New method for the onset point determination of the petroleum asphaltene aggregation

A M Gorshkov\textsuperscript{1}, L V Shishmina\textsuperscript{2} and A T Roslyak\textsuperscript{3}
Tomsk Polytechnic University, Tomsk, Russia

E-mail: \textsuperscript{1}gorshkovam89@mail.ru, \textsuperscript{2}shishmina@tpu.ru, \textsuperscript{3}RoslyakAT@ignd.tpu.ru

Abstract. Work has been devoted to investigation of the process of asphaltenes aggregation in a model system asphaltene-toluene-heptane. The procedure of the onset point determination of the petroleum asphaltenes which is based on the method of photon correlation spectroscopy has been described. Two ways have been developed to determine the onset of asphaltenes aggregation by means of method of photon correlation spectroscopy. The first method allows defining the onset of asphaltenes aggregation of light scattering intensity depending on the quantity of \textit{n}-alkane in the model system. The second method allows determining the onset point of asphaltenes aggregation parameter \( k \) depending on the quantity of \textit{n}-alkane. A comparative evaluation of onset points, obtained in different ways has been given. The influence of the model system composition on the process of asphaltenes aggregation has been studied. The characteristic diffusion time of asphaltenes has been calculated.

1. Introduction
Asphaltenes, the high molecular weight and the most aromatic component in the oil, are the subject of many studies, due to the ever increasing share of the heavy oil in the world's hydrocarbon reserves. There is a change of thermobaric conditions, leading to the aggregation of asphaltenes colloidal particles in the process of fields exploitation. They can plug the pore medium of productive layers and lifting pipes column in the process of oil production and form deposits in the manifold during transport.

Currently asphaltenes considered as oil fraction which is insoluble in \textit{n}-alkanes, and soluble in aromatic compounds such as toluene or benzene. The average composition of asphaltenes as a class is well known. Typical asphaltenes molecule consists of \( 3 \) – \( 10 \) condensed aromatic rings and the alkyl chains (about \( 3 \) – \( 5 \) carbons). Polycyclic nucleus contains a small amount of heteroatoms (N, O, S), and metals (Va, Ni, Fe) \cite{1}. High polarity, aromaticity and heteroatom content in asphaltenes causes a strong tendency to self-association and the formation of molecular aggregates even in very dilute organic solvents. Asphaltenes aggregation in toluene solution at the concentration of 1.7 – 3.0 mg/L is accompanied by the nanoaggregates formation of 4 – 6 molecules with size from 0.5 to 4 nm \cite{2}. Increasing the concentration of asphaltenes to 2 – 5 g/L results in the nanoclusters formation \cite{3}.

Asphaltenes can lose the sedimentation stability depending on the amount of the dispersed phase (asphaltenes) and the ratio in the dispersion medium precipitant/solvent the initial demonstration of them is onset of their aggregation. In modern publications the start of asphaltenes aggregation can be evaluated by using method of the point onset determination \cite{4}. This procedure allows defining the parameter of start aggregation of asphaltenes by the deviation from the linearity dependence of the optical density of the asphaltenes solution from concentration \textit{n}-alkane in accordance with the
Bouguer-Lambert-Beer law. The main difficulty of determining the onset point asphaltenes in this way is that the research results are strongly dependent on the laser wavelength [5]. We should look for new ways to determine the onset of the aggregation process due to the imperfection of this method.

We propose a new method for onset point determination of asphaltenes which is based on the method of photon correlation spectroscopy.

2. Experimental procedure

2.1. Materials

The asphaltene samples were extracted from crude oil of Taymurzinskoe field by means of «cold» method Golde. The elemental composition of asphaltenes is presented in table 1.

Table 1. The elemental composition of asphaltenes.

| Content, % wt. | Degree of aromaticity | Molecular weight, a.m.u. |
|---------------|-----------------------|--------------------------|
| C  | H  | N  | S  | O  | H/C | 1900 |
| 81.5 | 8.2 | 1.9 | 6.2 | 2.2 | 1.2 | |

The data of table 1 shows that the investigated asphaltenes have high molecular weight and value of degree of aromaticity. Sulfur predominates among the heteroatoms in asphaltenes.

Asphaltene aggregation was studied in a model system asphaltene-toluene-heptane which is the most common system for investigating the process of asphaltenes aggregation [6–9]. We used chromatographic grade toluene as a solvent and n-heptane of the same grade as a precipitant. All experiments were performed on freshly prepared solution of the asphaltene in toluene. Concentration of asphaltene in toluene was 0.4 and 0.6 g/L. Initiation of asphaltene aggregation was performed by adding a certain amount of precipitant – n-heptane. After preparing investigated solutions the cell with sample was placed in an ultrasonic bath for 15 seconds to thoroughly mix the components together, prior to each experiment, and then measurements were conducted. A new cell has been chosen for each ratio n-heptanes/toluene. We used a round cell 15 mm diameter for all measurements of the aggregation process.

2.2. Method and equipment

The method of photon correlation spectroscopy (PCS) or method of dynamic light scattering which allows determining the particle size in the dispersion system in real time during their growth is became widespread among the optical methods recently.

PCS method is based on determining of the diffusion coefficient $D$ of the colloidal particles by measuring the autocorrelation function of light scattering intensity fluctuations. If the particles take a spherical shape their radius $R$ can be calculated by Stokes-Einstein equation (1) [8]:

$$ R = \frac{k_B \cdot T}{6 \cdot \pi \cdot \eta \cdot D} $$

where $k_B$ – the Boltzmann constant, $T$ – absolute temperature and $\eta$ – shearing viscosity of the medium.

We used PhotoCor Complex system to measure the size of asphaltene associates and study the aggregation process. The device includes two parts: the optical-mechanical unit and control and data analysis unit.

A semiconductor laser beam with a wavelength $\lambda = 654$ nm was used as a radiation source. The main measuring tool of PhotoCor Complex device is photoelectron multiplier tube (PMT) operating in the photon counting mode. Light scattering intensity values increase amplify by a decade due to the greater sensitivity of the sensor through the use of an additional photodetector (Photocor-PC3), the main element of which is an avalanche photodiode. As a result, it becomes possible to track small changes in dispersion system. Thus in our work Photocor-PC3 was set at a $90^\circ$ angle to determine the
light scattering intensity. To study the asphaltenes aggregation and particle size determination second PMT (Photocor-PC1) is used. It is less sensitive but more effective for the study of the process. Photocor-PC1 was set at an angle of 40°. To avoid the influence of the «thermal lens» effect (occurrence of convection flows as a result of the liquid heating by laser beam) on the validity of the particle size determination the optimum neutral glass filter mounted on the laser for reduce the radiation power was selected for each experiment.

The main element of the control and data analysis unit in the PhotoCor Complex device is a programmable correlator which provides automatic control of the instrument operation according to the algorithm. It can also measure the correlation function and the integrated intensity of the light scattering. The autocorrelation function of the light scattering intensity fluctuations is recorded by cycles in our study. Duration of cycle is 1 minute, number of cycles is 1000.

3. Experiments and results
3.1. Onset point of asphaltenes
The particle size growth occurs, which leads to an increase in the light scattering intensity in the process of asphaltenes aggregation. It is known that the scattering intensity for polarized incident light depends on the particle radius, ceteris paribus, as power function $I \sim R^6$ according to Rayleigh's theory [10]. As a result a sharp increase of the light scattering intensity is observed, when the particles go from molecular-dispersed to colloidal state. The process can be detected by optical photodetectors.

Figure 1 shows the dependence of the light scattering intensity on the amount of $n$-heptanes in a model system.

![Figure 1](image)

Figure 1. Dependence of the light scattering intensity on the volume fraction of $n$-heptanes in a model system.

A linear increase in the light scattering intensity from the amount of added $n$-alkanes for both asphaltenes concentrations in toluene (reliability approximation $\chi^2 > 0.95$) is observed with increasing volume fraction of $n$-heptanes to 0.4. For a given quantity of $n$-heptanes in solution the asphaltene aggregation does not occur but increasing transparency of the system asphaltenes-toluene-heptane takes place by the addition of $n$-alkanes. Moreover, the growth rate of scattering intensity for a solution with a asphaltene concentration of 0.6 g/L is more than that of a solution with concentration 0.4 g/L, since it is more absorbing medium (figure 1).

There is a sharp growth in the light scattering intensity with increase volume fraction of $n$-heptanes over 0.4 for the asphaltenes solution with concentration of 0.4 g/L and over 0.45 for the solution with a concentration of asphaltenes of 0.6 g/L, that is evidence of the onset of aggregation. The particle size detection of asphaltenes order of several hundred nanometers using the method PCS confirms the aggregation when that value volume fractions of $n$-heptanes in a model system. In addition, this area of the experimental data is good approximated by an exponential dependence ($\chi^2 > 0.98$). The crossing
point of linear and exponential functions will define the onset point of aggregation. Thus, for the asphaltenes concentrations in toluene 0.4 g/L the onset point is 0.43 volume fraction, while for a concentration of 0.6 g/L is 0.48 volume fraction of \( n \)-heptanes in a model system.

3.2. Process of asphaltenes aggregation

Aggregation process, the variation with time of the particles number and the degree of their aggregation is described by Smoluchowski’s equation. Solutions of the Smoluchowski’s equation are known explicitly only for special cases, the appropriate modes of diffusion-limited aggregation (DLA) and reaction-limited aggregation (RLA). DLA mode dependence of the mean radius of aggregate \( R \) from the time \( t \) is given by [8]:

\[
R = R_0 \left(1 + \frac{t}{\tau_D}\right)^{\frac{1}{d_f}},
\]

where \( d_f \) is fractal dimensionality, \( R_0 \) is an initial particle size, \( \tau_D \) is the characteristic diffusion time. The value \( d_f \) is in the range \( 1 \leq d_f \leq 3 \) [8].

Figure 2 shows the results of a research of the aggregation process of asphaltenes with different concentrations in toluene by adding of \( n \)-heptanes. Solid curves are the processing result of the experimental data by least-squares method (LSM) on the power law in accordance with the expression (2).

![Figure 2. Process of asphaltenes aggregation upon adding of different \( n \)-heptanes quantity: a) – asphaltenes concentration is 0.4 g/L; b) – asphaltenes concentration is 0.6 g/L.](image)

Figure 2 demonstrates the aggregation process is satisfactorily described by a power law \( (\chi^2 \geq 0.93) \). This suggests that the aggregation of asphaltenes occurs on the DLA mode. It should be also noted that the addition amount of \( n \)-heptanes is near to the threshold value the reliability approximation of the experimental data decreases. Probably, this is due to the fact that asphaltenes are a complex polyaggregative system in which molecules differed in physic-chemical properties, including the tendency to association are presented [11]. When the \( n \)-heptane/toluene ratio is close to onset point, aggregation of different types asphaltene passes with different speed that leads to uneven growth process of the particles and, as a result, to a deviation from the DLA mode.

The characteristic diffusion time has been calculated experimentally for investigated asphaltenes concentrations in accordance with the decision of the Smoluchowski’s equation for the DLA mode. In addition, the time of aggregation \( t_{agr} \), in other words, the time during which there is growth of particles
in solution to the critical size after which the aggregates start to precipitate and measurement becomes impossible, has been determined in this study. Results are presented in table 2.

**Table 2. Parameters of petroleum asphaltenes aggregation.**

| Concentration of asphaltenes in toluene, gL⁻¹ | Volume fraction of n-heptanes | Equation approximation on the method (LSM) | Reliability approximation | Parameters of asphaltenes aggregation |
|---------------------------------------------|-------------------------------|------------------------------------------|--------------------------|--------------------------------------|
| 0.4                                         | 0.43                          | $R=31.7t^{0.36}$                         | 0.83                     | $t_{agr}$ min, $\tau$, and $k$, min*: 31.7 |
|                                             | 0.51                          | $R=207.3t^{0.35}$                       | 0.95                     | 166, $4.4\cdot10^{-7}$, 207.3         |
|                                             | 0.61                          | $R=310.2t^{0.36}$                       | 0.99                     | 39, $2.1\cdot10^{-7}$, 310.2          |
|                                             | 0.47                          | $R=105.4t^{0.30}$                       | 0.95                     | 300, $4.4\cdot10^{-7}$, 105.4         |
|                                             | 0.51                          | $R=163.2t^{0.29}$                       | 0.98                     | 208, $4.6\cdot10^{-8}$, 163.2         |
|                                             | 0.56                          | $R=273.4t^{0.31}$                       | 0.94                     | 64, $3.4\cdot10^{-8}$, 273.4          |
|                                             | 0.61                          | $R=452.9t^{0.26}$                       | 0.93                     | 27, $1.9\cdot10^{-10}$, 452.9         |

*In processing the experimental data initial size was given $R_0=1.25$ nm.

Table 2 demonstrates the characteristic diffusion time of asphaltenes decreases with increasing concentration of asphaltenes in toluene and with increasing quantity of n-heptanes. Time of aggregation has a similar dependence.

Equation (2) for the DLA mode has no unique solution because it includes three indeterminate. Table 2 shows that the characteristic diffusion time is much shorter than the asphaltene aggregation $\tau_D<<\tau_{agr}$, thus in the expression (2) can throw away a unit. The result is a power law dependence of the form $R=kt^\alpha$ which contains all the indeterminate in the parameter $k$ [9].

$$k = R_0\tau_D^{-1}a, \quad \alpha = \frac{1}{D_f}.$$ (3)

We construct the dependence of parameter $k$ on the volume fraction of n-heptanes for different asphaltenes concentrations in toluene (figure 3). The parameter $k$ values dependence on the quantity of n-alkanes is described by a linear function ($\chi^2\geq0.96$). The parameter $k$ is equal 0 only if the characteristic diffusion time of asphaltenes equals infinity and this in turn is possible only in the absence of aggregation. The extrapolation of the linear function to the horizontal axis can define a threshold volume fraction of n-heptanes or the onset point.

**Figure 3.** The parameter $k$ dependence on volume fraction of n-heptanes for different asphaltenes concentration in toluene.

Thus, this method allows determining the onset of asphaltene aggregation the parameter $k$ of aggregation depending on the quantity of n-alkanes. The threshold volume fraction of n-heptanes for the
asphaltenes solution in toluene with a concentration of 0.4 g/L was 0.4, for the asphaltenes concentration of 0.6 g/L was 0.44.

4. Conclusion
The study introduces a novel procedure of determining the onset point of asphaltenes which is based on the method of photon correlation spectroscopy. Two ways have been developed to determine the onset of asphaltenes aggregation. The first method allows defining the onset of asphaltenes aggregation of light scattering intensity depending on the volume fraction of \( n \)-alkanes. The second method allows determining the threshold amount of \( n \)-heptanes aggregation parameter \( k \) depending on the volume fraction of \( n \)-alkanes.

The onset point values, calculated by the second method, is less than the values determined from the light scattering intensity. Perhaps this is due to the fact that asphaltenes are a complex polyaggregative system in which molecules with different tendency to association are presented. The light scattering intensity depends not only on the size of asphaltenes aggregates but also by their number. Because of non-simultaneity of the aggregation process of asphaltenes molecules of different types the onset of aggregation identified by the light scattering intensity is observed in more \( n \)-heptanes quantity. The amount of \( n \)-alkanes enhances the aggregation rate, which leads to a significant increase in the concentration of asphaltenes aggregates sufficient to fix the change in the light scattering intensity. Thus, the value of the onset point of asphaltenes can be previously estimated within 5% error in the light scattering intensity and by calculation of aggregation parameters \( k \) can be updated an obtained value by means of photon correlation spectroscopy method.

5. References
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