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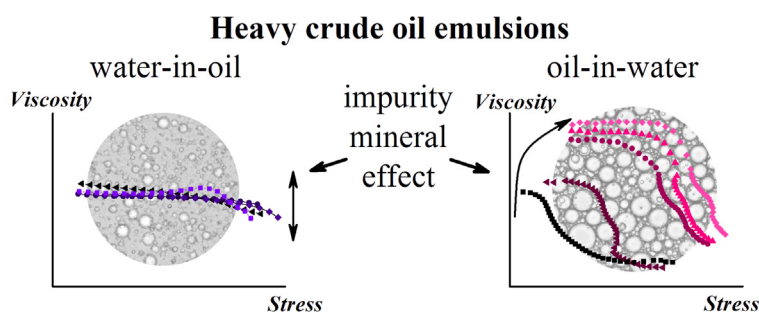
## Effect of silica and clay minerals on rheology of heavy crude oil emulsions

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Researchers studying oil-in-water emulsions practically always deal with the oil and water purified of mineral admixtures. In reality, a water/crude oil emulsion obtained from a well contains solid clay- and sand particles, which may act as surfactants. In the present work, the solid particles' effect on the morphology and rheological behavior of heavy crude oil emulsions are studied. Water-in-oil emulsions are fluids with the weakly non-Newtonian behavior and viscosity exceeding that of the crude oil. Solid particle admixtures have practically no effect on the viscosity of these emulsions. Oil-in-water emulsions, on the contrary, are viscoplastic systems, the yield stress of which increases with silica- and clay admixture content. The transition from water emulsions to the oil ones was realized using surfactants (cetrimonium bromide, sodium dodecyl sulfate, Tween 85, and Triton X-100), the success of the phase inversion depending on the hydrophilic-lipophilic balance of a surfactant. The effective viscosity of the oil-in-water emulsions is demonstrated to depend on the shear rate and solid particle- and surfactant concentrations, this providing the opportunity to optimize the compositions of crude oil emulsions for transportation.

## 1. Introduction

Crude oil and oil products consumption has grown considerably in the recent decades. The main extraction volumes fall on the low-density oil called “light oil”. Heavy oil, though, is given growing interest now, because of gradual exhaustion of the known fields. Basically, the heavy oil's viscosity is higher than that of the light oil [1,2], which makes heavy oil piping more complicated. Different ways to decrease oil viscosity are used in the world practice of oil production [3–6]. One of

the most popular methods is heavy oil dilution with lighter fractions [1,7] or with various organic solvents (liquid hydrocarbons, alcohols, ethers, etc). Thus, it is proved experimentally that the addition of light oil in 7:3 ratio decreased the heavy oil's viscosity to about 1/3 of its original value. However, the method has certain drawbacks. In some cases, heavy oil dilution may lead to the precipitation of asphaltenes, whose solubility is determined by an oil medium solubility parameter [8]. Oil viscosity reduction by heating the oil right in a pumping station is equally popular [7,9]. Authors [10] have succeeded in medium-

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density oil's viscosity reduction from 0.7 to 0.3 Pa·s by the crude oil heating from 283 to 303 K. The method is rather energy consuming and requires taking into account a lot of factors: heat loss to the environment, pipeline corrosion enhancement, etc.

An alternative method for heavy and extra heavy oils' viscosity reduction is formation of oil emulsions of the oil-in-water type [11–13]. In these emulsions, the oil phase (crude oil) is dispersed in a continuous aqueous phase. The method can be quite efficient for transportation of oils with the viscosity exceeding 1 Pa·s, especially in the regions with cold climate. In order to increase the stability of emulsions, the additions of surfactants of different chemical structure are used [14–16].

Besides the traditional surfactants, solid particles are also used as emulsifiers and emulsion stabilizers. This kind of emulsions is called "Pickering emulsions" [17,18]. Hydrophilic particles are the stabilizers of the direct (i.e., oil-in-water) emulsions. With hydrophobic particles, the invert emulsions of the water-in-oil type are formed. Combination of surfactants and solid particles in the same emulsion can sometimes produce a synergic effect preventing the breakup of the emulsion [19,20]. It should also be mentioned that crude oil contains asphaltene molecules as the nano-sized particles [21,22] capable of acting as water-in-oil emulsion stabilizers [23–25] and thus hindering oil-in-water emulsion formation, due to the competition between the asphaltene nanoparticles and surfactant molecules for the place in the interfacial layer.

Crude oil extracted from a reservoir formed within sedimentary rocks contains a certain amount of mechanical admixtures such as clay and silica. These particles' effect on the oil-based emulsion formation is ambiguous. From one hand, they may serve the system stabilizers; on the other hand, they are the detrimental impurities increasing the system's viscosity. The aim of the present work is to estimate mineral particles' effect on the morphology and rheological properties of emulsions and also to decide on the expediency of oil purification of these admixtures for it further transportation in the form of emulsion.

The structure of our work will be as follows: first, silica particles' effect on the rheological behavior of water-in-oil emulsions modeling the emulsions extracted in oil production will be studied; after that, silica- and clay particles' effect on oil emulsification in the presence of traditional surfactants of different structure and the rheological properties of the emulsions formed will be considered.

## 2. Experimental

### 2.1. Materials

A sample of the crude oil from Yaregskoye field (Lukoil JSC, Russia) was used as an object for study. The oil gravity at 15 °C, according to the standard of the American Petroleum Institute (API), made 18.1°, that is, the oil belonged to the class of heavy crude oils. Sulfur and paraffin wax mass concentrations were 1.24 and 0.8 wt%, respectively. The rheology of this crude oil was discussed in detail earlier [2].

As the solid particles simulating natural impurities, Cloisite Na<sup>+</sup> (Southern Clay Products Inc., USA) sodium montmorillonite with the specific surface of 750 m<sup>2</sup>/g and pyrogenic silica with the specific surface of 395 m<sup>2</sup>/g supplied by Aldrich were chosen. The surface of the particles has not been chemically modified, and so we can consider them as hydrophilic, that is, the ones favoring oil-in-water emulsion formation.

The choice of surfactants was determined by the necessity to prepare the direct oil–water emulsions, which meant that the surfactant's HLB (hydrophilic-lipophilic balance) value should exceed 9 [26]. The exact number for the best emulsification depends on the composition of the crude oil: the heavier it is, the higher the surfactant HLB should be (e.g., the required HLB number for emulsifying of linear paraffin in water is 9–11, whereas for the preparation of toluene emulsion is 12–16 [27]); otherwise emulsions may not be stable. The following surfactants were used in experiments (Fig. 1):

- Cetrimonium bromide (CTAB) cationic surfactant with HLB = 10 (Sigma production);
- Tween 85 nonionic branched surfactant with HLB = 11 (Sigma production);
- Triton X-100 nonionic linear surfactant with HLB = 13.5 (AppliChem Panreac production);
- Sodium dodecyl sulfate (SDS) anionic surfactant with HLB = 40 (Sigma-Aldrich production).

The emulsions were prepared by a specified oil volume gradual addition to the aqueous solution of a surfactant containing solid particles. For the dispersion of fluids, IKA T10 Ultra-Turrax rotary homogenizer was used. The rotation velocity varied within the range of  $8 \times 10^3$  to  $30 \times 10^3$  rpm. Mixing was carried out over the period of 10 min.

The following emulsion series were prepared:

- Invert emulsions with 35 vol% water containing 1, 3, 5, or 10 wt% SiO<sub>2</sub>;
- Emulsions containing 35 vol% aqueous dispersion of SiO<sub>2</sub> ( $c_{\text{SiO}_2} = 3$  wt%) with 5 wt% surfactant;
- Direct 65 vol% emulsions containing Triton X-100 (5 wt%) and SiO<sub>2</sub> (0, 1, 3, 5, or 7 wt%) in the aqueous phase;
- Direct 50 vol% emulsions containing 3 wt% SiO<sub>2</sub> and 3, 5, or 7 wt% Triton X-100 in the aqueous phase;
- Direct emulsions with the oil concentration varying within the range of 20 to 65 vol% containing 3 wt% SiO<sub>2</sub> and 3 wt% Triton X-100 in the aqueous phase;
- Direct emulsions with the oil concentration of 50 and 65 vol% and Triton X-100 and Cloisite Na<sup>+</sup> in the equal concentrations of 5 wt% in the aqueous phase.

There was no droplet coalescence in all emulsions, but there often was creaming in dilute direct emulsions without solid particles after a day of storage. For the latter reason, emulsions without solids were prepared only with a high oil droplet content (65 vol%); as a result, creaming did not occur. The obtained emulsions remained stable within a few weeks; no phase separation has been observed.

### 2.2. Methods

Rheological testing of the oil emulsions was carried out on the RheoStress 600 rotational rheometer (Thermo HAAKE, Germany) at 25 °C. For measurements in stationary and dynamic modes, a cone-and-plate geometry measuring unit was used (the cone diameter: 60 mm, the cone to plate angle: 1°). Shear deformation was measured in the controlled shear rate mode within the shear rate range of 0.0001–100 s<sup>-1</sup>. Shear rate changes were stepwise; at a constant shear rate, measurement duration was 240 s. The dynamic testing was carried out within the frequency range of 0.05–600 s<sup>-1</sup> at the constant shear stress of 1 Pa, this referring to the systems' linear viscoelasticity region.

The morphology of the oil emulsions was studied using Biomed 5P laboratory optical microscope. Emulsions' droplet size distribution was estimated by the dynamic light scattering method using Zetasizer Nano ZS analyzer (Malvern Instruments, UK). The samples were prepared by an oil emulsion droplet dilution with 5 ml of distilled water. The tests were carried out at 20 °C.

## 3. Results and discussion

### 3.1. Effect of impurities on water-in-oil emulsion properties

Due to water invasion, the oil is extracted from the subsurface as an emulsion. Let us consider the effect of contamination with solid particles, namely, with silica (the use of clay particles gives almost the same), on the rheological properties of these emulsions.

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