3).

| No. | Oil | 10% emulsion | 50% emulsion |
|-----|-----|--------------|--------------|
|     | \(\eta, \text{Pa}\cdot\text{s}\) | Eact, kJ/mol | \(\eta, \text{Pa}\cdot\text{s}\) | Eact, kJ/mol | \(\eta, \text{Pa}\cdot\text{s}\) | Eact, kJ/mol |
| 1   | 3.8 | 41.4         | 4.2          | 56.3         | 10.1         | 32.2         |
| 2   | 4.3 | 45.3         | 4.9          | 61.5         | 12.5         | 40.7         |
| 3   | 5.8 | 68.5         | 7.5          | 81.0         | 28.0         | 64.9         |

The maximum activation energy is characteristic of the oil sampled from the well No. 3. Introduction of water to the oil system up to 10% leads to an increase in Eact values by 16-27% compared to Eact of oil, which indicates to an increase in intermolecular interactions and an increase in the degree of the system associativity due to the formation of adsorption (solvation) sheaths consisting of resin-asphaltene components at the oil-water interface.

With a further increase in water cut to 50%, the Eact values decrease relative to the Eact of the 10%-th emulsion and oil. This is due to a significant decrease in the proportion of the oil phase in the composition of emulsion and in the content of emulsifying components, which is accompanied by a decrease in the strength of the formed associative combinations.

To assess the role of the dispersed phase in the formation of emulsions, the group composition of oils and intermediate layer of 10% emulsions was analyzed (Table 4). The formation of an intermediate layer during the separation of the emulsion is the result of incomplete destruction of the armor shells on droplets of emulsified water in oil during the retarded coalescence and fall of these drops.

Analysis of the group composition revealed that the Usinsk oil can be classified as a low-paraffin containing 1.8-2.1 wt% of solid paraffin hydrocarbons and highly resinous oil. The content of asphaltenes (A) in the oil of the Usinskoye oilfield sampled from various wells is approximately the same and amounts to 7.0 - 7.7 wt %.

The total mass fraction of benzene (BR) and alcohol-benzene resins (ABR) varies significantly: 12.6 wt % in the well No. 1 and 22.1 wt % in the well No. 3. The largest amount of resin-asphaltene components was found in the oil from the well No. 3, which explains its high density and viscosity. The proportions of saturated (SHs) and aromatic hydrocarbons (AHs) are the highest in the well No. 1.
Table 4. Composition of the oil from the Usinskoye oilfield and that of intermediate layers of oil-water emulsions

| Sample                  | n-alkanes | SHs | AHs | BR | ABR | A  |
|-------------------------|-----------|-----|-----|----|-----|----|
| Well 1                  | 1.9       | 61.5| 17.0| 5.4| 7.2 | 7.0|
| i/l of the well 1       | 1.2       | 51.1| 15.0| 10.3| 13.5| 8.9|
| well 2                  | 1.8       | 56.9| 18.0| 6.3 | 9.3 | 7.7|
| i/l of the well 2       | 1.5       | 45.0| 17.4| 9.3 | 15.3| 9.3|
| well 3                  | 2.1       | 52.6| 15.6| 9.5 | 12.6| 7.6|
| i/l of the well 3       | 1.9       | 47.4| 13.3| 11.2| 16.4| 9.8|

It is evident from Table 4 that an increase in the content of resin-asphaltene components is observed in the group composition of the intermediate layers isolated from 10% oil-water emulsions. Hence, the content of asphaltenes has increased by 18 - 23% and that of alcohol-benzene and benzene resins by 20 - 50%. The maximum increase in resin-asphaltene components reaching 70% was observed in the intermediate layer of emulsion of oil from the well No. 1, which was due to the increase in the proportion of resins.

4. Conclusion
By the example of similar in oil composition and physicochemical properties high-viscosity oil sampled from three wells at the Usinskoye oilfield, it has been shown that the stability of the emulsion and the strength of supramolecular structures depend on the component composition of the oil. The appearance of water in the oil from the well 1 containing the smallest amount of resin-asphaltene components compared to other wells leads to a significant increase in the proportion of resins in the composition of the intermediate layer. Moreover, 10% emulsions formed from this oil are characterized by minimum viscosity values and a maximum average droplet diameter. The increase in the proportion of resins and asphaltenes in the oil well 3 leads to the formation of emulsions characterized by higher values of the activation energy of viscous flow and viscosity, which is indicative of the formation of more stable supramolecular systems in the objects under study. At the same time, a high content of resin-asphaltene components promotes the formation of emulsions with a minimum droplet diameter in comparison with other emulsions based on oil sampled from the wells 1 and 2.

References
[1] Wong S F, Lim J S and Dol S S 2015 J. Petrol. Sci. Eng. 135 498
[2] Mousavi M, Abdollahi T, Pahlavan F and Fini El. H. 2016 Fuel 183 262
[3] Shi Ch, Zhang L, Xie L, Lu X, Liu Q, He J, Mantilla C A, Van den berg F G and Zeng H 2017 Langmuir 33 1265
[4] Speight J G J. 1999 J. Petrol. Sci. Eng. 22 (1-3) 3
[5] Speiecker M, Gawrys K L, Trail C B and Kilpatrick P K 2003 Colloids and Surf., A 220 9
[6] Nebogina N A, Prozorova I V, Yudina N V and Savinykh Yu V 2010 Petroleum Chemistry 50 (2) 158
[7] Sullivan A P, Zaki N N, Sjöblom J and Kilpatrick P K 2007 Can. J. Chem. Eng. 85 (6) 793
[8] Peralta-Martinez M V, Arriola-Madelin A, Manzanares-Papayanopoulos E, Sanchez-Sanchez R and Palacios-Lozano E M 2004 Petroleum Science and Technology 22 (7-8) 1035
[9] Evdokimov I N, Eliseev N Yu and Eliseev D Yu 2004 Fuel 83 (7-8) 897
[10] Loskutova Y V, Yudina N V, Volkova G I and Anufriev R V 2017 International Journal of Applied and Basic Research 10-2 221.
[11] Volkova G I and Yudina N V 2017 South Siberian Scientific Bulletin 4 (20) 282