The dynamics of asphaltene aggregates in heavy crude oils on a nanometer scale studied via small-angle X-ray scattering in situ

Yu.V. Larichev [a,b,*], O.N. Martyanov [a,b]

[a] Boreskov Institute of Catalysis, 5 Academican Lavrentiev Avenue, 630090, Novosibirsk, Russia
[b] Novosibirsk State University, 2 Pirogov Street, 630090, Novosibirsk, Russia

ARTICLE INFO

ABSTRACT

This work presents the results of the *in situ* SAXS study of the asphaltene aggregate transformations due to dilution of several heavy crude oils by heptane within the time range from 5 min to 3 days. The main growth of the asphaltene aggregates was usually observed within first minutes. The analysis of the SAXS data obtained *in situ* for the oils having significantly different relative content of resins showed their great influence on the dynamics of aggregates formation on a nanometer scale. In particular, it has been shown that the resins can prevent the asphaltene aggregation via certain mechanism which usually leads to the high anisotropy of the aggregates. Therefore the relative content of resin and asphaltenes as well as aromatics and aliphatics lead to the asphaltene aggregates with different shapes and different density of deposits.

1. Introduction

The depletion of reserves of light fossil hydrocarbons inevitably leads to a significant increase in the share of heavy oils produced in the world. One of the most serious problems in the extraction, transportation and processing of heavy oils is their high viscosity and propensity to form asphaltene based deposits (Akbarzadeh et al., 2007; Hammami and Ratulowski, 2007; Mullins, 2011). The addition of light oil fractions or specific solvents can significantly reduce the viscosity of heavy oils and their blends but on the other hand can lead to uncontrolled aggregation of asphaltenes followed by their sedimentation and precipitation under certain temperature and pressure (Chilingarian and Yen, 1994; Simanzhenkov and Idem, 2003; ASTM, 2012). The fouling and deposit formation usually occurs when mixing so-called "incompatible" oils (Hammami and Ratulowski, 2007, Wiehe and Kennedy, 2000, Gabrienko et al., 2015a). This phenomenon is highly undesirable in case of joint transportation of different crude oils and/or preparation of multicomponent hydrocarbon feedstock for catalytic processing (Chilingarian and Yen, 1994; Simanzhenkov and Idem, 2003). It is clear that the understanding of the key factors which determine aggregate stability of the oil disperse systems, phase behavior of their heaviest components in different external conditions is the crucial step for the development of any effective technologies for the production and processing of heavy oils.

The development of the methods and approaches to predict and control the stability of oils and their blends are of particular importance. Unfortunately the behavior of heavy crude oils and their blends of various compositions, in particular their stability under certain conditions (temperature, pressure, and additives), still remains poorly predictable despite a lot of efforts spent to solve this problem using sophisticated physical methods. For instance the so-called oil stability index (Guzmán et al., 2017) used to assess the stability of oils depending on the relative content of asphaltenes, resins, aromatics, and aliphatic hydrocarbons often leads to mistakes and can only be used for rough estimates of the blend stability.

The interrelationship between the composition of hydrocarbon dispersed systems of heavy oils and their stability may be established via *in situ* methods which can directly detect the evolution of asphaltene aggregates under certain conditions. The different qualitative and quantitative composition of the oils and their blends can lead to the various fouling mechanisms having substantially different temporal and spatial characteristics. Earlier some techniques including optical microscopy (Mohammadi et al., 2016a), light-scattering methods (Anisimov et al., 1995; Yudin et al., 1998), two-dimensional ATR FTIR spectroscopy (Gabrienko et al., 2014a, b), electron spin resonance (ESR) (Trukhan et al., 2014, 2017) and nuclear magnetic resonance imaging (MRI) (Gabrienko et al., 2015b; Morozov and Martyanov 2016; Morozov et al., 2016) were used to study the aggregation and precipitation processes *in situ*. In particular the light-scattering techniques allowed elucidating

---

* Corresponding author. Boreskov Institute of Catalysis, 5 Academican Lavrentiev Avenue, 630090 ,Novosibirsk, Russia.
  E-mail addresses: larichev@catalysis.ru, ylarichev@gmail.com (Yu.V. Larichev).

various aggregation mechanisms depending on the flocculant concentration in the asphaltene solution (Yudin et al., 1998; Mohammadi et al., 2016b). The optical microscopy showed that the pressure drop at different temperatures can lead to the growth of the asphaltene aggregates from 1 to 20 μm (Mohammadi et al., 2016a). ATR-FTIR spectroscopic imaging study of the crude oil fouling process allowed correlating between some crude oil properties (chemical composition) and its stability and the rate of deposit precipitation induced by n-heptane or supercritical CO_2 (Gabrienko et al., 2015b, 2016; Morozov et al., 2014). In particular it was shown that the sulphoxides and oxygen containing species are less stable and precipitate first. Afterwards the precipitation of pyridine and pyrrole containing species and finally thiophenes is observed. The works done allowed some correlation with the polarity and the stability of the constituent to be established (Gabrienko et al., 2014a, b). MRI technique showed that the growth of asphaltene aggregates and a significant changes in their morphology occur in the bulk of the oil samples starting from the first seconds after the addition of flocculant and continue in a long run (hundreds of hours) leading to the formation of a complex secondary structure of asphaltene based deposits (Gabrienko et al., 2015b; Morozov and Martyanov 2016).

Unfortunately, the spatial resolution of the visualization methods mentioned above makes it impossible to monitor and investigate the aggregation processes on a nanometer scale. This leads to a lack of information about the initial stages of the formation of asphaltene aggregates in the bulk of crude oils and their blends. At the same time the initial stages of aggregation depending primarily on the oil composition and local intermolecular interactions determine the scenario for the aggregation process, its characteristic time, the size and morphology of final deposits. Understanding the importance of this problem a lot of efforts have recently been spent to study the asphaltene aggregation process via Transmission Electron Microscopy *in situ* using liquid cell operating within the 10^4–10^5 Pa range (Janssen et al., 2016). For the first time it was shown *in situ* that the asphaltenes aggregation process is driven by the initial formation of 10–20 nm spherical clusters which agglomerate into larger globular structures. The data obtained follows the widely adopted Yen model (also known as the Yen-Mullins model) despite the initial clusters visualized were slightly larger as compared to the sizes proposed by this model. Some discrepancy in this case can be connected with the technical limitation of the *in situ* cell and the locality of the TEM method used.

Here we first report the results of a comparative study of the asphaltene aggregation dynamics in various crude oils in the presence of n-heptane as a flocculating agent by Small-Angle X-ray Scattering (SAXS) technique *in situ*. The SAXS method is widely used *ex situ* for the analysis of the sizes and shape of asphaltene aggregates depending on external conditions or additives to the oils or their blends (Gawrys et al., 2006; Hoepfner et al., 2013; Eyssautier et al., 2011, 2012; Tuzikov et al., 2011). The objective of this work was to study quantitatively the kinetics of the initial stages of asphaltenes aggregation process on a scale of tens of nanometers in various crude oils in the presence of flocculant. It was found that the most significant changes in the size and shape of aggregates occur at the initial stage within the first tens of minutes after the addition of the flocculant followed by sufficiently slow relaxation of multicomponent system into the energetically favorable state, where the size and morphology of asphaltene aggregates are determined preferentially by the chemical composition of crude oils.

2. Experimental section

The properties and chemical composition of the crude oils studied are shown shortly in Table 1. The samples having different content of asphaltenes and resin as well as aromatics and aliphatic compounds are labelled as A, B, C, D, E and F. The n-heptane (>99.5% purity) was purchased from Sigma-Aldrich and used without further purification as the flocculating agent to induce asphaltene precipitation. To study the kinetics of asphaltenes aggregation process the oils were mixed with

Table 1
Composition of the heavy crude oils.

	Crude oil samples					
	A	B	C	D	E	F
Density, g/cm^3	0.936	0.865	0.938	0.971	0.978	0.957
Aromatics, wt%	41.9	31.6	42.9	49.5	45.6	37.2
Aliphatic, wt%	18.8	28.9	23.2	29.8	21.3	21.0
Aromatics/Aliphatic ratio	2.2	1.1	1.8	1.7	2.1	1.8
Total S (wt%)	2.20	0.93	1.98	1.98	4.60	4.54
Total N (wt%)	0.38	0.15	0.08	0.62	1.01	0.70
Asphaltenes, wt%	6.0	1.7	2.2	8.1	6.7	6.7
Resins, wt%	8.8	3.8	6.7	19.2	30.2	35.1
Resins/Asphaltenes ratio	1.5	2.2	3.0	2.4	4.5	5.2

heptane in a volume ratio of 1:2 respectively followed by intensive stirring for 2 min using a Bio Vortex V1 device. Afterwards the sample taken from the mixture was placed in a quartz capillary with inner diameter of 1.5 mm. In order to maintain a constant oil/heptane ratio that can be affected by the evaporation of heptane and light oil fraction, the capillary was flame-sealed after filling it with a portion of the crude oil-heptane mixture. The Small-Angle X-ray Scattering curves were acquainted and registered starting from 5 min after the addition of n-heptane into the oils and during next 3 days.

Small-angle X-ray scattering (SAXS) was registered by a S3-MICRO diffractometer (Hecus, Austria) with a Cu anode ($\lambda_{CuK\alpha} = 1.541$ Å) and the point collimation system. SAXS patterns were reistered over the $0.01 < q < 0.6$ Å^{-1} range where q is the wave vector determined as $q = 4\pi \cdot \sin(\theta)/\lambda$, 2θ is the scattering angle, and λ is the wave length of the applied radiation with the 1.5 mm quartz capillaries used. SAXS patterns of initial solvents were subtracted from the corresponding SAXS patterns of asphaltene solutions taking into account X-ray absorption coefficients. The radius of gyration of the particles (R_G) was determined by the slope of the small angle curve in coordinates $(\ln(I(q); q^2)$, and the radius of gyration of the cross section of the particles ($R_{G(cross)}$) was determined by the slope of the small angle curve in coordinates $(\ln(I(q) \cdot q); q^2)$ in range of $q \cdot R_G < 1.3$ (Feigin and Svergun, 1987). The ATSAS program package was used for data processing (Konarev et al., 2006).

3. Results and discussion

Fig. 1 shows some initial SAXS data for mixture oil A – heptane as example. For the initial oil samples the SAXS curves in the range of large angles ($q > 0.15$ Å^{-1}) can be well described by a power law $I(q) \sim q^{-x}$,
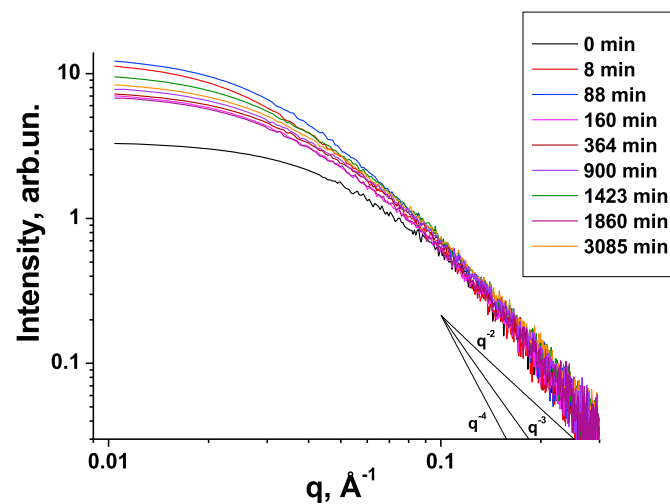

Fig. 1. SAXS curves for mixture oil A-heptane depending on the time of mixing. Curve of 0 min is corresponding to initial oil A. Additionally, for best visibility has been shown functions of $I(q) = q^{-2}$, q^{-3} and q^{-4}.