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I. V. Loskutova, N. A. Nebogina, G. I. Volkova, and N. V. Yudina



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Effect of Natural Surface-Active Substances on the Rheological Properties of Emulsions

I. V. Loskutova^{a)}, N. A. Nebogina^{b)}, G. I. Volkova, and N. V. Yudina

Institute of Petroleum Chemistry SB RAS, Tomsk, 634055 Russia

^{a)} Corresponding author: loskyu@ipc.tsc.ru

^{b)} nebogina@ipc.tsc.ru

Abstract. The effect of natural surface-active substances on the formation of emulsions in oils with different content of resin-asphaltene components (RAC) and paraffin hydrocarbons (PHC) (RAC/PHC from 0.7 to 95) is studied. The influence of oil composition and content of aqueous phase on microstructure, rheological properties, and activation energy of viscous flow of water-oil emulsions is shown. For oils with the ratio RAC/PHC < 1, the increase in water cut results in an increase in viscosity, activation energy of viscous flow, and pour point.

INTRODUCTION

The stability of water-oil emulsions is determined by the amount and composition of natural surface-active substances (surfactants). Among these are asphaltenes, salts of naphthenic acids and heavy metals, mechanical impurities, microcrystals of paraffins and resins. These substances, adsorbed at the interface, form adsorption layers with a high structural viscosity on the water droplets. These adsorption layers impede coalescence and reduce interfacial tension, which results in a decrease of free energy of the system and increase of its stability. Stabilization of emulsions is a dynamic process, which is determined by the laws of competing adsorption on water drops of various emulsifying substances [1].

Asphaltenes play a major role in the stabilization of water-oil emulsions. A large number of works are devoted to the role of asphaltenes in the stabilization of water-in-oil emulsions [2–4]. It was shown in [5–7] that oils subjected to deasphalting are incapable of forming stable emulsions, because their stability depends on the percentage of asphaltenes. When asphaltenes are in a colloidal dispersed state close to the point of their flocculation, they exhibit the highest emulsifying ability [8, 9]. If a significant part of the emulsifiers is converted from a colloid solution to a regular one, the emulsifiability of the oil will be significantly reduced. Colloid aggregates of asphaltenes are sterically stabilized by solvating shells from resin molecules [7].

Significant differences in the quantitative and qualitative compositions of the main emulsifying components of oils are reflected in the process of emulsion formation, its stability and structural and mechanical properties. The problem is particularly acute for breaking of water-oil emulsions of heavy oils, which form highly stable intermediate layers. The latter are usually spontaneously organized at the interface boundaries as a result of the adsorption of surfactants from the solutions. Knowledge of the composition of the emulsifying components allows us to determine the type of emulsion stabilizer and to recommend an effective method for the breaking of water-oil emulsions. To improve the technologies of demulsification, a clearer understanding of the processes occurring at the level of the water-oil emulsion structure is required.

The aim of the work was to study the effect of the composition of natural surfactants on the formation of water-oil emulsions, their rheological and colloidal properties.

EXPERIMENTAL

The objects of investigation were paraffinic oils with a ratio of the content of resinous-asphaltenic components to paraffinic hydrocarbons RAC/PHC = 0.7–5.5 and highly resinous oils with a RAC/PHC ratio 25 to 95.

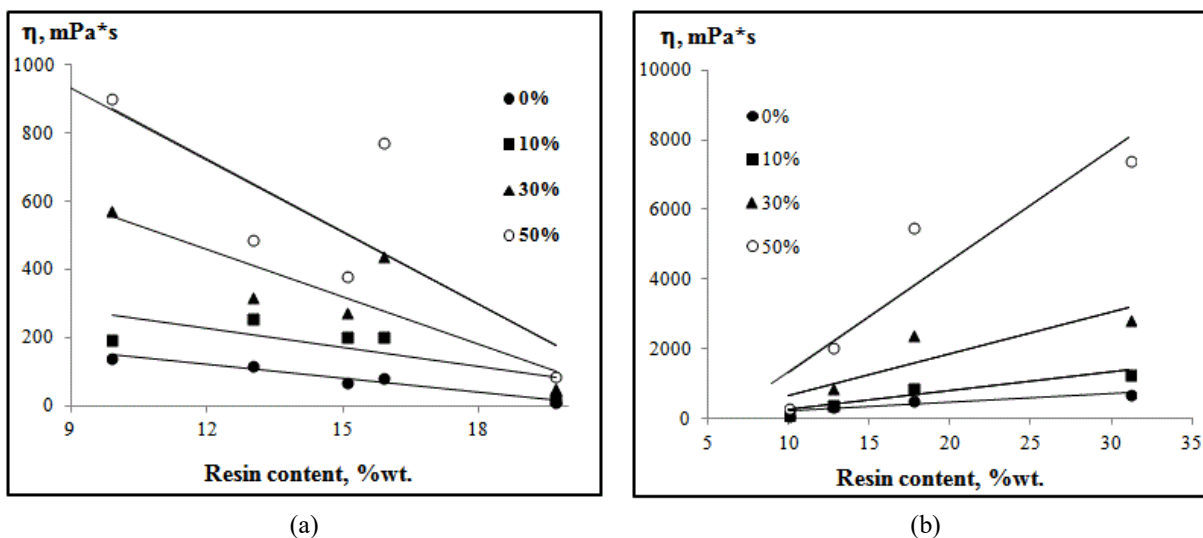


FIGURE 1. Plastic viscosity η of oils and emulsions versus resin content: (a) paraffinic oils; (b) highly resinous oils

A PE-0118 mixing device with 150 W of power and 1500 rpm blade rotation speed was used to prepare the emulsions with the produced water. Mixing was carried out for 10 min, followed by keeping the resulted emulsions for 2 hours at 20°C. The precipitation of asphaltenes was carried out according to the Golde “cold” method. The content of saturated and aromatic hydrocarbons, benzene and alcohol-benzene resins in oils was determined by column liquid-liquid adsorption chromatography. The dispersion of water-oil emulsions was assessed by optical microscopy (Axio Lab A1, Carl Zeiss) at 400 and 800 times magnification. The rheological parameters of the initial oils and emulsions were measured using a Brookfield LVDV-III Ultra rotary viscometer (USA). The activation energy of viscous flow E_{act}^{vf} was determined as the slope of the linear effect of viscosity against the temperature in coordinates $\ln \eta = f(T-1)$. For nonlinear dependences it was determined from the slope of the selected straight line portion or by the slope of the curve.

RESULTS AND DISCUSSION

Analysis of the rheological properties of oils and water-oil emulsions on their basis made it possible to establish a relationship between the content of resins in the initial oils and the structural-mechanical characteristics of emulsions. The increase in resin content in paraffinic oils is accompanied by a decrease in the viscosity of oils and emulsions. Increase in the amount of the aqueous phase in emulsions of oils containing resins up to 10 wt. % results in a sharp increase in viscosity (Fig. 1a). For emulsions based on oils with a resin content of about 20 wt. % the effect of aqueous phase on viscosity of the systems under study is insignificant.

Highly resinous oils and emulsions are characterized by a linear dependence of the viscosity on the resin content: the higher the content of resins in the system, the more significant the contribution of aqueous phase into viscosity. An increase in the aqueous phase in emulsions based on oils with a fraction of resinous components of not more than 10 wt. % has an insignificant effect on the viscosity characteristics (Fig. 1b). The water-oil emulsion with the maximum content of water and resinous components is characterized by the highest viscosity.

The formation of stable water-oil emulsions depends mainly on the RAC/PHC ratio, which is associated with the formation of rigid films on water globules and affects the structural and mechanical properties of water-oil systems [10]. The increase in the RAC/PHC value in emulsions of paraffinic oils results in a decrease in the plastic viscosity and pour point. The increase in water cut in oils, whose dispersed phase contain predominantly paraffins ($RAC/PHC < 1$) contributes to the increase in structural strength (viscosity, activation energy of the viscous flow E_{act}^{vf} , and pour point). The study emulsions are characterized by an inverse linear dependence of the activation energy and the pour point on the content of the components of the dispersion medium (Fig. 2b). In emulsions with a predominance of the RAC fraction, the values of E_{act}^{vf} necessary for the structure destruction are observed to decrease.

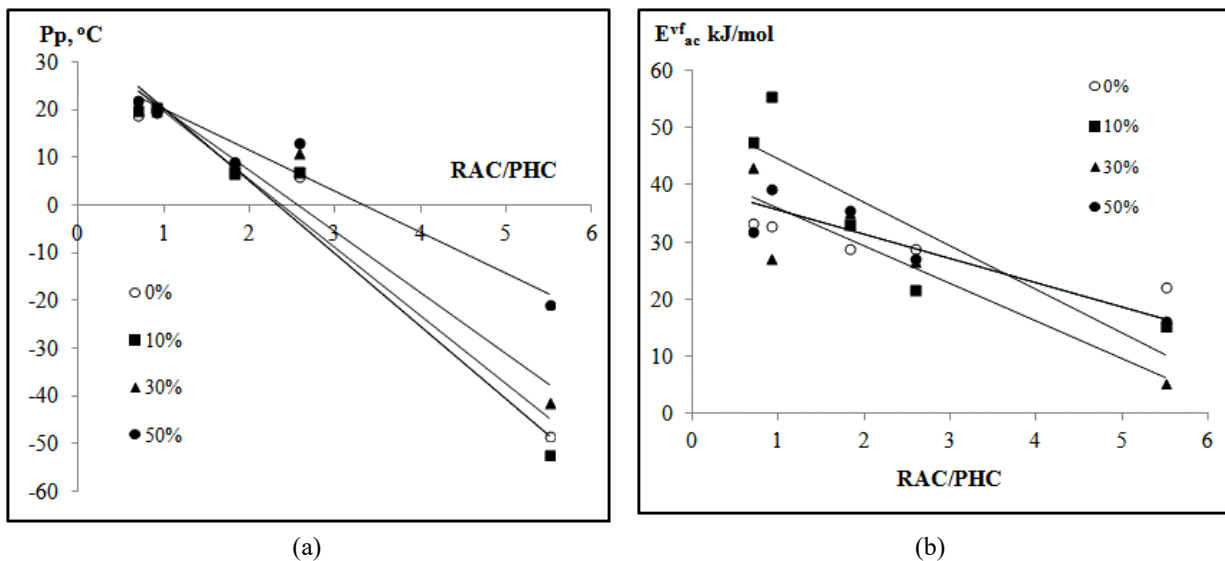


FIGURE 2. Dependence of pour point (a) and activation energy of viscous flow (b) of paraffinic oils and emulsions on the RAC/PHC ratio

Analysis of microphotographs of 30 vol. % emulsions of resinous paraffinic oils under study (RAC/PHC = 0.7/5.5) allowed to calculate average values of droplet diameters (D_{av}) of the water phase (Fig. 3).

The content and size of the aqueous phase droplets significantly affect the stability of water-oil emulsions [11]. Depending on the physical and chemical properties of oil and water, as well as the conditions for the formation of emulsions, the droplet sizes can be most diverse. In water-oil emulsions with the predominance of paraffinic hydrocarbons (RAC/PHC < 1), large stable globules with a diameter of 11–14 μm are formed. The high content of solid paraffinic hydrocarbons enhances the stabilizing effect of asphaltenes in the formation of water globules.

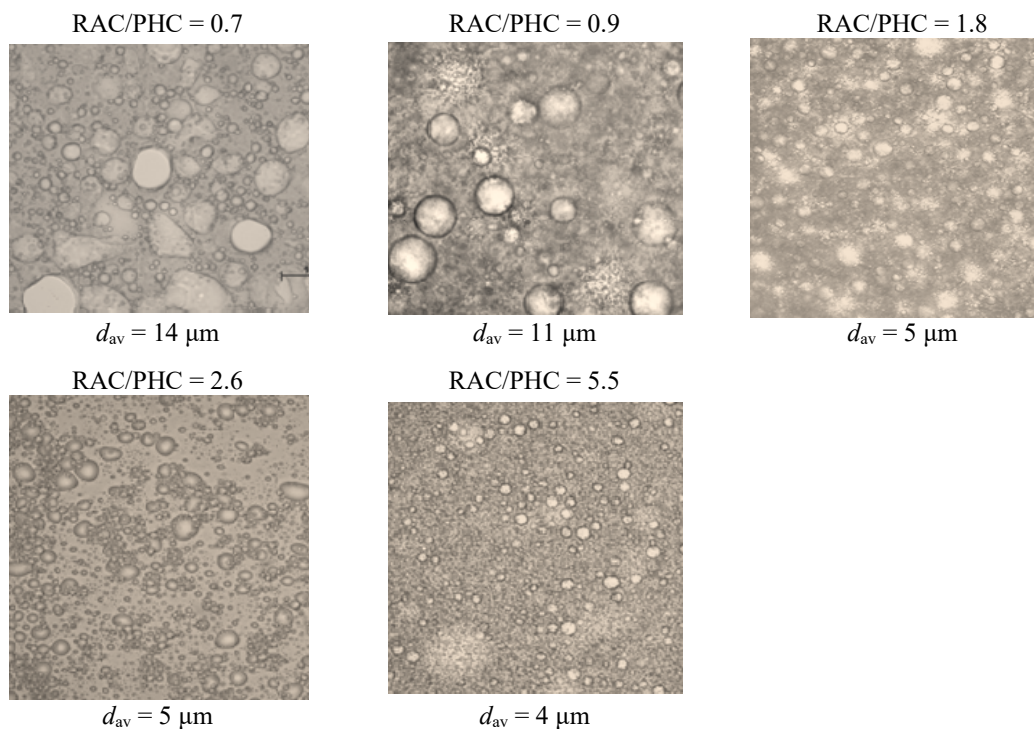


FIGURE 3. Micrographs of 30 vol. % emulsions of oils with different RAC/PHC ratios

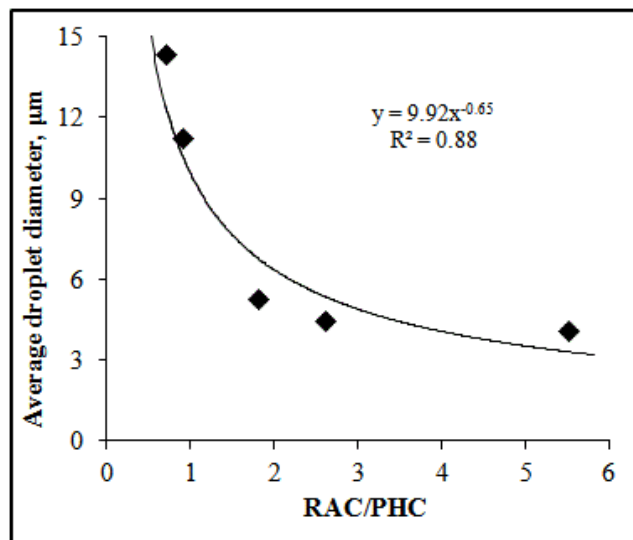


FIGURE 4. Dependence of the average droplet diameters in 30 vol. % emulsions of paraffinic oils on the RAC/PHC ratio

At a higher RAC/PHC ratio 1.8–5.5, the dispersed phase is represented by particles of smaller diameter (4–5 μm). The dependence of changes in the size of water droplets in the water-oil emulsions under study on the RAC/PHC ratio in oils is a power function with a high correlation coefficient (Fig. 4).

CONCLUSIONS

The effect of the composition of natural surface-active substances on the formation of water-oil emulsions and their stability is shown. In water-oil emulsions with a predominance of paraffinic hydrocarbons ($\text{RAC/PHC} < 1$) large stable water globules are formed and the pour point, viscosity, and activation energy of the viscous flow increase. With the increase in the water phase in oil, the amount of natural surfactants in the adsorption layers at the interface decreases, which results in a decrease in the structure strength. For emulsions of highly paraffinic oils, a presence of phase transition is characteristic when the temperature is raised and the structure of high molecular weight paraffins is destroyed. Emulsions of highly resinous oils are characterized by the formation of fragile structures with small water globules, high viscosity, and low values of activation energy of viscous flow.

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