The influence of dispersing additive on the paraffin crystallization in model systems

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Abstract. The work is dedicated to investigation of the influence of dispersing additive on the paraffin crystallization in model systems. A new method to determine the paraffin saturation point of transparent solutions based on the phenomenon of light scattering has been proposed. The linear relationship between the values of critical micelle concentrations of the additive and the quantity of paraffin in solution has been obtained. The influence of the model system composition on the paraffin crystallization has been studied.

1. Introduction
One way to improve rheology properties of high-paraffin oils is application of additives. They inhibit deposit formation or decrease its intensity. Mechanism of dispersing additives action has been researched in diesel fuel and oils [1, 2]. However, mechanism of dispersing additives action in terms of hydrocarbon paraffin solution has not been studied yet. High-molecular paraffin hydrocarbons were the reasons for paraffin build-up in oil pipelines. Therefore, the important task is to study the influence of additive on high-molecular paraffin hydrocarbons when ambient temperature decreases. The aim of the work is to study the influence of dispersing additives C-5A on the process of paraffin crystallization in model systems.

The effectiveness of dispersing additives C-5 action on the process of paraffin crystallization was evaluated by two parameters: the paraffin saturation point of model system and the paraffin pour point.

2. Experimental procedure

2.1. Materials
The process of paraffin crystallization was investigated using model paraffin–heptane system, which is one of the most common solutions in research of paraffin crystallization. Solid paraffins correspond to GOST – 23683-89 (the Russian Federation). Chromatographic grade *n*-heptane was used as a solvent. All experiments were performed on freshly prepared paraffin solutions in *n*-heptane. Paraffin concentration in *n*-heptane was 4%, 6% and 10% of the total mass.

Alkenylsusinimide C-5A was used as dispersing additive, which is 40% concentrate of alkenylsussinimide group in mineral oil and unreacted polybutylene. The additive was a viscous liquid, which was dissolved in toluene with mass ratio 1:1. To study the influence of dispersing additive on the paraffin crystallization, additive concentrations in paraffin solution were 0.03; 0.06; 0.08 and 0.1% of mass. At the beginning of every experiment, the cuvette with the studied solution was dispersed 15 seconds by ultrasound wave to mix all components. Every cuvette was used for one model system. Cuvettes had a cylinder form with diameter 15 mm.

2.2. Method and equipment

Paraffin saturation point is a main parameter which characterizes phase state «liquid phase – solid phase». However, it should be noted that standard method to determine the paraffin saturation point has not been found. Some methods to determine this characteristic can be listed: visual, refractometric, photometric, ultrasonic and viscous method.

The "PhotoCor Complex" equipment was used to determine the paraffin saturation point by the method of photon correlation spectroscopy [3, 4]. To determine temperature models more accurately, the equipment was modified by a temperature sensor DS18B20, which was placed in the thermostat (interval measurement is from -10 ºC to 85 ºC, accuracy ±0,5 ºC). The use of temperature sensor is caused by the cooling process. The cooling process is a dynamic process, in which cooling speed is faster than the speed of temperature distribution in the thermostat. As the result, temperature of the thermostat and the temperature in the cuvette were different. Temperature difference increases in growth of cooling speed. In this paper model system was cooled from 50 ºC to 5 ºC with the speed 0,05 ºC per minute. All experiments were conducted at atmospheric pressure.

A semiconductor laser beam with a wavelength λ = 654 nm was used as a radiation source. The main measuring tool of "PhotoCor Complex" device is photoelectron multiplier tube (Photocor-PC1), which operates in the photon counting mode. The present element of the equipment allows tracking a light scattering intensity change and consequently to determine the beginning of the phase transition in the disperse system. Photicor-PC1 was placed at an angle 90^0C in all experiments.

The main element of the control and data analysis unit in "PhotoCor Complex" equipment is a programmable correlator which provides automatic control of the instrument operation according to the algorithm. It can also measure integrated light scattering intensity. In our research, autocorrelated function fluctuation of light scattering was recorded repetitively in cycles. The time of the cycle was 3 minutes. The cycle interval is from 1 to 1000 (figure 1a). Thermosensor data was represented in log. By the input data the dependence of the light scattering intensity on the temperature was drawn (figure 1b).

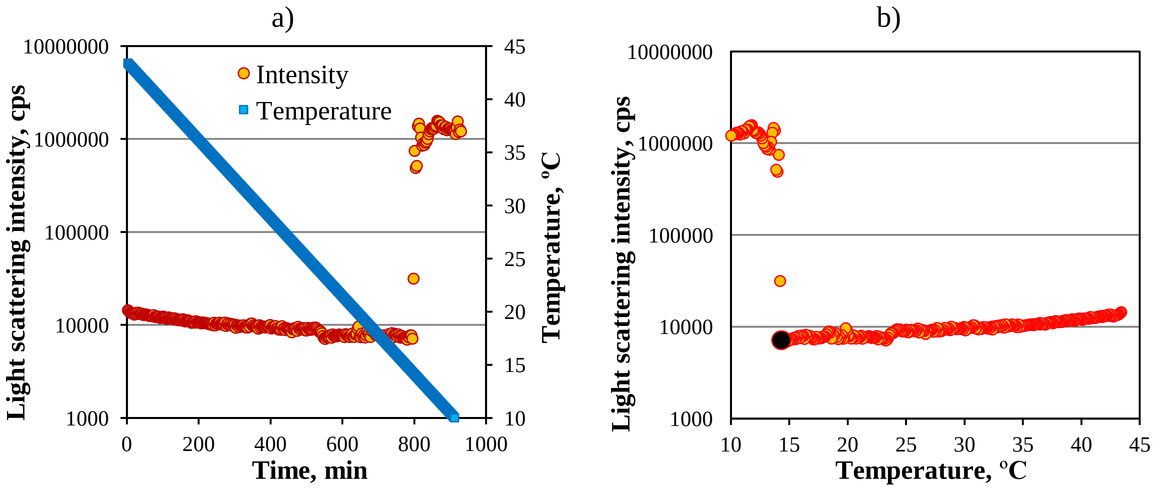

Figure 1. Procedure to determine the paraffin saturation point model system in "PhotoCor Complex" equipment: a) – input data; b) – dependence of the light scattering intensity on the temperature.

In this dependence, the transition change light scattering intensity was shown in the cooling process of the model system. According to the Rayleigh theory, light scattering intensity depends on particle radius (all other conditions being equal) by equation $I \sim R^6$ [5]. The intensity growth for two orders of magnitude indicated increasing radius of paraffin particles and consequently their crystallization. Therefore, the observed break corresponds to initiation of the new coexistent phase (paraffin crystals). We can assume that temperature at the first point of the break is the paraffin saturation point of the model system (figure 1b).

The paraffin pour point of solution was determined by the "CRYSTALL" device which has been created at the Institute of Chemistry of oil Siberian Branch Russian Academy Science (accuracy $\pm 0{,}5^0$C). The main element of the device is a head sensor. In the cooling process, the head sensor rotates and contacts the model system. The rotation speed of the head sensor decreases in the cooling process. The pour point was measured by the speed rotation of the head sensor.

3. Experiments and results

3.1. Critical micelle concentration of the additive in paraffin–heptanes solution

During the work phase, behavior of the additive in paraffin–heptane system was investigated. The model system contains two components which were dissolved in *n*-heptane. Therefore, it is necessary to determine the behavior of each component and the joint impact they have on model systems.

The experiment was performed as follows: the cuvette was placed in the thermostat; the temperature rose up to 50^0C; then the temperature was stabilized for 30 minutes and the light scattering intensity was studied when investigated parameters change (paraffin concentration and additive concentration). It should be noted that to study the phase behavior of dispersing additives, model solutions with additive concentrations of C-5A from 0.03% to 2% of total mass were prepared. Figure 2 shows the dependence of the light scattering intensity on the system composition.

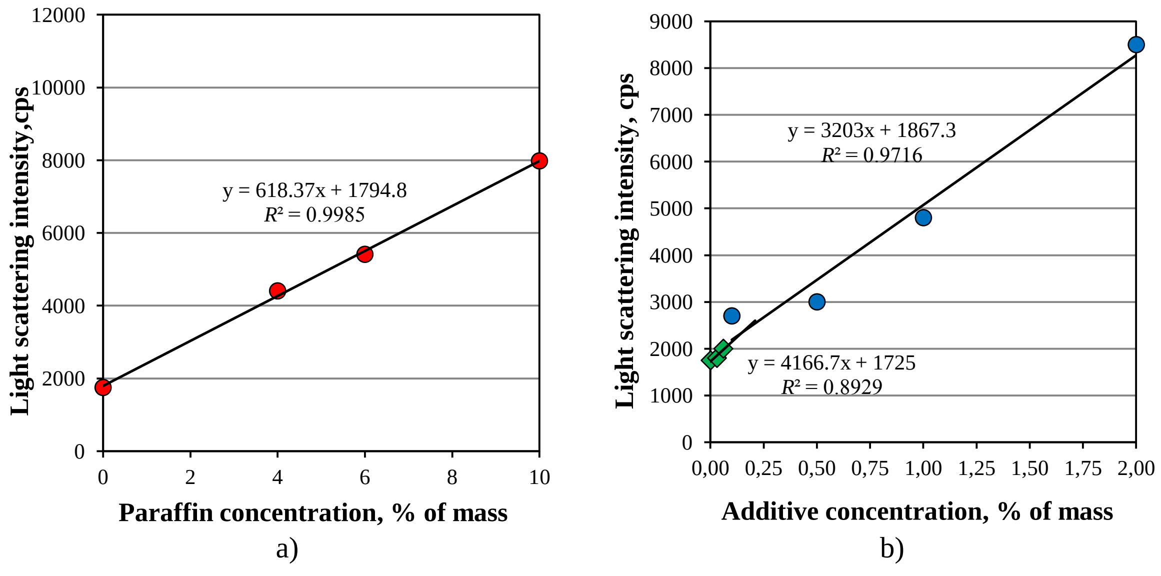

Figure 2. Dependence of the light scattering intensity on the model system composition: a) paraffin–heptane system; b) additive–heptane system.

Figure 2a demonstrates that the light scattering intensity was linearly dependent on paraffin concentration of the system. The reliability of approximation (R^2) was close to unity. This dependence indicates the paraffin presence in *n*-heptane in molecular state. The assumption corresponds to the Rayleigh theory, in which light scattering intensity is directly proportional to concentration of particles at constant value of their radius [5]. A small break of the curve, approximating the dependence of light scattering intensity on additive C-5A concentration, has been revealed (figure 2b). The break indicates the phase transition. When the threshold concentration of additive was exceeded, the additive entered colloid-dispersed state and formed micelles. The point of intersection between two approximating straight lines is the critical micelle concentration (CMC) of additive C-5A in *n*-heptane. Thus, the value of the additive CMC in *n*-heptane was 0.15% of total mass.

Then, the phase behavior of model paraffin–additive–heptane system was considered (figure 3).

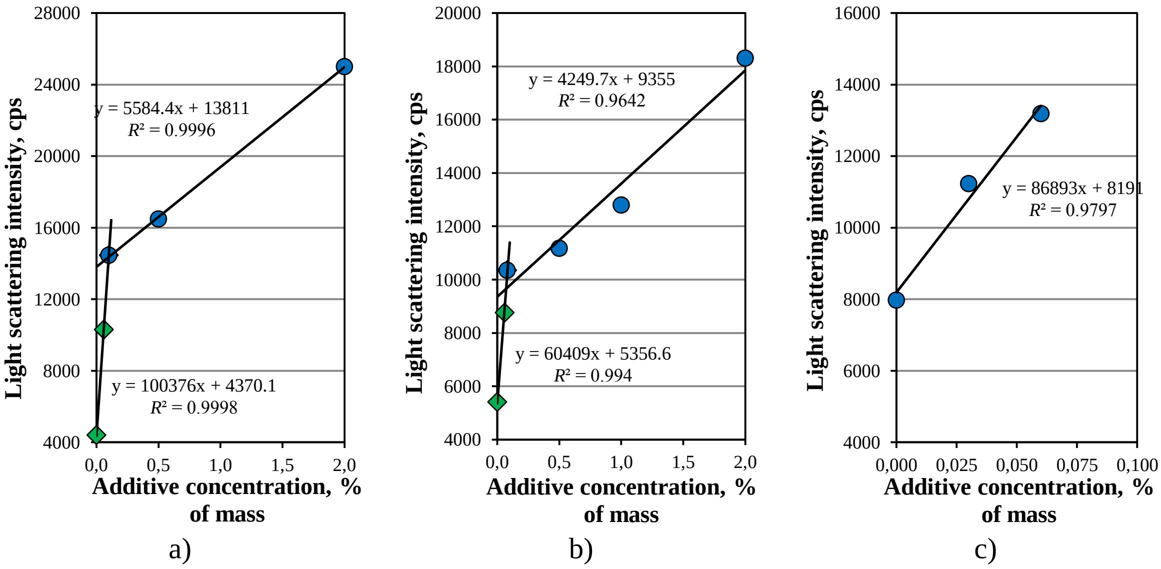

Figure 3. Dependence of the light scattering intensity on the additive concentration system with changes in the paraffin quantity: a) – paraffin concentration 4% of mass; b) – paraffin concentration 6% of mass; c) – paraffin concentration 10% of mass.

As a result (figure 3a and figure 3b), dependences indicate the same phase behavior of the additive in the investigated paraffin–heptane solutions, which is characterized by a clear break in the approximating curve. This break indicates the existence of dispersing additive CMC in paraffin–heptane solution. The high reliability of approximation of the dependences obtained by the linear functions (R^2 was close to unity) confirmed this assumption. Figure 3b shows a linear dependence of light scattering intensity on additive concentration, which indicates the absence of the CMC in this model system composition. This fact can be explained if the dependence of the critical micelle concentration of C-5A additive on the paraffin quantity in *n*-heptane is drawn (figure 4). It should be noted that obtained values of additive CMC are approximated by the linear function ($R^2 > 0.998$). The high reliability of approximation indicates that there is a significant relationship between these two parameters for different paraffin concentrations. Based on figure 4, the additive CMC should be about 0.02% of mass in the solution, which paraffin content is 10% of mass. This value is less than the investigated additive concentrations, which ultimately resulted in the absence of CMC in figure 3b.

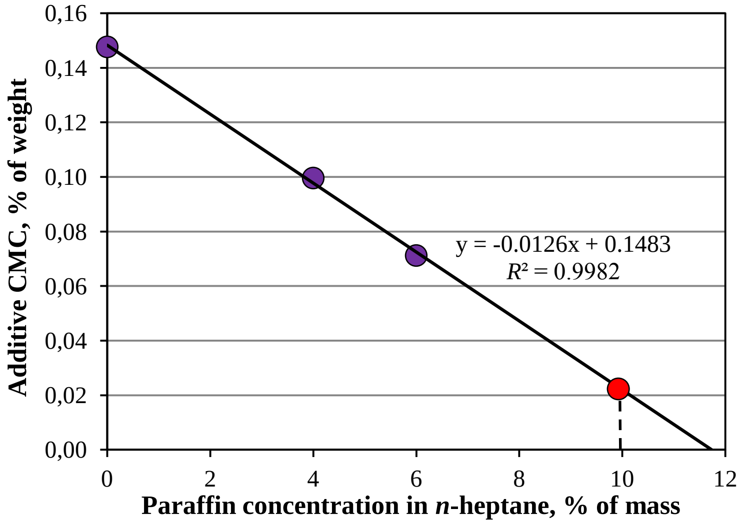

Figure 4. Dependence of the additive C-5A CMC on the paraffin concentration in *n*-heptane.

Thus, it has been established that the paraffin concentration in the model system affects the CMC value of additive C-5A: the higher the paraffin concentration, the lower the CMC value. Hence, additive C-5A may be either in molecular state or in colloid-dispersed state with certain concentrations in different paraffin–heptane solutions. This fact needs to be considered in future with interpretation of data on the additive effect on the saturation point and the paraffin pour point.

3.2. The influence of the additive on the saturation point and the paraffin pour point in model system
The paraffin crystallization occurs due to cooling or changing composition of solution in isobaric process. Ashmyan and co-authors [6] indicate that the paraffin saturation point of oil depends on paraffin hydrocarbons content in oil. When oil paraffin concentration increases, its saturation point will be higher.

The obtained results are represented in figure 5.

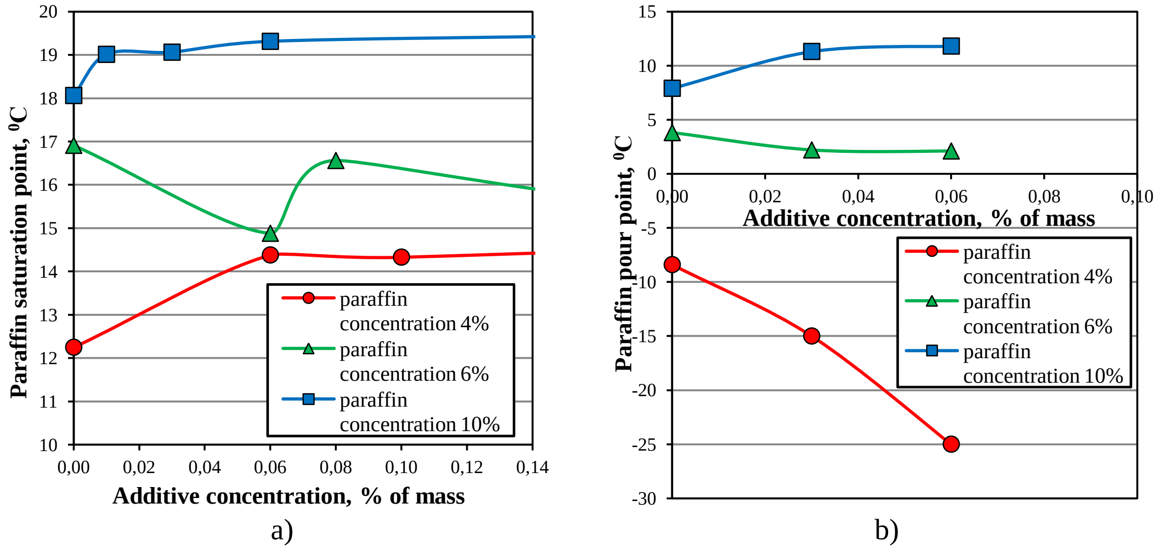

Figure 5. Influence of the additive concentration in a model system on the paraffin saturation point of solution (a) and the pour point of solution (b).

Figure 5a shows that by increasing the paraffin concentration in the model system (all other conditions being equal) the paraffin saturation point increases. Its dependence coincides with sequencing the conclusion of the work [6]. It should be noted that the C-5A additive does not generate the conclusive results on the paraffin saturation point of model system. A positive additive effect is observed in paraffin solution with concentration 6% of mass. It means that the saturation point decreases when the additive concentration less than 0.06% of mass. The negative C-5A additive effect is observed in paraffin solutions with concentrations 4% and 10% of mass. It means that the saturation point increases in all additive concentrations. Having analyzed figure 4 and figure 5a, it can be concluded that the excess of additive concentration higher than the CMC leads to the increase in the paraffin saturation point of model paraffin–heptane system. It might indicate the change in the mechanism of additive action.

Figure 5b shows that the effect of additive on the pour point decreases with the growth of paraffin concentration in model system. When the paraffin concentration grows up to 10% of mass the pour point increases. This fact also confirms the assumption on the change of additive action mechanism in excess of the CMC, as all investigated additive concentrations exceed the CMC value in solution with paraffin concentration 10% of mass (figure 4). It should also be noted that by increasing the paraffin content in the model system (all other conditions being equal) the pour point increases as well as the paraffin saturation point does in the model solution.

4. Conclusion

This paper evaluates the effectiveness of the dispersing additive action in model paraffin solutions with two parameters. They are the paraffin saturation point and the pour point.

It is the first time when the method to determine the paraffin saturation point of transparent solution by means of the method of photon correlation spectroscopy has been proposed. The optical methods are the most informative for transparent solutions, since they allow detecting small changes in the system at the initial moment of paraffin crystallization with high accuracy.

According to the results of experimental data, the following conclusions are made:

1. The CMC of C-5A additive in *n*-heptanes has been established.
2. The influence of the paraffin concentration of model system on the value of additive C-5A CMC has been revealed.
3. It is shown that the phase state of C-5A additive has a significant influence on the paraffin crystallization in the investigated model systems.

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