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Effect of Composition and Interfacial Tension on the Rheology and Morphology of Heavy Oil-In-Water Emulsions

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ABSTRACT: Rheological and morphological properties of heavy crude oil-in-water (O/W) emulsions have been studied. Two series of emulsions were considered: first, the surfactant type remained constant, while the continuous phase content was varied and second, the surfactant type was varied while the continuous phase content remained constant. Under stress-controlled shearing, all samples exhibit viscoplastic behavior. The rheological properties are directly related to the morphology of the emulsions which vary in size of dispersed phase droplets and their inherent structure. Adding a surfactant characterized by a high value of interfacial oil—water tension results in a decrease in the yield stress (which is a measure of the interparticulate structure strength). The same effect is attained by increasing the water content. Meanwhile, these two factors determine the viscosity which can be much lower than that of the basic heavy crude oil if the O/W type of emulsions has been created. Special attention was paid to the viscoelastic properties which have been scarcely reported. Correlations were found between the surfactant properties, composition of the emulsion, and rheological characteristics of emulsions (yield stress, apparent viscosity, and viscoelastic properties), which allows for reduction in the crude oil viscosity down to a low enough level acceptable for pipe transportation.

1. INTRODUCTION

The global pipeline network runs to more than 1 million km, and approximately, three-quarters are utilized for crude oil transportation. An inevitable transition to unconventional petroleum resources is being caused by the depletion of light crude oil for which the existing pipeline system was constructed and built. It seems highly unlikely that other transportation methods will be applied instead of pipelines because the latter are the most convenient, cheap, and environmentally friendly means to transport oil from a field to refineries. The transport-related properties of oils are directly determined by their viscosity which is determined by the content of heavy fractions (asphaltenes and resins).¹⁻⁴ In addition, these components promote the formation of water-in-oil (W/O) emulsions. The W/O emulsions appear spontaneously, for instance, during offshore petroleum production. Emulsions of this type with brine as a dispersed phase are widely highlighted in the literature.⁵⁻⁷ The formation of W/O emulsions leads to high viscosity which makes the transportation of these unconventional oil resources challenging.^{8–10}

Hence, there is a global problem in reducing the heavy crude oil (HCO) viscosity. The modern classification of the viscosity reduction methods is formulated in ref 10. The most evident

method is heating: an increase in temperature results in viscosity decrease. This method allows for reducing viscosity up to several orders though the cost of this operation can be unacceptably high. Then, one of the most popular methods is dilution with low viscous hydrocarbons and light oil, in particular. This approach is reasonable in practice if these sources are located relatively close to each other. It is necessary to mention the partial upgrading method, which belongs to the enhanced oil recovery (EOR-methods) and allows for deeper oil extraction. It consists of transition of high molecular-weight components (asphaltenes and resins) into lighter hydrocarbons through thermal or catalytic reactions, thus leading to viscosity decrease. The lubricated transportation (by addition of water) and core annular flow (is close to the latter by the mechanical nature) consist of creation of the low-viscous near-wall layer. This layer

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provides higher shear rates in comparison with viscous fluids and leads to the increase of the net flow stream at the same pressure.

The method of creation oil-in-water emulsions is one of the oldest and still one of the most promising because of the possibility of varying the emulsion structure and thus viscosity.^{11,12} Emulsification with water as a continuous phase can be also attributed to the methods of lubricated transportation. So far, its major application has been found in Venezuela (ORIMULSION). Nevertheless, the interest toward this method has not faded up so far.

Emulsification consists of the formation of micron size oil droplets dispersed in water. A significant viscosity drop can be reached only when the water acts as a continuous phase. From the economic point of view, the oil concentration should be as high as possible, but at an oil concentration of ca. 70–80 vol %, a phase inversion occurs.^{13–15} Conditions of the phase inversion should be predicted to avoid this undesirable phenomena during transportation. Indeed, the formation of W/O emulsions is undesirable as their viscosity is usually higher than that of the HCO itself.

The phase inversion of oil-in-brine emulsions was found to be related to the surfactant depletion from the aqueous phase.¹⁶ Conditions of the phase inversion for the oil-based emulsions have been discussed in the Salager's reviews.^{17,18}

Meanwhile, there is a definite difficulty in dealing with O/W emulsions, which is due to their instability. The discussed systems belong to so-called macroemulsions (the typical droplet size lies in the range from 1 to 100 μ m), and they are rather sensitive to gravity-induced creaming. Hence, the technological issue is to create a stable colloidal system for transportation which can be easily decomposed in the refinery. The dispersed phase in the O/W emulsion can be also of a submicron size. A thorough investigation of the nanoemulsions including selection of the surfactants with ultra-low interfacial tension values and the stability of such systems can be found in ref 19.

A lot of latest publications are devoted to the investigation of the in situ formed O/W or W/O/W emulsions regarding the EOR. Yu et al.²⁰ evaluated the properties of the emulsions with weak and strong emulsifying agents generated during the surfactant flooding. The viscosity reduction via in situ emulsification was also studied in ref 21. The authors showed that the O/W emulsion undergoes a decrease in the droplet size while migrating through the porous media. The same effect could be reached by the increasing the surfactant content in the surfactant-polymer system. The mechanisms of the in situ O/ W emulsion propagation and plugging in pore and macro scale were investigated in ref 22. The effectiveness of the emulsion flooding compared to the conventional water flooding for Iranian oil reservoir is highlighted by Yazdani Sadati et al.²³ The appliance of the viscosity reducer in the steam flooding process leads to the synergistic effect shown in ref 24.

The search of the most suitable emulsifying systems remains important. There is a certain division in this field, such as

- commercial synthetic surfactants. For example, in the recent work,²⁵ Span 60 and Tween 80 mixed with NaOH and used for the O/W emulsification showed 99% permeability reduction in sandpack flow tests.
- New polymers with amphiphilic properties.²⁶
- Surfactant-nanoparticle systems. The majority of researchers used silica particles.^{27,28} An interesting example of silica nanoparticles with a grafted polymer

allowed the authors to reversibly stabilize, recover, and break O/W emulsions via pH variation.²⁹

- Surfactant-polymer (see, for instance ref^{21,30,31}).
- Surfactant-polymer-nanoparticle systems. The latter system was synthesized on the basis of silica nanoparticle and implemented for the O/W emulsion stabilization in ref 32. The comparison of the chemical injection of the surfactant-polymer-nanoparticle fluid to the water flooding proved to extract more than 25% of oil.

The appliance of surfactants is needed to prevent coalescence and phase separation¹² despite the fact that HCO contains natural surfactants (asphaltenes, naphthenic acids, resins, porphyrins, etc.). Asphaltenes in the HCO cause main technological problems with its extraction, transportation, and further processing. There is still lack in understanding the behavior of this class of compounds, so they are subject to the most intensive studies. For example, recent work³³ highlights asphaltene chemical modification as a way of preventing their aggregation, thus causing viscosity reduction. Another interesting matter concerns the asphaltene behavior at the interface layer. It can be achieved by means of interfacial rheology, as presented in ref 34. Stability of the asphaltene aggregates and conditions of their disaggregation are the other important technological and fundamental issues. The presence of emulsified water was found to be a factor influencing the stability of asphaltenes. The authors of ref 35 investigated the matter on several samples of crude and model oils and suggested a technique to evaluate the effect of water on asphaltene stability valid at different temperatures and ambient pressure.

The presence of a surfactant also affects the emulsion type. It has been shown that the addition of 20 wt % water, alone, leads to a twofold increase in the viscosity as compared with the oil and emulsion remains of the W/O type.³⁶ In contrast, the viscosity of an emulsion with 20 wt % water and an anionic surfactant can be many times less than that of a sample without a surfactant, and this is an O/W emulsion. The formation of multiple emulsions (e.g., W/O/W) can create a challenge at the technological stage of the W/O emulsion separation.³⁷ Breakage of the formed emulsions is the main goal of many research studies.^{38–40}

Rheological properties of the O/W emulsions have been widely studied to evaluate the effect of various factors on the viscosity, for example, type and concentration of the surfactant, the content of the dispersed phase, processing factors, temperature, and composition of the aqueous phase (see, for example ref^{14,41,42}).

The rheological behavior of the O/W emulsions also depends on the ratio between the oil and water and droplet size distribution. It was shown in ref 43 that the emulsions under study behaved as Newtonian fluids when the dispersed phase concentration did not exceed 60 vol %. More concentrated samples exhibited shear-thinning behavior, and the viscosity strongly depended on the droplet size. The shear-thinning is typical for O/W emulsions of moderate concentrated emulsions.^{47–46} while yield effect is often observed for concentrated emulsions.⁴⁷ In overall the behavior of the oil-based emulsions mainly depends on the crude oil rheology as it can exhibit Newtonian^{45,48} or non-Newtonian flow.^{49–51}

The goal of this study was to find correlations between the physicochemical properties of surfactants illustrated by the interface tension (IFT) and hydrophilic–lipophilic balance (HLB) values, the emulsion composition, and the rheological

parameters (the viscosity and yield stress values) of these heavy oil-based colloidal systems. Special attention is paid to the viscoelasticity of the emulsions which has usually been omitted from the studies of crude oil emulsions but can be rather informative in discussing the structure of emulsions.

2. EXPERIMENTAL SECTION

2.1. Materials. *2.1.1. Heavy Crude Oil.* The basic object of our studies HCO was obtained from the Yarega oilfield (Ukhta, Komi region, Russia). The crude oil density was 944 kg/m³ at 20 °C, which corresponds to 19.5 API. The surface tension was 33.4 mN/m (at 21 °C). The oil composition was determined by liquid absorption chromatography and gas chromatography—mass spectrometry (GC–MS). The results are presented in Supporting Information, Tables S1 and S2, respectively. The detailed description of the analysis procedure can be found elsewhere.⁵²

2.1.2. O/W Emulsions Composition. Two series of emulsions were prepared using the double distilled water with IFT equal to 72.8 mN/m at 20 °C and conductivity not exceeding 1 μ S/cm. In the first series (S1), only one surfactant (Triton X-114, Fisher Chemical) was used and the continuous phase (aqueous solution) content was varied from 25 to 40 vol %. The concentration range was limited, on the one hand, by emulsion stability, and on the other hand, by phase inversion. The composition of the emulsions and designations of the samples are shown in Table 1. Besides, in order to get stable O/W

Table 1. Composition of the O/W Emulsions with Varying Water Content (Series S1)

		composition of aqueous solution		
sample designation	content of water, %	HEC ^a , wt %	surfactant ^b , wt %	
X1	25	0	5	
X2	25	0.25	5	
X3	30	0.25	5	
X4	40	0.25	5	
^{<i>a</i>} HEC—hydroxyethyl cellulose, viscosity enhancer. ^{<i>b</i>} Triton X-114.				

emulsions with water concentrations higher than 25 vol %, a polymer viscosity enhancer (hydroxyethyl cellulose, HEC, trademark Natrosol 250 HHBR, Ashland) was added.

For the detailed information regarding the selection of the surfactants, the preparation methods, and the emulsions stability, see ref 53.

In the second series (S2), the type of surfactant was varied, while its concentration and the ratio of the continuous to disperse phases were fixed (25/75 vol %). Four pure surfactants and one mixture differing in IFT and HLB values, listed in Table 2, were chosen. The interfacial tension was measured on the boundary between the surfactant solution and air, as well as HCO. In further discussion, under IFT, we will understand the values on the boundary with HCO. The main characteristics of the surfactants used in the work are listed in Supporting Information (Table S3).

2.1.3. Preparation of O/W Emulsions. For the preparation of both series of samples, the surfactant was dissolved in distilled water and then mixed with the crude oil. To obtain stable emulsions with higher water content, a polymer viscosity enhancer was used—a water solution of 0.25 wt % HEC with the later addition of the definite amount of surfactant.

Table 2. Composition of the Aqueous Phase in Emulsions (Series S2) and Their IFT for Both Series^a

		IFT, mN/m	
sample designation	composition of the aqueous phase	with air	with HCO ^a
Т	2.5 wt % Tween 80^b	37.6	8.6
Α	2.5 wt % Syntanol ALM10	32.3	2.3
S	2.5 wt % SLES	33.3	3.9
OS	10 wt % OP-7 + 2.5 wt % SLES (1:1)	32.5	1.5
0	10 wt % OP-7	32.7	0.6 ^c
X1	5 wt % Triton X-114	29.7	0.3 ^c
X2	5 wt % Triton X-114 + 0.25 wt % HEC	30.0	0.1 ^c

"HCO—heavy crude oil. ^bInterpretation of surfactants names—see Table S3 in Supporting Information. ^cThese values lie under the specified limit of the force tensiometer, but due to their reproducibility, they are used in the paper.

The following protocol was used for preparing the O/W emulsions:

- preheating of the definite volumes of the aqueous phase and the oil phase at 60 °C for 30 min;
- adding 100 vol % of the aqueous phase to the oil and emulsifying via the rotational disperser Ultra-Turrax T10 (IKA, Germany) at the lowest speed (8000 rpm at no load) for 1 min;
- subsequent mixing using a magnetic stirrer MR Hei-Tec (Heidolph, Germany) at 60 °C for 45 min;
- final emulsifying using a disperser (like step 2) for 2 min.

The samples containing 30 and 40 vol % of the continuous phase were obtained using different procedures in the final stage. Half of the volume of the aqueous phase was added into the crude oil. Then, the batches were mixed for 1 min in the disperser and for 30 min in the magnetic stirrer. After that, the rest of the aqueous phase was added into the emulsion and then mixed for 15 min in the magnetic stirrer.

The above described protocol allowed for the preparation of emulsions which were stable for months without phase separation.

2.2. Measurements. 2.2.1. Interfacial Tension. The interfacial tension values were measured using a K20 tensiometer (Krüss, Germany) based on the Wilhelmy plate standard method at a temperature of 21 ± 1 °C. To obtain reproducible results, not less than 3 parallel tests were carried out, and the absolute error was 0.05 mN/m.

2.2.2. Thermodynamics and Morphology. Differential scanning calorimetry (DSC) and optical microscopy were used to determine the type of the prepared emulsions. According to Dalmazzone,⁵⁴ the DSC thermograms of the undiluted oil emulsions can be used to get information about the emulsion type and the water content, calculated based on the solidification and melting properties of the samples. The type of emulsions was established using MDSC 2920 (TA Instruments, USA). Each sample was cooled from 20 to -60 °C with subsequent heating from -60 to 30 °C at a rate of 2 K/min under an inert (argon) atmosphere.

The microphotographs were taken using an optical microscope Polam L-213 (LOMO, Russia) at ambient temperature. The average size of the dispersed phase and the size distribution were evaluated by "ImageJ" software.

2.2.3. Rheological Tests. The rheological tests were carried out using Physica MCR 301 (Anton Paar, Austria) with the both

smooth and rough cone-and-plate pair. The latter test allowed us to be sure that the wall slip is negligible in measuring the flow curves discussed below. The working pair had a diameter of 50 mm, and the angle between cone and plate was equal to 1° . The temperature was varied from 0 to 50 °C with a 10 °C step. At each temperature, the properties of the samples were measured using the following regime:

- oscillation to obtain frequency dependences of the storage and loss moduli. The strain value was 0.05% and the frequency varied from 0.01 to 100 Hz;
- shear rate control mode to obtain flow curves; the shear rate was increased from 0.05 to 600 s^{-1} in a step-wise mode, with a duration of deformation of 30 s at every shear rate.

In some cases, for more precise determination of the yield stress, we carried out experiments in the shear stress control mode. For the rheological tests, not less than 2 parallel experiments were carried out for each sample and temperature, the error limit did not exceed 5%.

3. RESULTS AND DISCUSSION

3.1. Series 1—Emulsions with Varied Water Contents. *3.1.1. Morphology.* In accordance with the DSC data (Figure 1)



Figure 1. DSC thermogram for the sample X3.

and optical microscopy, the emulsions relate to the O/W type. In the cooling mode, only one exo-peak at around -18 °C was detected which corresponds to the aqueous phase crystallization. During the following heating, the continuous phase melts at around 0 °C.

This type of morphology is quite rare for HCO emulsions. Usually, they have more complicated (multi-phase) structures.^{20,53,55} For example, all the emulsions in S2 (as presented in Section 3.2) are of the W/O/W type. The observed simple morphology within S1 may be caused by the extremely low IFT between the oil and the aqueous solution of Triton X-114. HCO itself contains surface active components which are responsible for the spontaneous formation of W/O systems. The presence of a surfactant with higher surface activity (in this case, Triton X-114) can lead to phase inversion of the self-forming W/O to the O/W emulsion.^{37,56}

The microphotographs of the Series 1 emulsions are presented in Figure 2. It should be stressed that the water content does not greatly affect the average droplet size. Introducing HEC leads to a small decrease in the oil droplet size (compared samples are X1 and X2) and a slight decrease in



Figure 2. Microphotographs (magnification 10×) of the S1 emulsions and average oil droplet sizes.

the IFT value (see Table 2). It is possible that HEC having hydroxy groups and Triton X-114 can also adsorb on the surface of the dispersed phase which results in a higher stability of the obtained emulsions.

3.1.2. Viscoelastic Properties. At first, it was necessary to determine the domain of the linear viscoelasticity (LVE) in the range of temperatures under study (Figure 3). The shaded area



Figure 3. Storage modulus vs strain amplitude for the sample X1 at different temperatures (at the frequency of 1 Hz). The red line designates a chosen amplitude for characterizing the viscoelastic properties of all samples.

on the graph shows the narrow region where the applied strain does not lead to any structural changes of the sample. For the further oscillation experiments, a strain amplitude of 0.05% was used. This value is rather low which demonstrates that interactions between the oil droplets are rather weak and can be easily broken.

The changes in the viscoelastic properties with temperature can be seen in Figure 4. For the emulsions with a water content



Figure 4. Frequency dependences of the storage (solid) and loss (open) moduli of S1 emulsions at (a) 0; (b) 20; (c) 50 °C.



Figure 5. (a) Typical viscosity curves of the emulsions with Triton X-114 at various temperatures (the data relate to sample X4). (b) Flow curves for the X2 sample at different temperatures drawn according to the Herschel–Bulkley equation (for visual clarity all curves except the one for 50 $^{\circ}$ C, are shifted by 50 units along the *Y*-axis).

of 25 vol % (samples X1 and X2), the storage modulus remains constant over a wide frequency range in the temperature range from 10 to 50 °C. This is a consequence of the solid-like structure of the samples (at the low stress limit). The viscoelastic behavior of X1 and X2 is rather similar. The slight predomination in the storage modulus for X2 is caused by presence of the HEC. Even a small content of this polymer considerably influences the rheology of the aqueous phase. For example, the aqueous solution containing 0.25 wt % HEC and 5 wt % Triton X-114 exhibits non-Newtonian behavior.

With an increase in the continuous water phase content, the drops are less densely packed and the rigidity of the structure formed by the oil drops with the polymer viscosity enhancer becomes weaker (the storage modulus decreases).

For clarity, Figure 4 only includes loss moduli data for samples X2 and X4. The difference between the samples is quite obvious: at 0 °C, the emulsion with 40 vol % of water mostly demonstrates a liquid-like type of behavior, and the crossover point lies at a rather low frequency (1.6 s^{-1}) . On the contrary, for the emulsion with 25 vol % of water, the transition from solid-like to a liquid-like behavior moves to high frequencies (ca. 250 s⁻¹). The X1 and X3 samples exhibit intermediate values of storage modulus.

3.1.3. Flow Behavior. Under shear deformations, the obtained emulsions with Triton X-114 behave as viscoplastic materials (Figure 5). The similar type of the rheological behavior was observed by Zadymova et al.⁵⁷ and Knudsen et al.⁴⁷ The analysis of the experimental data (see Figure 5b) shows that the yield stress is expressed quite distinctly. It means that under low stress, the sample does not undergo any structural changes that correspond to the results obtained in the oscillation experiments. If the shear stress reaches a certain level, the sample structure breaks. This threshold is the yield stress which characterizes the structure strength. Unlike solid materials, new bonds between the dispersed particles in O/W emulsions quickly rebuild so that the breakup of the structure can be spread over a range of shear stress values.

For example, in Figure 5a, the X4 viscosity curves are plotted on a semilog scale and the yield stress region is scaled up. After passing the yield stress, all S1 emulsions flow as non-Newtonian fluids. In the region of high shear rates or stresses, the viscosity reaches its minimal values. For example, at 20 °C, the minimal viscosity values for the most viscous sample are 200–300 mPa·s, that is, all the emulsions meet the requirements for the tube transportation at a temperature of 20 °C and above.

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In Figure 5b, the data for X2 emulsions are presented using the Herschel–Bulkley approximation: $\sigma = \sigma_{\rm Y} + K \cdot \gamma^n$. This was used to obtain the yield stress values which are summarized in Table 3, and the coefficients of the equation for the samples

Table 3. Results and Errors of the Herschel-Bulkley Approximation for Emulsions X2 and X4 at Certain Temperatures

sample	X2 (25 vol % I	$H_2O)$	X4 (40 vol % I	$H_2O)$
temperature, °C	10	30	50	10	30	50
$\sigma_{\rm Y}$, Pa	4.94	1.49	1.25	0.61	0.39	0.18
K	8.06	2.87	1.85	0.21	0.10	0.06
n	0.53	0.61	0.64	0.95	0.92	0.88
reduced χ^{2a}	0.138	0.622	0.417	0.049	0.088	0.002
$R^2 (COD)^b$	0.998	0.991	0.991	0.999	0.999	0.999

^{*a*}The reduced χ^2 value is equal to the residual sum of square divided by the degree of freedom. A reduced χ^2 value close to 1 indicates a good fit result. ^{*b*}The coefficient of determination (COD) is a statistical measure to qualify the regression.

whose viscoelastic properties differ mostly from each other. At the same temperature, $\sigma_{\rm Y}$ for X2 is ten times higher than that for X4 which contains more water. An increase in temperature leads to a corresponding decrease in the yield stress and the viscosity (the latter is characterized by the coefficient *K*). The exponent *n* also indicates differences in the inner structure of the samples. The X4 emulsion flows almost as a Newtonian fluid $(n \rightarrow 1)$, whereas X2 flows as a typical non-Newtonian material $(n \sim 0.6)$.



Figure 6. Yield stress values vs water content (a) and temperature (b) for S1 emulsions. Temperature dependence of viscosity for the HCO and S1 emulsions in the coordinates of the Arrhenius equation; the apparent flow activation energies are indicated in the graph (c).

The correlations between the yield stress, water content, and temperature for all the emulsions S1 are shown in Figure 6a and Figure 6b, respectively. The yield stress increases if the



Figure 7. Thermogram of the emulsion A indicating the W/O/W morphology.

concentration of the inner phase grows. A drastic jump of σ_Y is observed when the water concentration is lower than 30 vol %. This effect is the most pronounced at low temperatures (Figure 6b). This peculiarity of the rheological properties explains the high stability of these samples against phase separation. The presence of HEC has a negligible effect on the yield stress, or its contribution is small for the highly concentrated emulsions. For the samples X3 and X4, the temperature dependence of the yield stress is linear.

Figure 6c shows the temperature dependence of the viscosity of the S1 emulsions in the Arrhenius coordinates. The viscosity values used for plotting are the minimal ones. These dependences are linear. In contrast to the emulsions, the temperature dependence of the viscosity for HCO cannot be described by the Arrhenius equation. The apparent flow activation energies, *E*, are displayed in Figure 6c. The values in question become smaller with an increase in the water content. **3.2. Series 2—Emulsions with Different Emulsifying Agents.** *3.2.1. Morphology.* All emulsions in the series S2 (O, OS, S, A, and T) were obtained using the same protocol as for samples of the series S1. Therefore, the surfactant chemistry was the only factor determining the difference in the morphology. Figure 7 shows two exo-peaks on the DSC thermograms during cooling. The presented transitions indicate the W/O/W type of the emulsions. The first peak corresponds to the freezing of the continuous aqueous phase (around -17 °C), and the second one (at ca. -40 °C) shows the crystallization of the "inner" water situated inside the oil drops. These data agree well with the analogous literature data for crude oil emulsions.^{54,58}

Figure 8 represents the microphotographs of the S2 samples and the average droplet sizes and IFT of the surfactant aqueous solution/HCO. As the preparation method was the same for all emulsions, it is evident that only the surfactant properties determine the droplet sizes and the viscoelastic behavior of the samples. We found a correlation that with the growth in the IFT values, the droplet size increases. It can be described by a power law equation (Figure 9a). The mixture of surfactants (OP-7 + SLES) has an intermediate IFT value and, consequently, an intermediate dispersed phase size in the emulsion OS, in comparison with the O and S samples.

The average droplets size (see Figure 8) and the droplets size distribution (Figure 9b) were obtained by means of the photographic analysis. The sample O contains droplets of very small size unsuitable for the photographic analysis, so it is absent from Figure 9b. It is worth noting that despite the noticeable average size growth with the IFT increase, all the samples contain an overwhelming quantity of $0.5-2 \mu m$ droplets. From the sample OS to T, the number of such droplets falls by 4-5 times, while at the same time, the number of large drops ($d > 10 \mu m$) increases considerably (see the enlarged region in Figure 9b). Polydispersity of the oil emulsions is one of the factors determining their inner structure strength and stability against sedimentation.



Figure 8. Microphotographs of the S2 emulsions and average oil droplet sizes.



Figure 9. Correlation between the IFT values and the average droplets sizes (a) and the droplet size distribution by the number of drops (b) for the S2 emulsions.



Figure 10. Frequency dependences of the S2 emulsions storage modulus at 20 $^{\circ}$ C (a). Frequency dependences of the storage and loss moduli for samples O (b) and T (c) at different temperatures.



Figure 11. (a) Plateau modulus vs IFT values for S2 emulsions at 20 °C. The G_{pl} values were taken at the frequency of 1 s⁻¹. (b) Correlation between yield stress and plateau modulus for various surfactants in the series at 40 °C. (c) Plateau modulus vs yield stress for emulsion A at different temperatures.

3.2.2. Viscoelastic Properties. Frequency dependences of the storage modulus of emulsions with different surfactants are given in Figure 10a. Along with the growth of IFT, the storage modulus decreases. In the region of low frequencies, the storage modulus achieves a plateau $(G_{\rm pl})$, which demonstrates that the emulsions behave as a solid-like medium.

The viscoelastic behavior of the samples T, S, and OS is characterized by an increase in the modulus at high frequencies as a reflection of the relaxation process, while the plateau for the O and A samples occupies two decimal orders, demonstrating a solid-like behavior (at low amplitudes of deformation).

The role of the droplets size is the most evident from Figure 10b,c. The emulsion O is almost 10-times more rigid than sample T because of a five-fold difference in the droplet size caused by the difference in the nature of the surfactant used. Besides, at all temperatures, the storage modulus of O prevails over the loss modulus. Hence, at low stresses, this emulsion behaves more in a solid-like mode than as a liquid. On the contrary, the emulsion T demonstrates the transition to the liquid-like behavior when the frequency grows. In both cases, the crossover point moves to higher frequencies with a temperature

increase. It is worth noting that at low frequencies, the storage modulus is independent from the temperature.

The plateau modulus clearly correlates with the IFT values (Figure 11a). This correlation is a consequence of the influence of IFT on the droplet size, which defines the interactions between the droplets and the structural strength.⁵⁹ The less the IFT is between the oil and surfactant solution, the smaller the drops of the dispersed phase and the more rigid is the emulsion. Meanwhile, the HLB of the surfactants does not correlate with the G' values.

3.2.3. Flow Properties. The emulsions with various surfactants behave similarly to the emulsions of series S1, and their flow curves are presented in Supporting Information (see Figure S1). An approximation by the Herschel-Bulkley equation was used to find the yield stress values. The results are shown in Table 4.

From sample O to T, the IFT and average droplet size increase, while $\sigma_{\rm Y}$ and viscosity index *K* decrease, as expected. Herewith, the index $n \rightarrow 1$, which means that the deviation from a Newtonian fluid becomes less prominent.

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Table 4. Coefficients and Errors of the Herschel–Bulkley Approximation for S2 at 40 °C

sample	$\sigma_{ m Y}$, Pa	Κ	Ν	reduced χ^2	R^2 (COD)
0	5.42	1.95	0.67	0.590	0.998
OS	3.97	1.12	0.70	0.461	0.997
А	3.67	0.54	0.75	0.019	0.992
S	3.12	0.40	0.86	0.097	0.993
Т	2.45	0.13	0.89	0.074	0.997

Figure 11 also represents the correlation between the yield stress and elastic (plateau modulus) properties of emulsions. The general tendency is the growth of the plateau modulus with increasing yield stress values. The tendency is the same for samples with various surfactants at the same temperature (Figure 11b) and for one surfactant at different temperatures (Figure 11c). But the surfactant properties (IFT in particular) have a stronger influence on the discussed rheological parameters than a decrease in temperature.

3.3. Viscosity Reduction. The emulsification is meant to be a method for decreasing the high viscosity of the HCO. The shaded area on the graph (Figure 12a) indicates the viscosity region in which tube transportation is possible. The presence of the two viscosity limits should not be confusing as there is no single accepted value in the literature or in engineering practice. Therefore, we used both of the most quoted ones, 0.2 and 0.4 Pa-s.^{8,60}

Among the samples containing 25 vol % of the aqueous phase, emulsion T is preferable for the purpose of transportation (Figure 12a) as suitable viscosity values are reached in the investigated temperature range (from 0 to 50 °C) after passing the yield stress (the viscosity values correspond to the shear stresses of the order of 200–300 Pa). An alternative way to decrease the HCO viscosity is to increase the water phase content in the emulsion; X4 is presented as an example.

The efficiency of the emulsification can be also estimated on the basis of the correlation between IFT and the viscosity reduction, which is described by a linear equation (Figure 12b). The viscosity reduction in this presentation is understood as the ratio of the HCO viscosity to the apparent viscosity of the emulsions, at shear stresses of the order of 200–300 Pa. Here again, it is worth comparing the influence of the water content as its contribution is strong enough. For example, emulsion X3 has an IFT value close to those of samples X1 and O and contains only an additional 5 vol % of water, but the viscosity drop for X3 is 2–3 times larger than that for O.

4. CONCLUSIONS

Rheological and morphological studies of the emulsions based on HCO revealed some important correlations for oil flowability. First of all, the choice of surfactant, depending on the IFT, influences the morphology type of the material. Simple O/W emulsions were only obtained for Triton X-114, which had the smallest IFT (0.3 mN/m). All emulsions are viscoplastic media. An increase in the interfacial tension leads to the formation of larger droplets and, finally, to a decrease in viscosity and yield stress. The reduction of the apparent viscosity in relation to HCO also correlates with the IFT and can be quite remarkable, reaching $0.1 \text{ Pa} \cdot \text{s}$ at 20 °C and $0.4 \text{ Pa} \cdot \text{s}$ at 0 °C (25times and 80-times viscosity drop, respectively). The obtained viscosity values guarantee the acceptability of these emulsions for pipe transportation.

The content of a continuous phase (water) also plays a dominant role in the viscous and viscoelastic properties of the emulsions. Samples with 25 vol % of water should be considered as highly filled materials with an elastic component of the complex modulus, up to 100 Pa, while the yield stress is less than 10 Pa. A sample with 40 vol % of water is characterized by frequency-dependent G', a weak structure ($\sigma_{\rm Y}$ is close to 1 Pa), and low viscosity at high shear stresses. In this case, the reduction of the viscosity in relation to the viscosity of heavy oil reaches 30-times at 20 °C (to 0.09 Pa·s) and 160-times at 0 °C (to 0.2 Pa·s). The temperature impact is less pronounced than the water content or surfactant IFT. An increase in temperature from 0 to 50 °C leads to yield stress and the apparent viscosity reduction of no more than 2–10 times.

The fulfillment of the technical recommendations for pipe transportation can be met by using the surfactant with a high interfacial tension and a low content of a continuous phase. The other way is to use a surfactant with a lower IFT and higher water content. Hence, a combination of these two parameters (surfactant IFT and the water content) is enough to obtain HCO emulsions with a suitable viscosity level.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00769.

HCO composition; viscosity curves for the S2 emulsions; and trademarks, chemical structure, and main physicochemical characteristics of surfactants (PDF)



Figure 12. (a) Temperature dependencies of viscosity for the HCO, S2 emulsions and sample X4. (b) Correlation between IFT and the viscosity reduction (at 20 $^{\circ}$ C) due to formation of emulsions.

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Notes

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ABBREVIATIONS

HCO, heavy crude oil; HLB, hydrophilic–lipophilic balance; IFT, interface tension; LVE, linear viscoelasticity

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