Influence of dispersing additive on asphaltenes aggregation in model system

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Abstract. The work is devoted to investigation of the dispersing additive influence on asphaltenes aggregation in the asphaltenes–toluene–heptane model system by photon correlation spectroscopy method. The experimental relationship between the onset point of asphaltenes and their concentration in toluene has been obtained. The influence of model system composition on asphaltenes aggregation has been researched. The estimation of aggregative and sedimentation stability of asphaltenes in model system and system with addition of dispersing additive has been given.

1. Introduction

Over the last decade, the share of unconventional Russian reserves has increased significantly, particularly, in high viscosity oil and natural bitumen. Today the commercial development of heavy oil is actively conducted in the Republic of Tatarstan. One of the main problems is the high content of asphaltenes, which can reach 20% in such oils [1, 2].

Asphaltenes are usually classified as the most polar fraction of crude oil that are soluble in aromatic solvents but insoluble in normal alkanes. Asphaltenes are identified as molecules having polyaromatic and polycyclic rings with short aliphatic chains and heteroatoms, such as nitrogen, oxygen and sulfur. Also asphaltenes contain some metals (vanadium, nickel, iron, etc.). The asphaltene molecule has diameter between 10 and 20 Å [1]. High polarity, aromaticity, and heteroatom content in asphaltenes causes a strong tendency to self-association and the formation of supramolecular aggregates even in very dilute organic solvents. In this regard the prevention of asphaltenes sedimentation stability loss is an important scientific and practical task.

One of the most common methods of asphaltenes stabilization in crude oils and hydrocarbon solutions is the use of amphiphilic surfactants, which inhibit or delay the phase separation process of asphaltenes in hydrocarbon solutions. Many scientists are trying to identify mechanisms of the additive structure influence on asphaltenes stability in organic model systems and crude oils. This research is focused on the influence of chemical additives due to their particular structure, composition, and mechanism of influence [1, 3-5]. A great interest is displayed towards dispersing additives among amphiphilic substances. Effect of dispersing additives has been investigated for diesel

fuel and oils [6, 7]. However, effect of dispersing additives in terms of hydrocarbon asphaltene solution has not been studied yet.

The aim of this work is to address the influence of dispersing additives on asphaltene aggregation in model system by the photon correlation spectroscopy method.

2. Experimental procedure
2.1. Materials

Asphaltenes have been extracted from heavy oil from one of the oil fields in the Republic of Tatarstan. Asphaltenes aggregation has been investigated in the asphaltene–toluene–heptane model system which is the most common system used to investigate the process of asphaltenes aggregation [8–11]. Chromatographic grade toluene and *n*-heptane of the same grade have been used as a solvent and as precipitant respectively. All experiments have been carried out on freshly prepared solution of asphaltenes in toluene. Initiation of asphaltenes aggregation is performed by adding a certain amount of *n*-heptane.

Alkenylsusinimide C-5A is used as dispersing additive, which is 40% concentrate of alkenylsussinimide group in mineral oil and unreacted polybutylene. The additive is a viscous liquid, which has been dissolved in toluene with mass ratio 1:1.

In the beginning of every experiment, the cuvette with the studied solution is dispersed for a 15 second period by ultrasound wave to mix all components. Cuvettes have a cylinder form with the diameter of 15 mm.

2.2. Method and equipment

The photon correlation spectroscopy (PCS) method allows determining the diffusion coefficient of colloidal particles by measuring the autocorrelation function of light scattering intensity fluctuations. If the particles take a spherical shape, their radius can be calculated by Stokes-Einstein equation [8–11]. Besides, PCS allows measuring the particle size in dispersion system in real time during its growth.

PhotoCor Complex system is based on the PCS method and is used to measure the size of asphaltenes associates and investigate aggregation process [8, 11]. A semiconductor laser beam with a wavelength $\lambda = 654$ nm is used as a radiation source. The main measuring tools of PhotoCor Complex device are two photodetector sensors, operating in photon counting mode. Light scattering intensity is observed in order to calculate the onset point of asphaltenes using a photodetector device Photocor-PC3 which is more sensitive. As a result, it becomes possible to track small changes in dispersion system. Photocor-PC3 is set at an angle of 90º. The light scattering intensity is measured for a short period of time (60 seconds). To research asphaltenes aggregation and particle size determination, second sensor (Photocor-PC1) is used. It is less sensitive but more effective for study of the process. Photocor-PC1 is set at an angle 40º. To avoid influence of the «thermal lens» effect (occurrence of convection flows as a result of the liquid heating by laser beam) on validity of particle size determination, the neutral glass filter has been selected for each experiment. The filter is installed on optical path of laser radiation. All experiments are carried out at the temperature of 27 °C and at atmospheric pressure.

3. Experiments and results
3.1. Onset point of asphaltenes

In this work, onset point of asphaltenes is determined from the dependence of the light scattering intensity on the amount of *n*-alkane in model system [11].

The PCS method has limitations due to the fact that highly concentrated asphaltenes solutions in toluene act as strongly absorbing media. The dependence of the light scattering intensity on the concentration of investigated asphaltenes is presented in figure 1.

The increase in asphaltenes concentration in toluene to 0.15 g/L leads to the growth of light scattering intensity to a maximum value of 218,000 cps. Further addition of asphaltenes to the solution

results in an intensity drop, indicating the onset of light absorption by the disperse system (figure 1). When concentration of asphaltenes in toluene reaches value of 1 g/L, the scattering intensity drop comes to a minimum value of 15,500 cps. Four solutions with different concentrations of asphaltenes in toluene have been chosen as objects of research: 0.05 g/L (concentration in range of transparent solutions), 0.15 g/L (concentration, corresponding to the maximum value of scattering intensity), 0.4 g/L and 0.625 g/L (concentrations in range of opaque solution) (figure 1). The threshold concentration of *n*-heptane (the onset point of asphaltenes) is determined by PCS method for each concentration of asphaltenes.
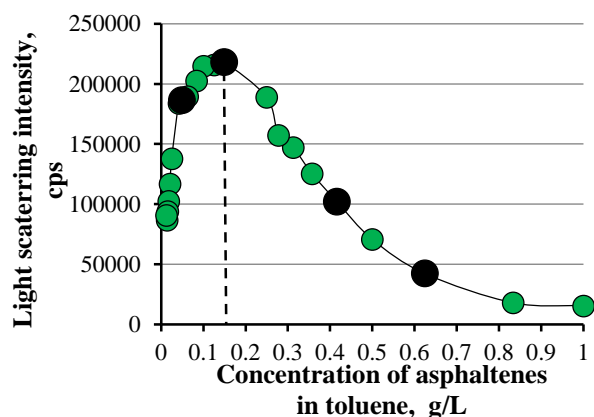

Figure 1. Dependence of the light scattering intensity on the asphaltenes concentration in toluene

The dependence of the light scattering intensity (*Ils*) on the amount of *n*-heptane (*C*) for different concentrations of asphaltenes in toluene is presented in figure 2.
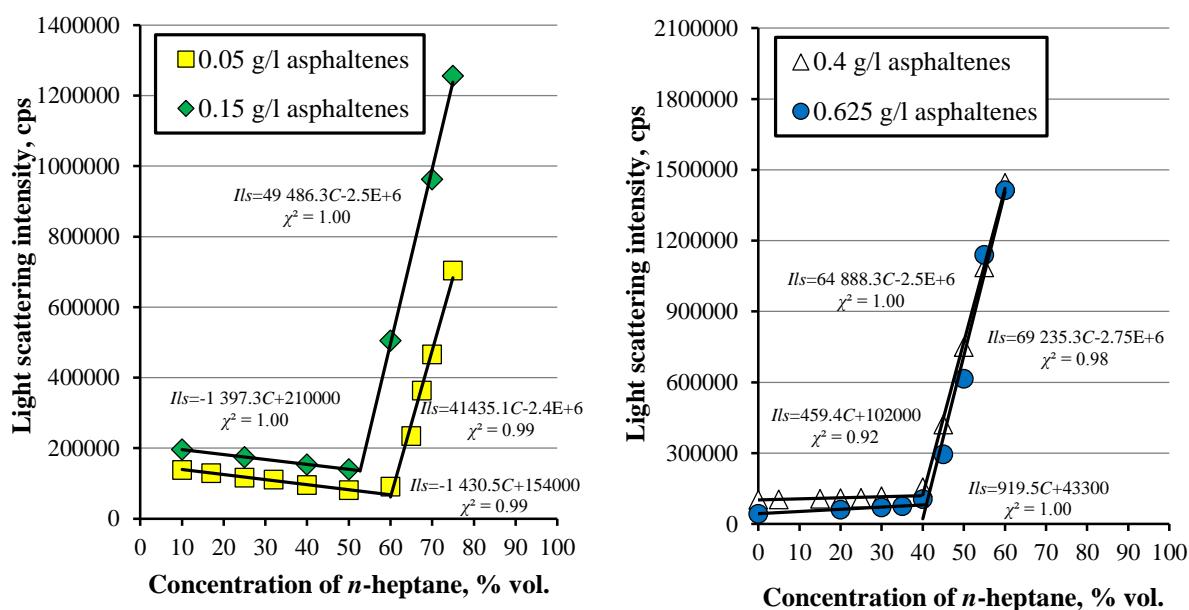

Figure 2. Identification of the asphaltenes onset point in model systems

Based on figure 2, it can be concluded that the dependence of the light scattering intensity on the amount of added *n*-heptane is approximated by linear functions (reliability of approximation $\chi2 \geq 0.92$) for all concentrations of asphaltenes in toluene. The cross point of these functions is the "onset" parameter of asphaltenes in investigated concentrations. It is worth mentioning that scattering intensity decreases with increasing amount of *n*-heptane to the threshold value for the transparent solution (concentrations 0.05 g/L and 0.15 g/L), while light scattering intensity rises in directly proportional

manner with amount of precipitator to the threshold value for the absorbing solution (concentrations 0.4 g/L and 0.625 g/L). This light intensity decreases due to the increasing fraction of *n*-heptane, scattering intensity of which is less than that of pure toluene in case of transparent solutions. In the second case, intensity rises due to the increase in solution transparency. Sharp growth of light scattering intensity is obtained when amount of *n*-heptane is above the threshold value. It indicates the transition of model solution from the molecular-dispersed to the colloidal state [11]. The growth rate of scattering intensity rises with increasing concentration of asphaltenes in toluene (figure 2). Findings once more confirm potential of using the PCS method to determine the onset point of asphaltenes.

The dependence of the onset point of asphaltenes on their concentration in toluene is presented in figure 3.
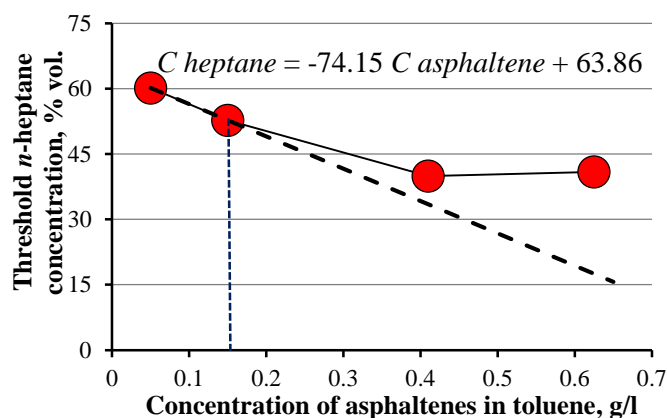

Figure 3. Dependence of the threshold *n*-heptane concentration on concentration of asphaltenes in toluene

Based on this figure, it can be concluded that the onset point of asphaltenes decreases linearly with increasing concentration of asphaltenes to the value of 0.4 g/L, after which it stabilizes at 40% vol. of *n*-heptane. However, asphaltenes aggregation is identified for the concentration of asphaltenes in toluene 0.4 g/L with lower addition *n*-heptane than the threshold value. A possible explanation for this phenomenon is that concentrated solutions of asphaltenes in toluene (0.4 g/L and 0.625 g/L) are strongly absorbing media, for which optical methods, including the PCS method, have their limitations. Thus, the PCS method allows precise defining of asphaltenes onset point only in the range of transparent solutions (for investigated asphaltenes up to concentration of 0.15 g/L). During the experiment, it has been assumed that in order to determine the onset of asphaltenes aggregation in absorbing media it is necessary to extrapolate the curve obtained for transparent solutions (figure 3, dotted line). Figure 3 shows that the more concentrated solution of asphaltene is the more deviation of experimental data from the approximating curve is observed. Thus, for asphaltenes concentrations in toluene 0.4 g/L and 0.625 g/L, the aggregation starts with *n*-heptane addition of 34% and 18% vol. respectively.

3.2. Process of the asphaltenes aggregation

Process of aggregation, i.e. time variation of particles number and degree of their aggregation, is described by the Smoluchowski equation. In the articles [8, 10, 11] it is shown that process of asphaltenes aggregation passes in accordance with the diffusion-limited aggregation mechanism in most cases.

An investigation of the asphaltenes aggregation process is conducted in toluene solution of asphaltenes with concentration of 0.4 g/L, which is an opaque medium (figure 1). The onset point of the asphaltenes concentration in the solution is assumed to be equal to 34% vol. of *n*-heptane.

The investigation results of the asphaltenes aggregation process during the addition of various *n*-heptane volumes are presented in figure 4. Solid curves are the result of the experimental data treatment to the power law dependence in accordance with the diffusion-limited aggregation mechanism by least-squares method.

Figure 4 displays that asphaltenes in toluene stay in the colloidal-dispersed state without the addition of *n*-heptane, with the average radius of particle *R* being approximately 225 nm. The asphaltenes aggregation process in all model systems is described by the power law dependence (reliability of approximation $\chi 2 \geq 0.89$), which suggests DLA mechanism. The only exception is the sample containing 35% vol. of *n*-heptane. In this case, the asphaltenes particles grow to a size of about 310 nm and remain stable throughout the experiment. This behavior is possible because the *n*-heptane concentration value is close to the threshold value (34% vol.) and the amount of *n*-heptane is not enough for a fast asphaltenes aggregation.
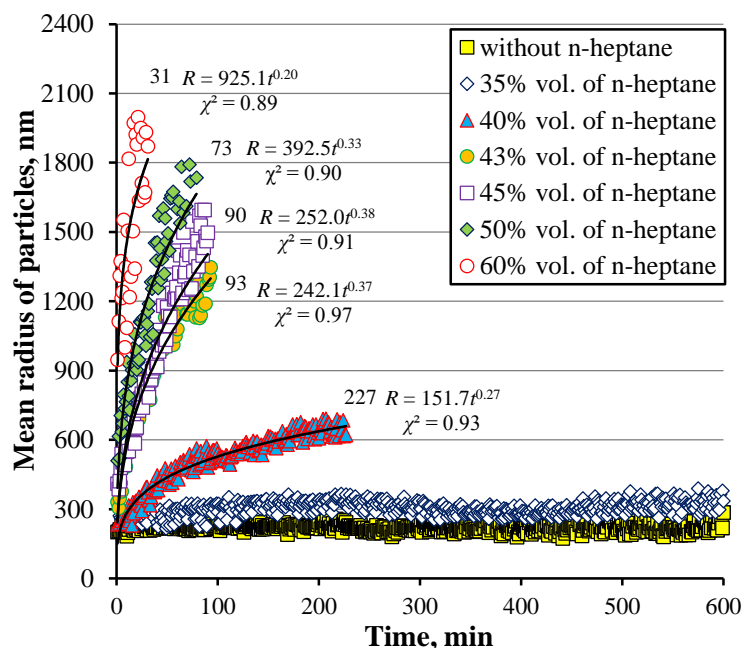

Figure 4. The asphaltenes aggregation process during the addition of various *n*-heptane volumes

In this paper an aggregation time *tagr* has been defined. It is the time during which the particles grow to critical sizes in the solution, and after reaching these sizes, aggregates commence to precipitate and measurements become no longer valid (figure 4). This parameter can be used to evaluate the sedimentation stability of asphaltenes.

Figure 4 displays that increasing amount of added *n*-heptane facilitates the aggregation rate because initial size of the particles fixed by the device is increased and the asphaltenes aggregation time is decreased. Ultimately, these facts lead to earlier precipitation of asphaltenes particles.

3.3. Influence of dispersing additive on the asphaltenes aggregation process
An investigation of the dispersing additive influence on the asphaltenes aggregation process is carried out on the asphaltenes–toluene–heptane model solution. The concentration of asphaltenes in toluene is 0.4 g/L. The amount of added *n*-heptane is 43% vol. for all additive concentrations.

The results of the asphaltenes aggregation process research in solution without additive and with addition of various dispersing additive volumes are presented in figure 5.

The dispersing additive efficiency is evaluated by two parameters: aggregative and sedimentation stability of the asphaltenes solutions. If the additive stabilizes the asphaltenes aggregates and sedimentation is not observed, the aggregative stability of asphaltenes is evaluated by the value of mean particle's radius in the solution. The sedimentation stability is determined by the asphaltenes aggregation time (*tagr*). The results of aggregative and sedimentation stability evaluation of the investigated asphaltenes is presented in table 1.
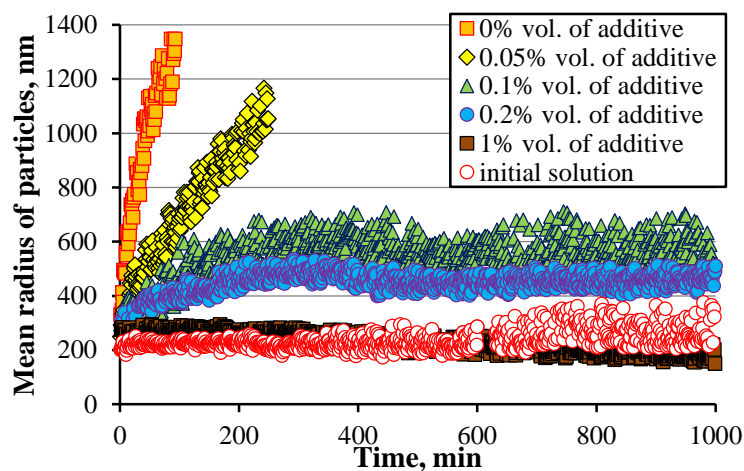
Figure 5. The asphaltenes aggregation process during the addition of various volumes of additive C-5A

Table 1. Influence of the additive C-5A on asphaltenes stability in model systems

Concentration of additive, % vol.	Time of aggregation $tagr$, min	Mean radius of particles R, nm
0	93	growth from 300 nm to 1300 nm
0.05	249	growth from 250 nm to 1130 nm
0.1	>1000	590±110
0.2	>1000	455±50
1	>1000	225±65
Solution of asphaltenes in toluene without n-heptane	>1000	225±35

With figure 5 and table 1 it can be concluded that addition of the additive in small amounts (up to concentration of 0.05% vol.) leads to the increase in the asphaltenes aggregation time, which ultimately increases the sedimentation stability of asphaltenes. With the increase in additive concentration by more than 0.05% vol. there is the decrease in mean radius of particles in the model solution. When 1% vol. of the C-5A is added to the solution, the additive prevents asphaltenes aggregation completely, as the size of particles in the system coincides with the size of particles in the initial solution of asphaltenes in toluene. These facts indicate the dispersing effect of the additive C-5A on the asphaltenes aggregates.

4. Conclusion

In this paper the onset point of asphaltenes in toluene solutions with different concentrations has been determined by the photon correlation spectroscopy method. It is shown that the PCS method allows reliably determining the onset point for asphaltenes only in transparent solutions. For opaque solutions to determine the asphaltenes aggregation onset, it is necessary to use the linear relationship obtained in this research. This assumption conforms to the article [12] where an inverse relationship between the concentration of asphaltenes in toluene and the amount of precipitant, which is necessary to reach the onset point of aggregation, are experimentally shown.

The influence of model system composition on the asphaltene aggregation process has been researched. It has been identified that investigated asphaltenes in toluene with a concentration of 0.4 g/L stay in the colloid-dispersed state and have a mean particle's radius of 225 nm. The asphaltenes aggregation obeys DLA mechanism.

In this research the estimation of asphaltenes aggregative and sedimentation stability in model system with addition different amounts of additive has been given. The dispersing effect of the additive C-5A on asphaltenes aggregates has been identified.

5. References

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