

Heavy Oil as an Emulsion: Composition, Structure, and Rheological Properties

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Abstract—Recent works devoted to studying the structure and rheological properties of water/oil disperse systems have been reviewed. Contemporary understandings of crude heavy oil as a water-in-oil emulsion have been discussed. Data on the mechanism of the stabilizing effect of natural lipophilic surfactants and ultradispersed particles of different natures contained in oil have been presented. Methods that are used to improve the transport characteristics of heavy oil—in particular, the formation of low-viscosity oil-in-water emulsions—have been listed. Colloidal and rheological properties of heavy oil-in-water emulsions, which are increasingly applied for pipeline transportation of oil, have been considered.

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1. INTRODUCTION

At present, the explored oil reserves are about 70% heavy and extraheavy oils, which are becoming increasingly in demand because of the growing consumption of oil products and the gradual depletion of oil fields being exploited [1]. The world geological reserves of heavy oils are of about 810 billion tons. The explored reserves of Russia are in third place after those of Canada and Venezuela [2]. The development of these resources requires the elaboration of novel technologies that would provide economically feasible extraction followed by transportation and processing of heavy and extraheavy oils.

The compositions and properties of natural hydrocarbons are extremely diverse, thus making classification of oils with respect to any criterion to be conventional. The high-usage system proposed by the American Petroleum Institute [3] is based on the API criterion, which is calculated by the following formula:

$$\text{API} = \frac{141.5}{\rho/\rho_w} - 131.5,$$

where ρ and ρ_w are the densities of oil and water, respectively, at 60°F (15.6°C)

Oil is considered to be heavy when its API criterion lies in a range of ~20–10 and extraheavy at $\text{API} < 10$, when it is heavier than water. The fact that high viscosity values correspond to low API values is the most significant circumstance from the point of view of oil extraction and transportation.

The peculiar composition of heavy oils results from biodegradation processes that have taken place over the course of geological periods of time. The life processes of microorganisms has enriched oil with resins, asphaltenes, and polyaromatic compounds [4]. Moreover, light fractions may be lost because of washing out and phase separation.

Water is a component, which is inevitably present in crude oil under the conditions of both bedding and extraction. Although oil and water initially coexist as two separate phases, their movement through wellbores, pipes, valves, and pumps results in emulsification [5]. Therefore, all types of crude oil are, as a rule, water-in-oil (W/O) emulsions stabilized with natural lipophilic emulsifiers. The initial properties of such disperse systems (especially their rheological characteristics) make the extraction, transportation, and processing of oil so difficult that these processes appear to be almost impossible, unless its rheological parameters are decreased to admissible values.

In this review, we discuss contemporary notions of the structure and properties of initial W/O emulsions and different approaches to decreasing the viscosity of these liquid-phase disperse systems. Special attention is focused on the methods leading to phase inversion with the formation oil-in-water (O/W) emulsions, the dispersion medium of which has a low viscosity that results in their several times higher mobility as compared with that of W/O emulsions.

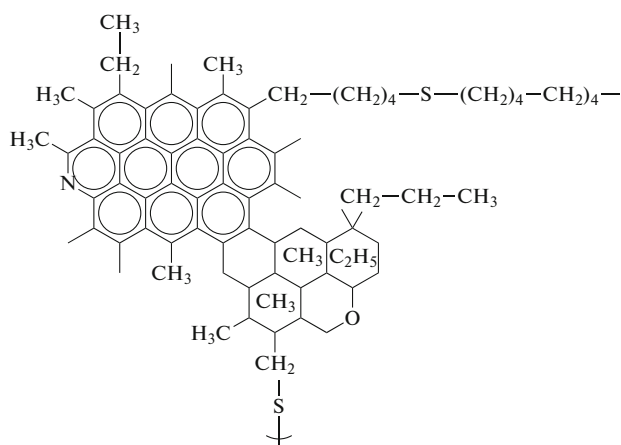


Fig. 1. The structure of asphaltene molecules according to [9].

2. WATER-IN-HEAVY OIL EMULSIONS

2.1. Stabilization of Water-in-Oil Emulsions with Natural Lipophilic Surfactants

A key technological problem of the oil industry is the formation of W/O emulsions, which hamper the transportation and processing of crude oil and necessitate its subsequent de-emulsification followed by dehydration, thereby causing additional expenditure [6]. These emulsions are stabilized by oil components, such as lipophilic surfactants (asphaltenes, resins, naphthenic acids, etc.) or ultradispersed particles (paraffin crystals, lyophilized clays and sands, iron oxides and hydroxides, etc.).

Among natural emulsifiers, asphaltenes are of greatest importance; they are polycyclic aromatic compounds containing different side alkyl substituents and heteroatoms (nitrogen, oxygen, sulfur, etc.) (Fig. 1) [7–11]. Asphaltenes are soluble in aromatic solvents

(e.g., toluene) cyclohexane, and some other organic liquids; however, they are actually insoluble in alkanes.

Different mechanisms are considered in the literature for the stabilizing effect of asphaltenes in emulsions. For example, the structure-related barrier that arises at an oil/water interface due to the formation of a gel-like layer from mutually crosslinked adsorbed aggregates of asphaltene molecules is thought to be the key stabilization factor in W/O petroleum emulsions [10, 11]. This idea correlates with the results of the compression–expansion experiments performed using a Langmuir film balance. These experiments have confirmed the presence of asphaltene molecular aggregates in an interfacial layer at the boundary with air [12]. Being amphiphilic substances, asphaltenes can form strong films 2–10 nm thick composed of crosslinked molecules or be adsorbed as resin-solvated aggregates on water droplet surfaces [13]. In subsequent works [14, 15], the pendant oscillating drop method was used to measure interfacial tension σ , instantaneous modulus of elasticity E_0 , and interfacial dilatational modulus. Interpretation of data based on the Langmuir equation and corresponding equation of adsorbed layer state, which are known to ignore the interaction between adsorbed molecules, has shown that asphaltene molecules are adsorbed from an oil phase in a manner such that polyaromatic fragments and aliphatic chains thereof are arranged in parallel and perpendicularly to a water surface (Fig. 2), respectively [14]. The stabilization in this model is realized due to the elasticity of an adsorbed asphaltene layer (the Marangoni–Gibbs effect). When the interfacial tension is reduced to 22 mN/m, the E_0 value is 40 mN/m [14].

For high-concentrated W/O petroleum emulsions, an exponential dependence of viscosity on asphaltene concentration has been revealed, which is explained by aggregation of water droplets “armored” with

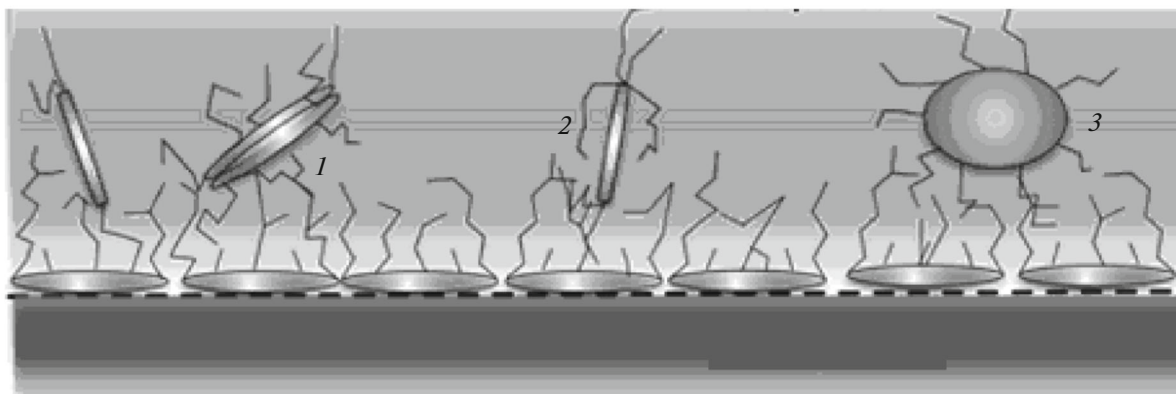


Fig. 2. Schematic representation of asphaltene adsorption at oil/water interface: (1) asphaltene molecule composed of a polyaromatic cycle and aliphatic chains, (2) nanoaggregate, and (3) cluster [14].

asphaltenes with the formation of a branched structure (network) up to the appearance of a gel [7, 16, 17]. A striking example is the formation of so-called “chocolate mousse” as a result of oil spills, in which the viscosity increases by 500–1000 times [5].

Petroleum resins are high-molecular-weight compounds ($M_w > 1000$ Da) containing condensed aromatic, naphthenic, and heterocyclic fragments in which alkyl, carbonyl, carboxyl, hydroxyl, sulfide, mercapto, and amino groups are present as substituents. In contrast to asphaltenes, they are readily soluble in low-boiling saturated hydrocarbons.

Since resins and asphaltenes are most typical components of heavy oil, their combined effect on the properties of W/O petroleum emulsions has been analyzed in detail in a number of works. For example, according to [18], as the content of resins increases, the stability of emulsions passes through a maximum, after which solubilization of asphaltenes with resins in the oil phase and their removal from the adsorption layer begin to prevail [13, 19, 20].

Oil-soluble acids (naphthenic, aliphatic, and aromatic) contained in oil also take part in stabilization of W/O petroleum emulsions [19]. Naphthenic acids prevail in the component composition; they contain one or several five-membered (more seldom, six-membered) carbon cycles. They possess the highest surface activity and interact with polyvalent cations (Ca^{2+} , Mg^{2+} , Fe^{3+} , and Al^{3+}) contained in reservoir water to yield salts with low values of the hydrophilic-lipophilic balance (HLB), these salts also being efficient stabilizers of W/O petroleum emulsions.

The authors of [21, 22] studied the surface activity of salts of naphthenic acids and bivalent cations at the water–oil phase interface. They have shown that the ability to decrease the interfacial tension increases with a reduction in the degree of cation hydration according to the following series: $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$. The maximum effect (a decrease in σ by 30–40 mN/m) is reached at high pH values in the presence of Ba^{2+} .

The colloidal disperse structure of heavy oil seems to be similar to the structure of petroleum bitumens, which was studied by the temperature-modulated DSC [23].

2.2. Natural Pickering Petroleum Emulsions

Submicron particles (paraffin crystals and hydrophobized particles of clays, SiO_2 , iron oxides, etc.) present in oil may serve as stabilizers of W/O petroleum emulsions. Hydrophobic layers are formed on the surface of mineral particles as a result of adsorption of lipophilic stabilizers present in oil [24, 25]. W/O emulsions stabilized with these particles appear, as a rule, to be much more stable than those stabilized with natural lipophilic surfactants [26, 27].

The possibility of stabilizing emulsions with solid particles has been known since the 19th century. Pickering was the first to describe in detail these systems in his original communication [28]. Moreover, he noted the existence of concentrated petroleum emulsions and discussed the relationship between the degree of hydrophilicity of particles and the type of an emulsion that they stabilize. In [29], Reh binder wrote that “[a] substance can play the role of a solid emulsifier, provided that its particles are capable of being selectively wetted with an external medium of an emulsion being formed. ... however, this selective wetting must not be complete, because, upon the complete wetting ... these particles remain in the bulk of the external medium and do not stick to droplet surface.” By analogy with classical surfactants, the concept of the HLB has been introduced for solid particles, which is characterized by a ratio between the increment of the Gibbs free energy due to wetting with a polar medium (commonly water) and the energy of wetting with a nonpolar liquid [30]. The value of HLB may be determined by the following equation [31]:

$$\text{HLB} = \frac{A_w}{A_o} = \frac{1 + \cos \theta}{1 - \cos \theta},$$

where A_w and A_o are the particle surface areas wetted with water and oil, respectively, and θ is the selective wetting angle counted toward water.

It has been experimentally established that O/W and W/O emulsions are formed at $\theta < 90^\circ$ and $\theta > 90^\circ$, respectively, thereby confirming the already-known Bancroft rule [32]. Since the contact angle for small particles with complex shapes can hardly be experimentally measured, the HLB of such particles may be indirectly estimated using their electrochemical potential, an increase in the absolute value of which improves particle surface wetting with water [33].

Adsorption modification of particle surface with surfactants makes it possible to change the type of an emulsion. For example, at a certain concentration of stearic acid in adsorption layers, the selective wetting of clay particles is inverted, thus leading to the inversion of an emulsion [34].

The factors that determine the stability of Pickering emulsions have been described in detail elsewhere [19, 26, 31, 35, 36]. The highest stability with respect to aggregation is observed at intermediate values of particle HLB, while, at its high or low values, the particles possess a lower stabilizing ability. The stability of emulsions increases with a decrease in the particle size [24] and an increase in the particle concentration [37]. It is thought that the particle size must be no larger than one-tenth of the dispersed phase droplet diameter, while the particle concentration must be sufficient to provide multilayer coverage of droplet surface [19].

Variations in the volume ratio between oil and aqueous phases in Pickering emulsions cause phase inversion that occurs without hysteresis and is referred

to as “catastrophic” [32, 38, 39]. Within the framework of a thermodynamic consideration, it has been proposed to predict the type of emulsion on the basis of the sign of difference ΔW between the formation works of an O/W (W_1) and W/O (W_2) emulsions [32]. At $\Delta W < 0$ the emulsion will be O/W and vice versa. It has been shown that the ΔW value is proportional to difference $(\varphi_1 - \varphi_2)$ between the volume fractions of emulsion phases, while the catastrophic phase inversion must be observed at $\Delta W = 0$, i.e., at $\varphi_1 \approx \varphi_2$. However, experiments have shown that, for emulsions stabilized with hydrophobized SiO₂ particles, a W/O emulsion is transformed into an O/W one only at a water volume content of 70% [40]. The difference between the results of the thermodynamic analysis and these experimental data has been explained as being a result of the influence of kinetic factors [32].

A study of model W/O emulsions, in which the dispersion medium was represented by a heptane–toluene mixture, while natural asphaltenes and clay particles with different dispersities played the role of emulsifiers, has shown that emulsions stabilized with small particles (50–500 nm) are most stable [27]. In the case of large clay particles (1–10 μm), the sizes of which are comparable with the sizes of water droplets, emulsions are destabilized even in presence of the stabilizing effect of asphaltenes. Moreover, large particles may provoke droplet flocculation via the bridge mechanism. As the concentration of large particles increases ($> 10 \text{ kg/m}^3$), they form multilayers on the droplet surface, thereby increasing emulsion stability.

Clay particles stabilize W/O petroleum emulsions more efficiently than any other mineral particles. Different regions of particle surface may have strongly different compositions, affinities to water or oil, and charge magnitudes and signs. Therefore, such particles are commonly amphiphilic (Janus-like) and form strong layers on the surface of water phase droplets [41, 42].

2.3. Rheological Properties of W/O Petroleum Emulsions

The general principles of describing the rheological properties of emulsions, in particular, concentrated ones, have been described in relation to their composition and structure in detail elsewhere [43–45]. Therefore, only some rheological peculiarities of heavy oils will be considered here.

Dehydrated heavy oils are, as a rule, Newtonian liquids [46, 47] with high viscosities (1–10 Pa s) [46–48]. At a high content of asphaltenes, the aggregates of which are prone to flocculation and structuring at low temperatures, a slightly pronounced non-Newtonian behavior is observed, which has been described in detail for oils from different deposits. For example, using the example of heavy oil (water content as low as 0.06 wt %) from the North Sea, variations in the rheological properties from Newtonian to anomalously

viscous ones have been monitored upon a decrease in temperature from 60 to 15°C [46] and even to –30°C [47]. For the high-viscosity heavy oil of the Yagerskoe oil field (Komi Republic, Russia), viscosity, yield stress, and thixotropic properties dramatically decrease in a temperature range of 20–40°C [49]. The decrease in the yield stress of crude heavy oil with API = 10.7 (Saskatchewan, Canada) upon heating from 25 to 65°C has been described in [50].

W/O petroleum emulsions with a small volume fraction of dispersed phase ($\varphi < 0.1$) are commonly Newtonian liquids, the viscosity of which is, in the simplest case, described by the Taylor equation, which takes into account the difference between the viscosities of a dispersed phase (η_1) and a dispersion medium (η_0) [51]:

$$\eta = \eta_0 \left((1 + 2.5\varphi(\eta_1 + 0.4\eta_0)) / (\eta_1 + \eta_0) \right).$$

As φ increases, the interdroplet interaction leads to an anomalous viscosity and the η value begins to depend on shear stress (τ) or deformation rate ($\dot{\gamma}$). In a number of cases, the rheological properties of non-Newtonian petroleum emulsions may be described by the following power law [52, 53]:

$$\tau = k\dot{\gamma}^n,$$

where n and k are empirical constants. Therewith, the larger the volume fraction of a dispersed phase in an emulsion, the lower the n value and the more pronounced the anomaly of viscosity [53].

The rheological properties of petroleum emulsions are determined by not only the viscosity of system components and the fraction of a dispersed phase, but also the droplet sizes. For example, an analysis of the flow curves and viscoelastic properties of W/O petroleum emulsions with different dispersed phase particle sizes, with the emulsions being stabilized, in addition to natural lipophilic surfactants, with sorbitan trioleate (Emsorb 2503, HLB = 1.8 [54]) and containing 55–76 vol % aqueous phase, has shown (Fig. 3) that finely dispersed emulsions (with average particle size $r_{\text{av}} = 12 \mu\text{m}$) have higher values of apparent viscosity and storage modulus G' and a more pronounced anomaly of viscosity than more coarsely dispersed ones ($r_{\text{av}} = 30 \mu\text{m}$) have [55]. The revealed phenomenon is explained by the fact that flocculation and structuring are more substantial for finely dispersed systems, which are characterized by solidlike properties. The existence of the solidlike state of an emulsion at low stresses is directly proven by the independence of the storage modulus on the frequency upon low-amplitude measurements of the viscoelastic properties of an emulsion [45].

It is of great importance that, even at a very high content of an aqueous phase (76 vol %), phase inversion is not observed for a W/O emulsion. At the same time, the apparent viscosity of such emulsions at low shear stresses is as high as 100 Pa s. The anomalous vis-

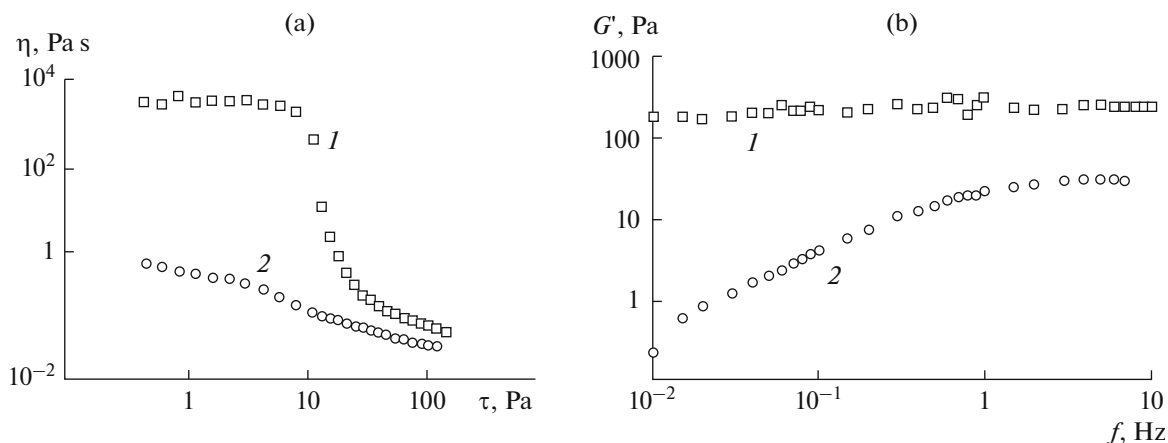


Fig. 3. Influence of average dispersed phase particle size of W/O emulsions with dispersed phase volume fraction of 0.76 on the dependences of (a) apparent viscosity on shear stress and (b) storage modulus G' on frequency: $d_{av} = (1)$ 12 and (2) 30 μm [55].

cosity caused by droplet flocculation and the formation of percolation structures has been found for W/O petroleum emulsions stabilized with natural components of oil alone [46]. Therewith, as the temperature is reduced from 50 to 20°C and the dispersed phase volume fraction is increased from 0.1 to 0.7, the apparent viscosity grows more pronouncedly as compared with the viscosity of initial oil (by a factor of as high as 40) in the absence of emulsion phase inversion.

Emulsions stabilized with solid particles are viscoplastic media characterized by a yield stress. Moreover, they exhibit thixotropic properties typical of gel-like structures [25]. The stability and rheological peculiarities of Pickering emulsions may be explained by the formation of a strong branched structure (network), which comprises “adsorption” layers of particles [56].

The existence of the yield stress and a high apparent viscosity of W/O emulsions of heavy oil are the main obstacles to the extraction and transportation of oil.

3. MODERN METHODS FOR IMPROVING TRANSPORT CHARACTERISTICS OF HEAVY OIL

Transportation of crude heavy oils can be optimized by means of destructive thermal actions, changes in flow regimes, or a decrease in oil viscosity. Different methods used for solving these problems are considered below.

3.1. Conversion of Heavy Oils in Resting Places

Interaction between high-molecular-weight components of oil and the formation of ordered structures are among the physicochemical factors providing heavy oil with high viscosity [57]. Cracking at even relatively low temperatures leads to removal of side aliphatic chains and rupture of aliphatic bonds in

asphaltenes. Cracking at $\sim 400^\circ\text{C}$ causes a substantial reduction the viscosity. This underlies numerous technological methods of the conversion [58–60]. In recent years, the THAI (Toe to Heel Air Injection) technology, i.e., a combination of in situ combustion and extraction of oil from a horizontal well, and its catalytic variant CAPRI (CAtalytic upgrading Process In situ), which manifested high efficiency, have been widely used. Catalytic hydrocracking leads to both the rupture of long-chain molecules and a reduction in the content of sulfur and nitrogen compounds, which are undesirable for oil processing. Subsequent catalytic hydrogenation occurring without destruction increases the fraction of saturated hydrocarbons. The method of in situ combustion is disadvantageous in that measures need to be undertaken for environmental protection and utilization of combustion products. In addition, valuable side components can be lost.

3.2. Changes in the Flow Regime

3.2.1. Transportation in pipelines with near-wall water layers [61–64]. A decrease in the viscous drag of a pipeline is provided by the formation of a low-viscosity liquid layer near its inside surface. The core-annular flow regime ensures the minimum pressure drop along a pipeline, as compared with other flow regimes of two immiscible liquids, and reduces the losses to 10% and below. This flow regime is stable, provided that the liquids are immiscible, have viscosities differing by several orders of magnitude, and close values of density (in another case, oil will float up in a pipeline, and the lubricating effect will disappear). The development of an instability (waves) at the interface may lead to the local formation of O/W emulsions, which also disturbs the flow regime. Another problem relevant to the annular flow is gradual oil sticking to pipeline walls, which, in the long run, blocks the flow. Deposits are formed on the internal surface of a pipe-

line due to wettability inversion caused by the presence of asphaltenes and naphthenic acids in oil. This effect can be substantially decreased by adding modifiers (e.g., sodium metasilicate) to an aqueous phase.

3.2.2. Laminarization of a turbulent flow [65–69].

According to the known Toms effect, in the case of a turbulent flow, the viscous drag may be decreased by adding small amounts (10^{-3} – 10^{-4} wt %) of a long-chain polymer. The effect becomes evident at some critical Reynolds number of about 2000, i.e., in the boundary region of the transition from a laminar to a turbulent flow. The efficiency of the action of polymers is enhanced with an increase in their concentration to a value at which an increase in the dynamic viscosity of a solution begins to be of significance. Micellar solutions of surfactants may be used in addition to polymers. Polymers with long hydrocarbon chains have a rather strong effect, which is, however, limited by the fact that they are degraded at high shear stresses. On the contrary, wormlike micelles may reorganize and restore their distorted structure under the conditions of shear stresses below some critical magnitude [70]. The use of micelle-forming surfactant–polymer mixtures noticeably extends the range of a laminar flow [71]. The Toms effect is widely used to reduce the viscous drag of both aqueous and hydrocarbon media. Polyethylene, polybutadiene, and polystyrene and its derivatives, as well as ethylene copolymers (in particular, with vinyl acetate) and other polymers, are used as additives for oil transportation. However, the application of this method to heavy oils encounters a number of difficulties associated with the low solubility of the additives, which causes their separation from oil being stored.

3.3. Decreasing Viscosity of W/O Petroleum Emulsions

3.3.1. Dilution with low-viscosity liquids. Dilution of heavy oil with light hydrocarbons or other solvents (gas condensate, kerosene, light crude oil, ethanol, ethers, etc.) have been used to advantage for a long time [72]. This makes it possible to decrease substantially both the viscosity and yield stress. For example, the addition of light oil (20%) decreases the viscosity by a factor of 26 and eliminates the yield stress, while the addition of ethanol (20%) leads to a tenfold reduction in viscosity [60]. The action of ethanol may be explained by the fact that, in addition to dilution, its presence prevents asphaltene molecules from aggregation [73]. The choice of an optimum ratio between the light and heavy fractions in oil composition has been described in [47]. Gas condensates (pentane and longer-chain paraffins) are more efficient than light oil is; however, they do not dissolve asphaltenes, the aggregation of which followed by sedimentation makes heavy oil instable in the course of transportation and subsequent storage [72].

Decreasing the viscosity of heavy oil by dilution requires large amounts of cheap and available diluents

(up to 20% for heavy oils and 25–50% for bitumens). Therefore, this method can be applied in places where, along with heavy oil, light oil or gas condensates are available [74]. Moreover, this method is economically sound only under the conditions of diluent recovery, which requires expenditure for its isolation, construction of an additional pipeline, etc. [72].

3.3.2. Thermal methods [58, 75]. Transportation of oil after heating or with heating along a pipeline (hot transportation) is a method widely used to decrease the viscosity of W/O emulsions of heavy oils. This method is rather efficient because of a high activation energy of viscous flow for W/O emulsions (it is ≈ 40 kJ/mol [57]). However, the thermal design of a pipeline requires taking into account many factors (heat transfer to an environment, heat of friction, oil heating due to paraffin crystallization, etc.), the action of which may cause local changes in the rheological properties of oil and, hence, instability of the flow. In addition, this method is disadvantageous in having high energy consumption, accelerated corrosion of pipes because of increased temperature, and ecological problems resulting from heating frozen ground in high latitudes. The application is especially limited for underwater pipelines. Moreover, an increased priming pressure is required when oil is thickened because of cooling under the conditions of a temporary interruption of the transportation.

3.3.3. Pour point decreasing [76]. An increased pour point is inherent in paraffinic crude oils with a high content of alkanes with a normal or slightly branched structure. Paraffin crystallization complicates the extraction and transportation of oil. One method for solving these problems is the use of depressants, the incorporation of which in small doses (commonly, 0.05–0.10%) substantially reduces the pour point and improves the fluidity of paraffinic crude oils at low temperatures. Being adsorbed on paraffin crystal nuclei, modifiers may hinder further nucleation, decelerate the growth of crystals [77], and prevent them from aggregation, which gives rise to the formation of extended structures, thus causing the appearance of a yield stress and a noticeable increase in viscosity. Poly(ethylene-co-vinyl acetate) copolymers, polymethacrylates, alkyl phenols, and numerous multifunctional polymer additives are used as depressants. Depressants are inefficient at temperatures higher than the pour point of heavy components of oil. The presence of water in W/O petroleum emulsions decreases depressant efficiency at low temperatures because of adsorption of the additives on ice crystals [78].

3.4. Inversion of Crude Oils into O/W Emulsions

Transformation of W/O petroleum emulsions into O/W emulsions is the object of many studies and patents, which have mainly been published within the last decade. The idea of transporting heavy oils in the form of O/W emulsions with low-viscosity dispersion

media was proposed as early as in the 1960s [79–81]. The feasibility of using this method in practice was successfully shown in 1963 on the island of Kalimantan (Indonesia), where an oil-trunk pipeline 238 km long was built with an annual flow rate of 3.7 million tons for transporting high-paraffin oil from an out-of-the-way deposit [82]. Works performed in the 1980s in Venezuela (Orimulsion® project [52]) stimulated the development of this approach to a great extent.

The authors of many reviews [19, 52, 83, 84] have arrived at the conclusion that this method has advantages over other technologies. It has appeared that the viscosity of O/W petroleum emulsions stabilized with hydrophilic surfactants is decreased as compared with crude oil much more strongly than it when oil is diluted with light hydrocarbons (Fig. 4). Moreover, this method is advantageous in its economy and higher ecological compatibility, because O/W bitumen emulsions can be used as fuels without preliminary removal of water, with CO₂ emission being decreased by 20% [52].

The colloid-chemical and rheological properties of O/W emulsions of heavy oil are discussed in detail in the next section.

4. O/W EMULSIONS OF HEAVY OIL

4.1. Formation Conditions of O/W Emulsions

The type of an emulsion is known to be determined by not only the nature of a stabilizing surfactant (the Bancroft rule), but also the ratio between the amounts of aqueous and oil phases in the emulsion (as a rule, a prevailing liquid plays the role of a dispersion medium). The presence of natural lipophilic stabilizers (surfactants and ultradispersed particles) in crude heavy oil strongly complicates the inversion of its W/O emulsions into O/W ones. This transformation can obviously take place only upon addition of a rather large amount of a hydrophilic surfactant with a high HLB value and a large amount of water. Sometimes, the phase inversion does not occur even in the presence of 70 vol % water. In this case, the apparent viscosity of an initial W/O emulsion may increase because of a rise in the volume fraction of a dispersed phase and the formation of a percolation structure [46].

At the same time, economic considerations dictate the necessity to minimize water content both upon oil pumping and at final stages of its transportation and processing. Therefore, in order to make emulsion phase inversion reasonable, it is necessary to properly select many parameters (surfactant HLB, optimum volume ratio between the phases, pH and ionic strength of an aqueous phase, etc.) that determine the stability, particle size distribution, and rheological properties of resulting emulsions [19, 52, 84–88].

Polyethoxylated nonionic surfactants, the efficiency of which is independent of water salinity, compose one of the classes of surfactants that are widely used for this purpose [19]. However, anionic surfac-

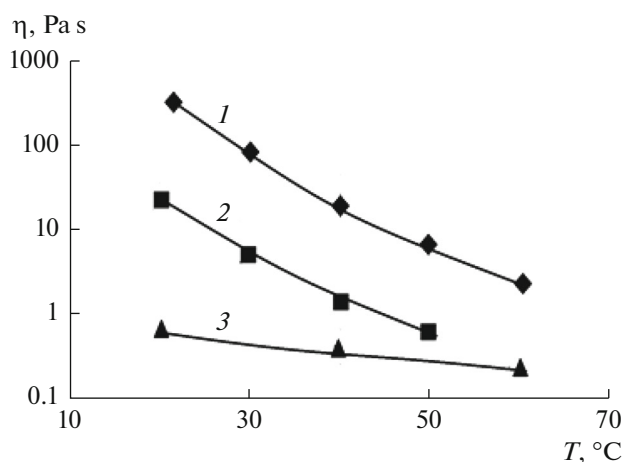


Fig. 4. Temperature dependences for viscosity of (1) initial heavy oil (API = 9, Orinoco), (2) oil containing a solvent (25 vol %), and (3) O/W emulsion containing 30% water [52].

tants are preferable because of a higher surface activity and a lower cost. In accordance with an increasing tendency toward stabilizing concentrated emulsions with mixed surfactants [89], attempts are being made to find an optimum combination of surfactants of different natures as applied to O/W emulsions with high concentrations of dispersed phases [90–94]. Therewith, hydrophilic surfactants synthesized in situ at interfaces by saponifying acidic lipophilic stabilizers present in crude oil upon addition of aqueous alkali solutions are used as system components (formation of so-called “in situ surfactants”) [19, 95, 96].

This method is widely used to obtain O/W emulsions at the stages of both oil extraction and transportation. The saponification is accompanied by an increase in HLB and the surface activity of surfactants (at aqueous phase pH ≈ 11, interfacial energy σ may decrease to 0.1 mN/m [97]). However, the interfacial energy may substantially increase (sometimes, by two orders of magnitude) with time, thereby destabilizing emulsions. Dynamics of variations in the interfacial tension depends on the character of variations in the nonequilibrium surface concentration of a surfactant, which, in turn, is governed by the ratio between the rates of adsorption, desorption, and diffusion of surfactants into aqueous or oil phases.

It has been shown [98] that the growth of σ may be prevented by adding surfactants exhibiting synergistic action with natural stabilizers. The incorporation of sodium dodecyl benzene sulfonate (SDDBS) at pH 11 is accompanied by a persistent reduction in σ to ultralow values (1.5×10^{-3} mN/m), while the addition of sodium dodecyl sulfate (SDS) or polyoxyethylene(40)isooctylphenyl ether (Triton X-405) to an aqueous phase has not a significant effect on the interfacial tension (Fig. 5). The strong influence of SDDBS is explained by the synergistic effect of the

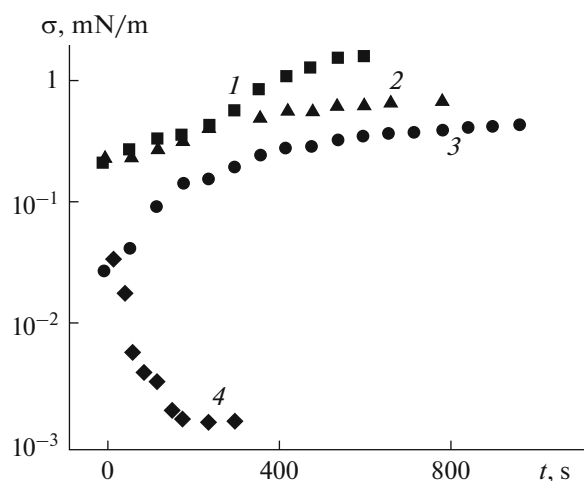


Fig. 5. Influence of hydrophilic surfactants on kinetics of interfacial tension of diluted heavy oil (containing 5% asphaltenes) at an interface with an aqueous 0.5 wt % NaCl solution at pH 11: (1) with no additives and in the presence of (2) 0.3% Triton X-405, (3) 0.1% SDS, and (4) 0.1% SDDBS [97].

formation of a stable layer from the incorporated and natural surfactants on the interface [97].

The addition of a surfactant with a high HLB to crude oil, which primordially contains natural lipophilic surfactants, may lead to their competitive adsorption and the formation of multiple water₁/oil/water₂ (W₁/O/W₂) and oil₁/water/oil₂ (O₁/W/O₂) emulsions [99]. The first-type emulsions consist of continuous phase W₂, in which large oil droplets O are distributed, with very small water droplets W₁ being contained in them. As a matter of fact, the dispersed phase in the double emulsion of this type is represented by an ultradisperse W/O emulsion. The sizes of internal small water droplets are, as a rule, no larger than 1 μm, whereas the sizes of the large oil droplets suspended in the continuous water medium vary in a rather wide range of 5–150 μm [98, 100]. Emulsions of the second type have a similar structure.

Double emulsions containing highly developed interfaces of different natures are much less stable than ordinary emulsions are because of the large sizes of external droplets and intense transfer of components between the internal dispersed phase and external dispersion medium under the action of osmotic pressure gradients [101–104]. However, the emulsions may retain their resistance to sedimentation and aggregation under the conditions of efficient stabilization.

Multiple petroleum emulsions of both types may arise during oil extraction and transportation [19, 52, 90, 105, 106]. However, information on the conditions of their appearance and rheological properties is scarcer. At the same time, W₁/O/W₂ emulsions may appear to be rather promising taking into account the goals of the oil industry.

4.2. Peculiar Rheological Properties of O/W Petroleum Emulsions

The high mobility of O/W petroleum emulsions, which is due to the low viscosity of aqueous dispersion media, is the main argument for their use in the oil industry. However, the rheological behavior of O/W emulsions depends on many different factors (composition of heavy oil, nature and concentration of a stabilizer, content of dispersed phase, sizes and polydispersity of particles, flow conditions, etc.). Therefore, numerous experimental results usually have a particular character, and the relevant regularities are, to some extent, approximate, as has been noted in a number of reviews [19, 52, 72].

The Newtonian behavior is inherent in emulsions of low and moderate concentrations (no higher than 50 vol % [43, 107]). For higher-concentrated emulsions, the viscosity anomaly is observed [19, 43, 72] due to interdroplet interactions leading, in the long run, to the formation of percolation structures.

As in the case of W/O emulsions, an increase in the total surface area of droplets with a reduction in their sizes (at a constant fraction of a dispersed phase) causes a growth in the emulsion viscosity (Fig. 6a); moreover, storage modulus G' is also significantly higher for finely dispersed emulsions in a wide frequency range [54] (Fig. 6b).

Emulsions with bimodal droplet size distributions are of particular interest, because they possess a decreased viscosity [54, 108, 109]. Indeed, mixing of two almost monodisperse emulsions yields a resulting emulsion with a substantially lower viscosity, provided that the average diameter ratio between the initial emulsions is rather high [54]. Therewith, bimodal emulsions are non-Newtonian liquids. However, at a certain volume fraction of a finely dispersed emulsion ($\psi = 0.35$), the viscosity anomaly is almost leveled (Fig. 7). In patent [110], an analogous method has been proposed for threefold decreasing emulsion viscosity, as compared with the viscosity of initial heavy oil by mixing two emulsions with average particle sizes of 20 and 5 μm in a ratio of nearly 3 : 1 (weight/weight). A stronger effect is achieved, when the fine fraction is initially polydisperse [52]. Thus, the targeted regulation of the dispersity of concentrated O/W emulsions as a method for decreasing their viscosity is a promising field of investigation.

Critical dispersed phase volume fraction ϕ_c corresponding to the closest packing of droplets without their deformation depends on the dispersity and pattern of the particle size distribution. For a monodisperse system, the value of ϕ_c is known to be 74%. This value increases for polydisperse systems with widening the particle size distribution and becomes still higher for a mixture of monodisperse particles of two different sizes.

Highly concentrated O/W emulsions ($\phi \geq 0.74$), in which deformed particles are separated by thin water

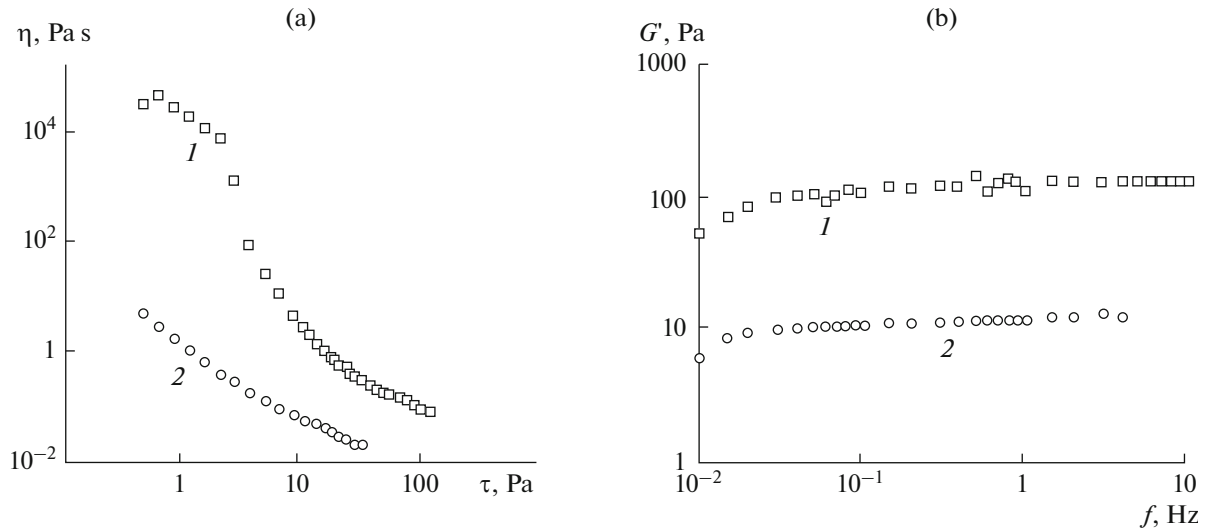


Fig. 6. Influence of average dispersed phase particle size of O/W emulsions with a dispersed phase volume fraction of 0.745 on dependences of (a) apparent viscosity on shear stress and (b) storage modulus on frequency: $d_{av} = (1) 5$ and $(2) 18 \mu\text{m}$ [55].

interlayers, are, as a rule, characterized by higher values of apparent viscosity [45]. For water–oil emulsions, this is observed when trying to decrease water content to 30 vol % and below (Fig. 8). In some cases, emulsions are thickened still greater because of the phase inversion. For example, emulsions with dispersed phase concentrations of 50–60 vol % and low apparent viscosities (<100 mPa s) were obtained in the presence of combined hydrophilic surfactants. However, a further rise in the oil content resulted in a three-fold increase in the viscosity, which grew with shear stress (rheopexy) (Fig. 9) [90]. The authors assumed that an $O_1/W/O_2$ double emulsion was formed in this case.

The stability and rheological behavior of emulsions at high pressures and temperatures were studied in [111], because such conditions are typical of enhanced oil recovery (EOR). O/W emulsions prepared from oil with the addition of a polymer (polyacrylamide) and a surfactant (SDS) containing and not containing nano-sized SiO_2 or clay particles at interfaces were compared. It was found that, in contrast to particle-free O/W emulsions, viscosity values of the Pickering emulsions remained unchanged at high temperatures (up to 100°C) and pressures (up to 30 MPa).

4.3. Destruction of Heavy Oil Emulsions

After being transported, O/W petroleum emulsions must be destroyed, with this destruction being a rather complex technological problem. First, since the density of heavy oil is close to water density, classical methods, such as gravitational separation or centrifuging, appear to be inefficient. Second, derivatives of asphaltenes and other natural surfactants may be retained at interfaces of O/W emulsions and hinder

the demulsification. Moreover, emulsion phase inversion, which is often difficult to prevent under the conditions of transportation, leads to the formation of ultradisperse systems, which are difficult to destroy because of the high viscosity and a large amount of present stabilizers.

Petroleum emulsions are destroyed by different methods, such as selective-wetting-based filtration, incorporation of de-emulsifiers destroying adsorption

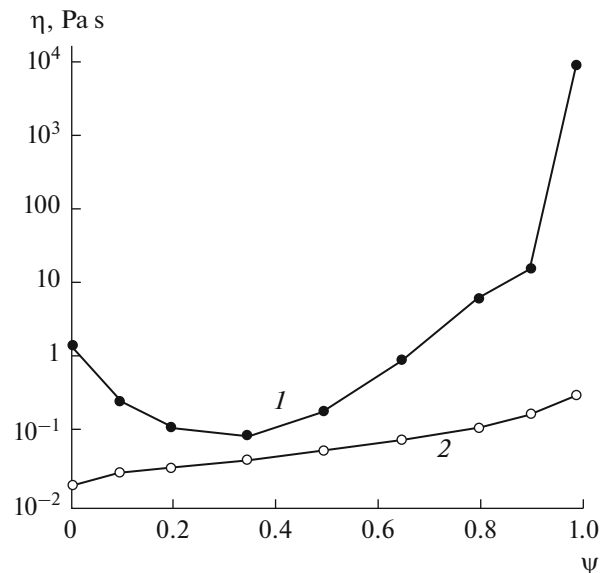


Fig. 7. Dependences of the apparent viscosity of emulsion resulting from mixing two emulsions with different dispersities (average diameters of 10 and $30 \mu\text{m}$) on volume fraction ψ of the finely dispersed emulsion at different shear stresses: $(1) 0.9$ and $(2) 30$ Pa. Dispersed phase volume fraction in both emulsions is $\phi = 0.745$ [55].

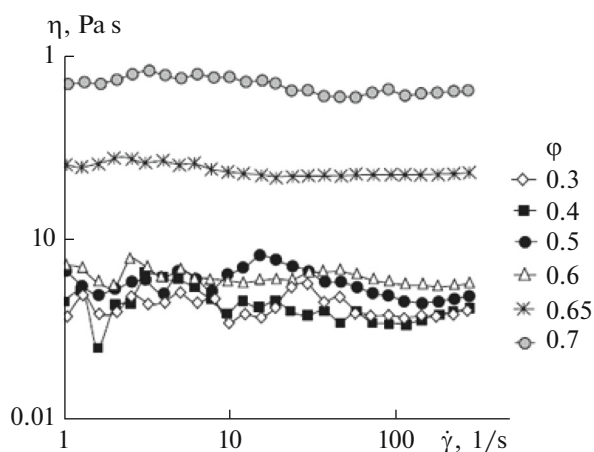


Fig. 8. Influence of dispersed phase volume fraction ϕ on the viscosity of O/W petroleum emulsions at different deformation rates [19].

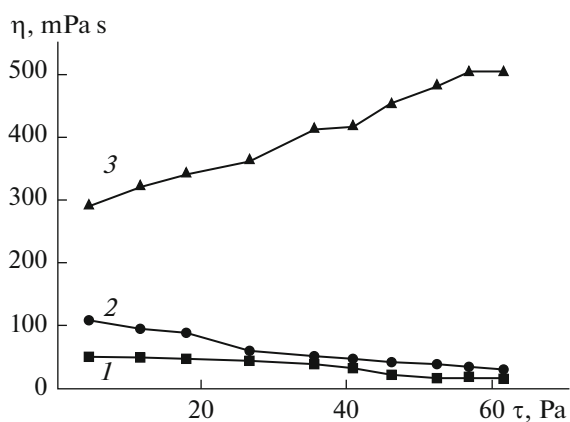


Fig. 9. Dependence of apparent viscosity on shear stress for O/W emulsions with different contents of oil: (1) 50, (2) 60, and (3) 70 vol % [90].

layers, the action of alternating or direct electric fields, etc. [112].

At present, methods are being developed for the formation of relatively stable petroleum emulsions that are easy to destroy after transportation. For this purpose, switchable ionic surfactants are used, the effect of which changes in the presence of volatile protonating or deprotonating agents. For example, saponification of fatty acids with ammonia solutions has been proposed for stabilizing O/W petroleum emulsions followed by heating for removal of ammonia (which can be than used repeatedly) and destruction of the emulsions [113]. Cationic and anionic surfactants have been shown to be efficient, with the former facilitating the formation of O/W emulsions in the presence of carbon dioxide and demulsification after its removal, with the latter acting in the opposite manner [114–116]. Good results were also obtained when using 2-(dimethylamino)ethyl methacrylate–butyl methacrylate copolymer for emulsification of extraheavy oil with an apparent viscosity of nearly 100 Pa s in the presence of CO₂. At a molar monomer ratio of 3 : 4, an emulsion with a viscosity of 31 mPa s was obtained, in which almost complete phase separation took place after CO₂ was removed by blowing nitrogen through the emulsion for 20 h [117].

CONCLUSIONS

Recently, the representation of heavy oil as a multicomponent colloidal system has become generally accepted. Numerous communications have been published devoted to the identification of natural adsorbable components, analysis of the composition and structure of interfacial layers, the study of the peculiar behavior of W/O water–petroleum emulsions, etc. Increasing preference is being given to the inversion of W/O petroleum emulsions into O/W emulsions as an

optimum method for facilitating its extraction and transportation. At the same time, some problems remain to be further studied (regularities of asphaltene adsorption, relation between the molecular structure of surfactants and their synergistic action, rheology of multiple emulsions, etc.).

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