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Formation of Emulsions in Paraffin and Highly Resinous Oils

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Abstract

The paper reports on the research results of the formation process of emulsions in paraffin and highly resinous oil varieties. The effect of the composition of resin-asphaltene components and aqueous phase content in oil on pour point, rheological properties, and the viscous flow activation energy of oil-in-water emulsions was demonstrated. As determined, large resistant globules of water were formed in oil-in-water emulsions where paraffin hydrocarbons, were prevailing; the pour point, viscosity, and the viscous flow activation energy were increased. Emulsions of highly resinous oils were characterised by the formation of structures with small globules of water, high viscosity and the low viscous flow activation energy. The power relationship of the size of water globules in oil-in-water emulsions on the ratio of the content of resin-asphaltene components and paraffin hydrocarbons was determined.

Key words: oil, emulsion, pour point, viscosity, viscous flow activation energy

INTRODUCTION

An increase in the fraction of the extracted watered hydrocarbon raw material requires the development of new methods for the adjustment of colloidal-chemical and structural-mechanical properties. Depending on the composition, properties of oil and reservoir water it is possible to form emulsions that are notable for high stability even under the effect of chemical reagents, *i.e.*, deemulgators, and electric fields. The stability of oil-in-water emulsions is determined by the quantity and composition of surfactants referred to as emulgators. The latter include asphaltenes, salts of naphthenic acids and heavy metals, mechanical impurities, paraffin microcrystals, and resins. Certain authors claim that the primary stabilizers of water-in-oil (W/O) emulsion are asphaltenes [1–4]. According to the data of [5, 6], asphaltenic molecules consist of small aromatic clusters, interconnected by aliphatic, sulphide, and ether/ester bridges. Peripheral substituents may be presented by unbranched and branched aliphatic

chains, and also by hydroxyl, carbonyl and other moieties. Components that have hydrophilic and hydrophobic properties may be distinguished in the molecular composition of emulgators. Such a composition of the species determines their trend towards aggregation even at relatively low concentrations [7, 8]. In the form of monomers, aggregates, and clusters asphaltenes are irreversibly adsorbed in the oil/water interface boundary, form adsorption layers with high structural viscosity on dispersed phase drops preventing coalescence, reduce interphase tension and therefore reduce the free energy of the system and increase the stability of the latter [9–11]. Asphaltene aggregation processes are accelerated when water is present. According to researchers [12], the driving force in this case is hydrogen bonding.

Resins play a significant part in the formation of emulsions. Being polar compounds with a lower molecular mass than asphaltenes, asphaltenes stabilise drops of water. However, when the asphaltenes/water ratio is increased above 0.6, emulsion formation is hindered, as resins make

solvate shells around asphaltenes increasing aggregate sizes and decreasing the migration of the latter towards drops of water [13].

The formation of emulsions is a dynamic process that is determined by regularities of the competitive adsorption on drops of water in various emulgators. Significant differences in the quantitative and qualitative composition of the major emulsifying components in oil have an effect on the formation process of the emulsion, the stability and structural-mechanical properties of the latter. The issue of separation of oil-in-water emulsions in heavy oil that form highly stable intermediate layers is especially acute. The latter are usually spontaneously organized at the interphase boundaries resulting from the adsorption of surfactants from solutions. In order to improve demulsification technologies, it is required to more clearly comprehend processes that proceed at a level of the composition of oil-in-water emulsions.

The objective of this research was to elucidate the effect of the composition of natural surfactants on the formation of oil-in-water emulsions, and also their rheological and colloidal properties of the latter.

EXPERIMENTAL

The research objects were paraffin and highly resinous oils. In order to prepare emulsions with reservoir water, the mixing device PE-0118 with a capacity of 150 W and a blade rotation rate of 1500 rpm was used. Mixing was carried out for 10 min followed by allowing to stand the resulting emulsions for 2 h at 20 °C.

The isolation of asphaltenes was carried out by the Golde cold method. The content of saturated and aromatic hydrocarbons, benzene and alcohol-benzene resins in oil was determined by column liquid adsorption chromatography.

Rheological parameters of the initial oil and emulsions were analysed using Brookfield LVDV-III Ultra rotational viscometer (USA). The temperature was maintained using a thermostat in the 20–30 °C range.

Viscosity is the exponential function of the viscous flow activation energy, E_a (kJ/mol):

$$\eta = A \cdot e^{E_a/RT}$$

where η , A , R , and T are dynamic viscosity, MPa · s, pre-exponential coefficient, universal gas constant, and absolute temperature, K, respectively.

The E_a value was determined as the angular coefficient of the linear relationship of the effec-

tive viscosity *vs* temperature in the coordinates $\ln(\eta) = f(1/T)$. The deviation against the linear law of the relationship for associated liquids is explained by the temperature effect on the value of the viscous flow activation energy due to the additional energy consumption for the breaking of structural bonds in the liquid.

The pour point of oil varieties and emulsions was analysed using the instrument of temperature indicators of oil products “Crystal”. The measurement error of pour point was 2 °C.

The dispersity (D) of oil-in-water emulsions was assessed by optical microscopy. Micrographs of the investigated samples were collected with Axio Lab A1 biological microscope (Carl Zeiss) equipped with Axiocam ERc 5s digital camera using 400- and 800-fold magnification. Relying on the analysis of micrographs of emulsions with distilled and reservoir water, the curves of the droplet size distribution (DSD) were plotted; the maximum (d_{max}) and minimum (d_{min}) diameters of globules of water were determined, and also the arithmetic average diameters (d_a) and dispersity were calculated.

RESULTS AND DISCUSSION

Table 1 reports physicochemical parameters of oil varieties. The ratio of the content of resin-asphaltene components (RAC) and paraffin hydrocarbons (PHC) is 0.7–5.5, in highly resinous oil – 25.2–95. Positive values of pour point are typical for paraffin oil, except for Verkhnechonskoe oil, wherein the RAC/PHC ratio is 5.5. The crystallization of PHC in oil determining pour point takes place according to classical mechanisms of nucleation and growth under certain thermodynamic conditions, which leads to the formation of submicron primary crystallites from a complex mixture of hydrocarbons. These crystallites are combined into micro-sized particles followed the association of the latter and the formation of structures that capture the liquid phase. In this case, RAC act as inhibitors, changing the crystallization of paraffin structures and reducing oil pour point.

Using the mathematical analysis of the submitted data, a linear relationship between the pour point and the RAC/PHC ratio for paraffin oil varieties and emulsions based therefrom was determined with an increase in the fraction of resins and asphaltenes: there is a steady reduction in pour point (T_p) (see Tables 1 and 2). Paraffins are prevailing in the composition of the dis-

TABLE 1

Physicochemical characteristics of oil varieties

Field	Content, mass %			RAC/PHC	T_p , °C
	Oils (PHC)	Resins	Asphaltenes		
<i>Paraffin oil</i>					
Verkhne-Salatskoe	95.1 (11.2)	4.9	Absent	0.4	+16.1
Mamurinskoe	87.3 (18.2)	9.9	2.8	0.7	+18.7
Festivalnoe	82.0 (20.0)	15.9	2.1	0.9	+20.0
Yuzhno-Tabaganskoe	85.8 (7.8)	13.0	1.2	1.8	+8.3
Archinskoe	84.3 (6.1)	15.1	0.6	2.6	+6.1
Verkhnechonskoe	77.2 (3.6)	19.7	0.1	5.5	-45.0
<i>High-viscosity oil</i>					
Tagulskoe, well 26	81.0 (0.2)	17.7	1.3	95.0	-30.0
Same, well 103.	88.6 (0.45)	10.0	1.4	25.2	-58.0
Usinskoe	59.0 (1.1)	31.1	9.9	37.3	-18.0

persed phase (RAC/PHC < 1) for oil varieties from Festivalnoye and Mamurinskoe fields. The effect of water cut on T_p of emulsions is minor. The pour point of emulsions based on oil varieties with the prevalence of RAC in the composition of these species (RAC/PHC > 2) is significantly increased with an increase in aqueous phase content.

An increase in the RAC/PHC ratio in emulsions of paraffin oil varieties results in a decrease in viscosity and pour point.

A rise in the water cut of oil varieties in the composition of the dispersed phase of which paraffins are prevailing (RAC/PHC < 1) contributes to an increase in the viscous flow activation energy.

There is a decrease in E_a required to destroy the paraffinic structure therein in emulsions where the RAC fraction is prevalent. When the stable paraffin structure is formed, both the condition of the entire thermodynamic system and the contribution of natural surfactants are cru-

TABLE 2

Rheological properties of paraffin oils and water-in-oil emulsions

Field	Water content in emulsions, mass %	η^{30} , MPa · s	E_a , kJ/mol	T_p , °C
Mamurinskoe	0	144.0	33.5	18.7
	10	196.0	47.4	19.8
	30	575.9	43.1	20.2
	50	1207.7	31.8	22.3
Festivalnoe	0	128.4	33.3	20.2
	10	203.1	55.6	20.5
	30	239.3	27.2	19.8
	50	375.6	39.4	19.6
Yuzhno-Tabaganskoe	0	119.9	28.8	8.3
	10	259.8	33.0	7.0
	30	319.9	34.9	6.6
	50	420.1	35.6	9.4
Archinskoe	0	72.3	29.0	6.1
	10	202.4	21.7	7.0
	30	276.1	26.5	11.0
	50	383.4	27.1	13.4
Verkhnechonskoe	0	9.1	19.9	-45.2
	10	11.7	20.2	-51.2
	30	22.3	-	-42
	50	88.4	16.2	-23

* η^{30} – viscosity at 30 °C.

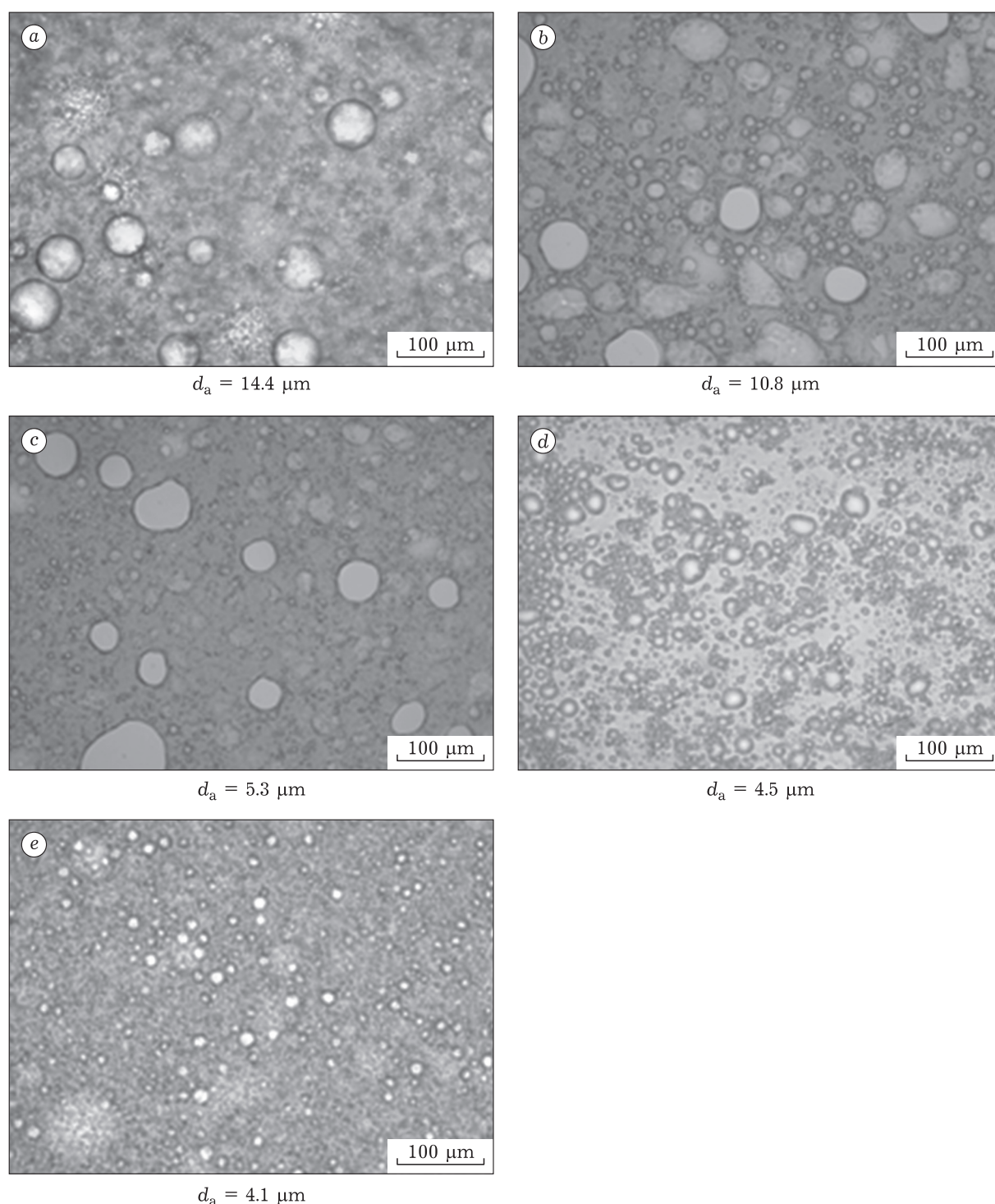


Fig. 1. Micrographs of 30 mass % water-in-oil emulsions based on oil varieties at a ratio of RAC/PHC < 1 (a and b) and RAC/PHC > 1.8 (c - e). RAC/PHC ratio: 0.7 (a), 0.9 (b), 1.8 (c), 2.6 (d), and 5.5 (e).

cial. As determined, there is a liner reversed relationship between the viscous flow activation energy (E_a) and a ratio of the content of components in the dispersed phase for paraffin oil varieties and oil-in-water emulsions. The more resins and asphaltenes the oil system contains, the lower

heat energy is required to be consumed in order to destroy the paraffin gel structure.

The data for plastic viscosity η at 20 °C were acquired for highly resinous oil (RAC/PHC > 25) varieties (Table 3). As determined, there is a direct linear relationship between viscosity and resin

TABLE 3

Plastic viscosity of highly resinous oil varieties and oil-in-water emulsions from different deposits at 20 °C, MPa · s

Field	Resin content, mass %	Viscosity η^{20} of emulsion with varying water content, mass %			
		0	10	30	50
Usinskoe	31.1	536	879	2420	5510
Tagulskoe, well 26	17.7	339	435	890	2048
Same, well 103.	10.0	79	113	191	330

content for the former. In other words, the higher is resin content in the system, the more significant is the contribution of the aqueous phase into viscosity. An increase in resin content by 1.7 times increases the viscosity of emulsions by 6–8 times. Herewith, the water-in-oil emulsion of Usinsk oil with the maximum content of water and resinous components shows the maximum viscosity.

In order to assess the contribution of natural surfactants into the formation of emulsions and the stability of the latter, research on the microstructure of the aqueous phase was performed. According to the literature data, the content and the size of aqueous phase globules have a substantial effect on the stability of water-in-oil emulsions [14]. Depending on physicochemical properties of oil and water, and also on formation conditions of emulsions, the size of globules of the aqueous phase presented by distilled water may be most diverse. Micrographs of 30 % emulsions with the varying RAC/PHC ratio in oil varieties are given in Fig. 1, *a* and *b*.

The analysis of the data of micrographs has enabled to calculate average diameter (d_a) values of water. There is the highest size of globules for unstable emulsions of Verkhne-Salatskoe oil at a ratio of RAC/PHC = 0.4. As determined, water-in-oil emulsions in reliance on oil with RAC/PHC < 1 in the composition of natural surfactants of which PHC are prevailing, are characterised by

the average diameter of globules of water between 10.8 and 14.4 μm (see Fig. 1, *a* and *b*). When the RAC/PHC ratio is increased, the size of globules is decreased. The aqueous phase in water-in-oil emulsions with a RAC/PHC ratio higher than 1.8 is mainly presented by globules of the same size – the average diameter (d_a) is varied in a range between 4.1 and 5.3 μm (see Fig. 1, *c–e*).

The relationship of the size of globules of water *vs* the RAC/PHC ratio was determined for water-in-oil emulsions. The former is presented by an exponential function with a high correlation coefficient (Fig. 2).

An increase in the water cut of emulsions leads to variations in the distribution of globules of water according to size (Table 4).

When aqueous phase content in emulsions at a RAC/PHC ratio of 0.7 is increased between 10 and 50 mass %, there is a significant increase in the size of large globules to 100 μm and a decrease in dispersity, D (the value reversed to average diameter, d_a). The maximum diameter (d_{max}) of globules for 50 % emulsions reaches 15 μm with an increase in the RAC/PHC ratio to 3.1. A decrease in the size of globules of water results in an increase of emulsion dispersity and stability.

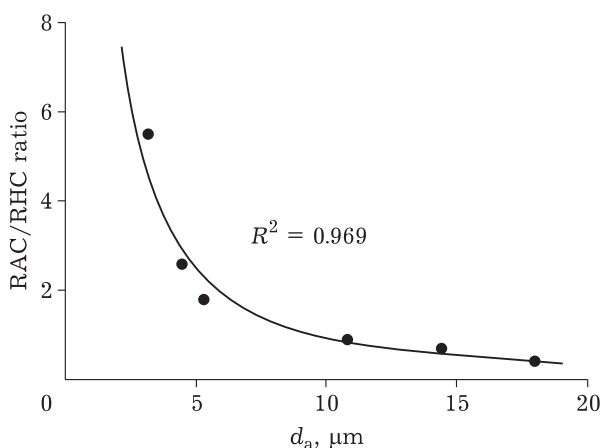


Fig. 2. Average globule diameter (d_a) in 30 mass % water-in-oil emulsions *vs* RAC/PHC ratio in paraffin oil varieties.

TABLE 4

Water phase content and RAC/PHC ratio in oil varieties *vs* globule diameter of water phase in emulsions

Water content, mass %	RAC/PHC ratio					
	0.7			3.1		
	d_{max} , μm	d_a , μm	D , μm^{-1}	d_{max} , μm	d_a , μm	D , μm^{-1}
10	24.4	6.4	0.15	6.0	3.7	0.27
30	36.0	8.3	0.12	12.0	4.1	0.24
50	99.0	10.8	0.09	15.0	6.3	0.16

Note. D – dispersity (the value reversed to the average radius, d_a).

CONCLUSION

The relationship between the ratio of the content of resin-asphaltene components and paraffin hydrocarbons, rheological characteristics and colloidal properties of water-in-oil emulsions has been determined. With increasing the RAC/PHC ratio in oil between 0.7 and 5.5, plastic viscosity and emulsion pour point are reduced. When blocking paraffin crystals, resin-asphaltene components (RAC) facilitate a decrease in the viscous flow activation energy required to destroy the paraffin gel structure in oil dispersed systems.

The effect of the composition of natural surfactants on the formation process of water-in-oil emulsions and the stability of the latter has been demonstrated. Unstable large globules of water capable of coalescence are formed in emulsions where paraffin hydrocarbons are prevailing (SAC/PHC < 1). When aqueous phase content is increased, the quantity of natural surfactants is reduced, which is accompanied by a decrease in the strength of the structure. The formation of strong structures with small globules of water, high viscosity and low values of the viscous flow activation energy is typical for emulsions of highly resinous oils.

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