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Assembly of asphaltene molecular aggregates as studied by near-UV/visible spectroscopy II. Concentration dependencies of absorptivities

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Abstract

The properties of molecular aggregation in toluene solutions of a crude oil and solid asphaltenes are determined almost solely by the concentration of asphaltenes, as shown by absorptivity measurements at 315–750 nm. From non-monotonic concentration dependencies of absorptivities, it is concluded that asphaltene monomers are abundant in solutions with asphaltene concentrations below 1–5 mg/l, while molecular aggregates are effectively formed above 20–25 mg/l. The most stable oligomers are a dimer and a dimer pair (Yen's "nanocrystallite" [NC]). Nanocrystallites act as building blocks for more complex aggregates at asphaltene concentrations exceeding 90–100 mg/l. These optical absorption results are supported by studies of Rayleigh scattering in asphaltene solutions.

Keywords: Petroleum fluids; Asphaltenes; Molecular aggregates; Colloidal suspensions

1. Introduction

Asphaltenes constitute a very important fraction of crude oils, petroleum residues, bitumens, as well as of oil- or bitumen-based emulsions. The tendency of asphaltenes to aggregate distinguishes them from other oil constituents. Asphaltene aggregation may be the cause of complex non-linear effects in such phenomena as adsorption at solid surfaces, precipitation/deposition, fluid's rheology, emulsion stability, etc. Until now, the structure of asphaltene molecules and the precise nature of the asphaltene–asphaltene interactions are not well known, which precludes reliable theoretical modelling of the properties of asphaltene aggregates. Hence, of primary importance are experimental studies, which may reveal new details of the aggregation process, especially at its initial stages of formation of the simplest aggregates.

In our previous publications (Akhmetov et al., 2002; Evdokimov et al., 2003), we have presented experimental evidence for the influence of asphaltene aggregation in dilute solutions on positions of absorption bands in the near-ultraviolet/visible spectroscopy (near-UV/Vis) range. On the basis of these results, we concluded that single asphaltene molecules are predominant only in solutions with asphaltene concentrations below 1–5 mg/l, while asphaltene dimers are most abundant species at concentrations close to 10–15 mg/l. The most stable aggregates are apparently 2 nm quasispherical dimer pairs or "nanosized crystallites" (Yen et al., 1961; Dickie and Yen, 1967), predominant at concentrations ≈ 90 mg/l. The observed multiple-stage aggregation process was regarded as quite distinct from conventional micellisation phenomena with a single critical micelle concentration.

In the present paper, we report new near-UV/Vis absorption results, which reveal non-monotonic concentration dependencies of asphaltene absorptivities. These results are supplemented by Rayleigh scattering measurements. The experimental data confirm our previous aggregation model, which is further substantiated by an analysis of asphaltene molecular weight (MW) distributions measured by other authors.

2. Experimental

2.1. Samples

The solid asphaltenes have been precipitated with *n*-heptane (40/1 dilution at room temperature) from a mixture of Tatarstan crude oils. The crude was collected directly from a

wellhead at Romashkinskoye reservoir and (after water separation) contained 3.5 wt.% asphaltenes (as determined by *n*-heptane precipitation). A “chemically pure” grade toluene was used as a solvent for all samples. The crude oil was used directly for preparation of the studied solutions. The solutions of solid asphaltenes were prepared by dilution of a concentrated (1.5 g/l) “primary solution” in toluene.

2.2. Apparatus and procedure

The optical absorption of asphaltene solutions in the near-ultraviolet/visible range (315–750 nm) has been measured in a KFK-2 Photocolorimeter — a spectrometer, widely employed in Russian in-field laboratories (Devlikamov et al., 1970). The sample cuvetts had the path length of 5.07 mm. Reproducible results were obtained with absorbances in the range of 0.005–1.90. Correspondingly (for the above path length), the studied ranges of asphaltene concentrations were from 1.6 mg/l to 1.5 g/l in solutions of solid asphaltenes (~150 samples) and from 5.1 mg/l to 1.5 g/l in crude oil solutions (~110 samples). For any sample measurements started 10–15 min after its preparation and optical transmittances at nine fixed wavelengths were determined for both the sample and the reference cuvetts. Hence, no more than 8–10 samples were studied during a single working day. There was no pre-determined pattern in selecting concentration value for each new sample; this value was chosen virtually at random. In all, the studies of more than 260 samples continued for more than 4 months and, over that lengthy period, the new data points kept falling onto the non-monotonic concentration dependencies presented below, confirming their reproducibility.

In optical adsorption studies of dilute solutions of asphaltenes/crude oils, it is customary to disregard the contribution of scattering (Acevedo et al., 1999; Bastow et al., 1997; Devlikamov et al., 1970; Groenzin and Mullins, 2000, 2001). Accordingly, we assumed that light extinction in any studied solution was determined entirely by optical absorptivity ε of asphaltenes.

The Rayleigh scattering measurements were performed in a 90° geometry with a photon correlation spectrometer (PhotoCor Instruments), as described in detail in Yudin et al. (1997).

3. Results and discussion

3.1. Wavelength dependencies of absorptivities

The measured absorptivities were strongly wavelength-dependent and ranged from $\varepsilon=1.8$ – $2.8 \text{ cm}^2/\text{mg}$ for $\lambda = 750 \text{ nm}$ up to $\varepsilon=45$ – $450 \text{ cm}^2/\text{mg}$ for $\lambda = 315 \text{ nm}$. The data sets, connected with dashed lines in Fig. 1, are the results for toluene solutions of solid asphaltenes (circles) and the crude oil (triangles). The respective asphaltene concentrations in solutions were 98 and 93 mg/l. In a zero-order approximation, $\varepsilon(\lambda)$ dependencies may be represented by power laws (solid lines in Fig. 1). Deviations from power laws are due to characteristic absorption by chromophores in the fused aromatic and porphyrin-like fragments of the asphaltene molecule (cf. Groenzin and Mullins, 2000; Akhmetov et al., 2002).

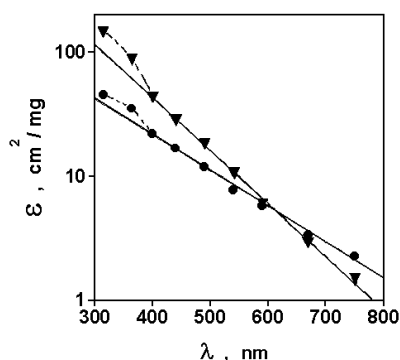


Fig. 1. Absorptivity spectra for toluene solutions of solid asphaltenes (circles) and of the crude oil (triangles). The asphaltene concentrations are 98 and 93 mg/l, respectively. Solid lines are power law approximations.

Fig. 1 shows that, in solutions of solid asphaltenes and of the crude oil, close ε values are observed at $\lambda > 550 \text{ nm}$, while at smaller wavelengths, absorptivities in oil/toluene solutions are systematically higher. The differences at shorter wavelengths are evidently due to oil constituents

other than asphaltenes (e.g., resins and heavy aromatics), which were not accounted for in calculating absorptivities. However, the presence of resins, etc. did not make a meaningful impact on the concentration dependencies of absorptivities. As shown below, the specific aggregation-dependent features of these dependencies were determined solely by the net concentrations of asphaltenes in all types of the studied solutions.

3.2. Concentration dependencies of absorptivities

The dependencies of ε at $\lambda = 670$ nm on the concentration of asphaltenes C are presented in Figs. 2 and 3; triangles and circles denote the data sets for oil/toluene and asphaltene/toluene solutions, respectively. To reduce a random scatter of the original experimental results, the data sets have been smoothed by a sliding five-point window. The results of Fig. 2 show that, in both types of solutions, a simple Beer's law (implying a constant, concentration-independent absorptivity) is fulfilled only at high asphaltene concentrations, exceeding 700 mg/l. In more dilute solutions, reproducible non-monotonic $\varepsilon(C)$ dependencies are observed, with well-resolved extrema at specific asphaltene concentrations. The sets of these specific concentrations for both types of solutions may be regarded as virtually identical. In particular, the presence of non-asphaltene species in oil solutions does not significantly alter the positions of the measured extrema and results mainly in the worse resolution of the $\varepsilon(C)$'s structure. For example, in Fig. 2, for oil/toluene solutions, there is a single maximum of absorptivity at $C \approx 197$ mg/l, while for asphaltene solutions, this maximum splits into two components, peaked at $C \approx 159$ and 225 mg/l. A wide oil/toluene maximum close to 500 mg/l develops local minima in asphaltene solutions (Fig. 2). On the other hand, in $\varepsilon(C)$ curves for oil solutions, there is a feature not observed for solutions of asphaltenes, namely a narrow local peak at $C \approx 34$ mg/l (Fig. 3).

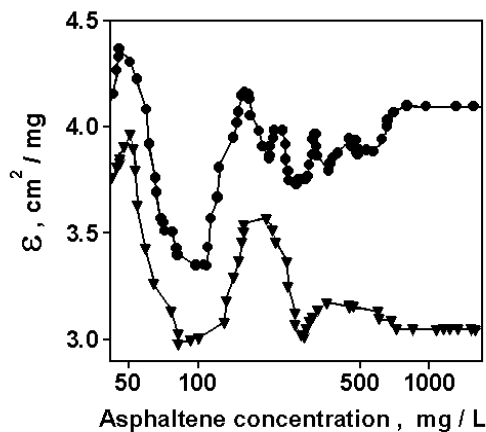


Fig. 2. Absorptivity ε at $\lambda = 670$ nm in toluene solutions of solid asphaltenes (circles) and of the crude oil (triangles). The behaviour expected for ideal solutions ($\varepsilon = \text{const}$) is observed for asphaltene concentrations 0.7– 1.6 g/l. Deviations from this behaviour at smaller concentrations are attributed to asphaltene aggregation

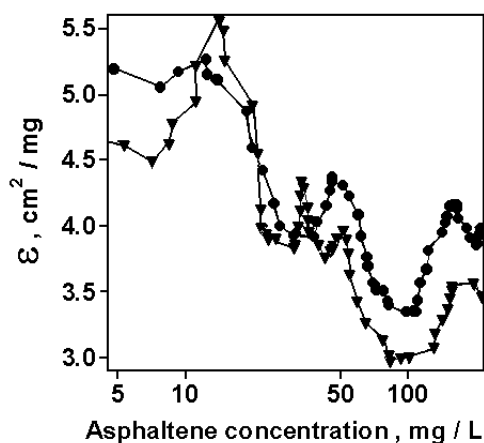


Fig. 3. Concentration dependencies of absorptivities at $\lambda = 670$ nm in dilute toluene solutions of solid asphaltenes (circles) and of the crude oil (triangles).

It is a common practice in optical absorption studies to assume that deviations from the simple Beer's law (implying constant absorptivity) are indicative of molecular aggregation (Sergienko et al., 1979; Rao, 1975; Haswell, 1991; Carroll et al., 1999). Hence, the specific $\varepsilon(C)$ behaviour in asphaltene solutions may be regarded as an evidence of multiple-stage aggregation of asphaltenes. The data of Figs. 2 and 3 show that, for both types of solutions, an increase of asphaltene content leads to a general decrease of ε interrupted by local minima at specific concentrations. We attribute these $\varepsilon(C)$ minima to consecutive stages of massive formation of specific asphaltene aggregates. In support of this attribution, absorption minima in solutions of organic dyes are regarded as indicative of predominance of particular molecular aggregates in the respective concentration ranges (cf. Carroll et al., 1999).

Fig. 3 shows that, at C close to 10 mg/l, there is an abrupt fall of ε terminating with a shallow minimum at about 7 mg/l. At still lower asphaltene concentrations, $\varepsilon(C)$ dependencies are evidently levelling off, indicating a transition to the aggregate-free solution, i.e., to a molecular solution of asphaltenes. In favour of the above conclusion are the data of Groenzin and Mullins (2000), who did not register the presence of molecular aggregates in asphaltene/toluene solutions with asphaltene concentration of ~ 6 mg/l. Consequently, the first $\varepsilon(C)$ minimum at higher concentrations (namely that at $C \approx 25$ –30 mg/l) should be ascribed to a stage of massive formation of the simplest molecular aggregates dimers. At concentrations 30–55 mg/l, an overall increase of absorptivity is interrupted by a local minimum at $C \approx 35$ –45 mg/l, attributed to the transient predominance of asphaltene trimers. The apparent preference of even-numbered asphaltene aggregates was discussed in detail in Akhmetov et al. (2002) and Evdokimov et al. (2003). We interpreted the following sharp decrease of ε and a well-defined deep minimum at $C \approx 85$ –110 mg/l as a stage of massive formation of the stacked four-membered dimer pairs or "nanocrystallites" (NCs). Finally, the absorptivity minimum at $C \approx 240$ –280 mg/l (Fig. 2) may be attributed to formation of such aggregates as [NC + dimer] or [NC + NC].

3.3. Correlation of optical absorption and Rayleigh scattering in asphaltene solutions

The effects of asphaltene concentration C in crude oil/toluene solutions on the intensity S of a laser light ($\lambda = 633$ nm) scattered at 90° were studied with a simplified technique of sample preparation. A single toluene-filled scattering cuvet was used for measuring the entire $S(C)$ dependence and the asphaltene concentration was increased by successive additions of pre-calibrated oil drops to the sample; the measurements were performed within 15–20 min after each change of concentration.

The cumulative data of three measured $S(C)$ dependencies are shown in Fig. 4. For comparison, in the same figure, we present the concentration dependence of absorptivity ε , measured in oil/toluene solutions at $\lambda = 670$ nm. In view of the simplified method of the scattering measurements, there is a sufficiently good correlation between the extrema of both sets of data in Fig. 4. A broad maximum of the scattering intensity (peaked at $C \approx 55$ –60 mg/l) is observed in the concentration range, which includes the main asphaltene aggregation stages, defined by the individually resolved minima of absorptivity curve at C close to 25–30 and 90–100 mg/l.

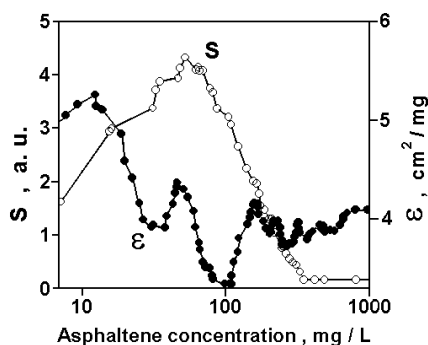


Fig. 4. The effect of asphaltene concentration in crude oil/toluene solutions on: (1) S = intensity of Rayleigh scattering at $\lambda = 633$ nm; (2) ε = absorptivity at $\lambda = 670$ nm.

Maxima of Rayleigh scattering in surfactant-containing petroleum fluids are routinely attributed to massive formation of large molecular aggregates (cf. Bansal and Shah, 1977 and references therein). Hence, the scattering data of Fig. 4 may be regarded as an additional proof of asphaltene aggregation in dilute solutions, with concentrations well below the frequently quoted “critical micelle concentrations” of about several grams per litre.

3.4. Aggregation-sensitive studies reported by other authors

At the time of completion of our experiments (August 2001), we have found only a small number of previous publications, in which certain experimentally observed effects have been interpreted as due to aggregation in solutions at asphaltene concentrations below 1 g/l, namely at 10–15 mg/l (Sergienko et al., 1979), at ~50 mg/l (Acevedo et al., 1999), at ~60 mg/l (Groenzin and Mullins, 2000) and in the range of 100–300 mg/l (Priyanto et al., 2001). A literature survey revealed also quite a number of publications containing experimental results, which, subjected to a proper analysis, show specific effects that may be attributed to the above discussed aggregation stages. These effects, however, have not been noticed by the authors.

As a representative example, consider the studies of asphaltene aggregation in toluene (Castillo et al., 2001). The authors present a “calibration curve”, i.e., a plot of absorbance at 532 nm (optical path length 1 mm) vs. asphaltene concentration in the range of 10–600 mg/l. They state that the linear absorption (i.e., at low light intensities) “is rather insensitive to aggregation processes in the observed concentration range” and that “this observation is confirmed by the almost perfectly linear calibration curve”. The reported concentration range is close to that in our measurements. Hence, we extracted the numerical absorbance values from the experimental points in their “calibration curve” and calculated the respective absorptivities in units of cm^2/mg , as used in our studies. The results of this data analysis are presented in Fig. 5. In spite of a small number of data points from Castillo et al. (2001), the main features of this concentration dependence correspond to those, as registered in our studies (cf. Figs. 2 and 3). Namely, there is an absorbance minimum close to 100 mg/l and two maxima at about 50 and 400–450 mg/l.

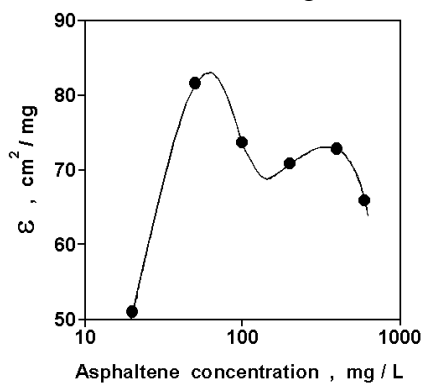


Fig. 5. Concentration dependencies of absorptivities at 532 nm in toluene solutions of solid asphaltenes, calculated from the data of Castillo et al. (2001).

3.5. Evidence for asphaltene oligomers in the published molecular weight data

The observed coincidence of aggregation stages for asphaltenes of different origin points to a similarity of properties of respective asphaltene monomers and oligomers. In other words, both types of asphaltenes evidently belong to the same “chemical species” consisting of “asphaltene molecules” with sufficiently narrow, though polydisperse, distributions of properties and atomic structures.

Asphaltene are still conventionally defined in terms of their solubility classification (cf., e.g., Speight, 1999 and references therein). From this point of view, asphaltene are complex mixtures of different molecular sizes and various functional types, which are characterised by wide structureless molecular weight distributions. The operational “solubility” definition combined with the active, order of magnitude, controversy over asphaltene molecular weight have obscured the existence of governing chemical and structural parameters that may define all asphaltene fractions as belonging to the same chemical species.

The implication that asphaltene may be a chemical entity is becoming more and more popular (Zhao et al., 2001; Kowalewsky and Behar, 1999; Morales-Izquierdo et al., 1999). It has been shown that monomers in seemingly disparate asphaltenes of different origin exhibit certain molecular invariants (cf. Lin et al., 1991; Yen, 1994; Groenzin and Mullins, 1999, 2000, 2001; Buenrostro-Gonzalez et al., 2001; Sharma et al., 2002). It is expected that solubility classification of asphaltenes may be derived from these invariants by accounting for the manner and the degree of asphaltene aggregation in the original crude oil, bitumen, etc.

According to the above cited references, the structural invariants of asphaltene monomer are primarily its shape of a flat sheet, its size of 1–2 nm and its molecular weight of about 750 Da. Another common property, relevant to our studies, is an apparent propensity of asphaltene monomers to form stacked even-numbered oligomers, the most stable being the 4-mer (dimer pair, nanocrystallite), which, in turn, is a main structural unit in more complex aggregates. For example, from the results of Siddiqui et al. (2002), it follows that the average numbers of monomers in asphaltene aggregates from fresh Arabian asphaltens are close to $N \approx 4$ and 8, while in aged asphaltens, there are also aggregates with $N \approx 6$. The studies of oilsand bitumen asphaltens from Canada, Nigeria and USA (Zhao et al., 2001) show that asphaltene aggregates form groups with the average numbers of monomers close to 2 and 8.

The direct evidences of existence of well-defined asphaltene monomers and even-numbered oligomers are observations of molecular weight distributions with multiple peak structures. In Fig. 6, we present such multimodal MW distributions reported by Vazquez and Mansoori (2000) for asphaltens precipitated by *n*-pentane and *n*-heptane from different crude oils. The weak, but easily detectable, maxima (labelled as ‘1’ and ‘2’) at $MW \approx 650$ –750 and 1300–1600 amu may be attributed to asphaltene monomers and dimers. Accordingly, we may attribute the common maxima at $MW \approx 2600$ –3300 amu (labelled as ‘4’) to four-membered NCs. The occurrence of more complex aggregates evidently depends on the method of asphaltene precipitation. For *n*-heptane asphaltens, there is a high peak at $MW \approx 9400$ amu, which may be due to association of three NCs. This peak reduces to a weak shoulder for *n*-pentane asphaltens, where the most prominent feature is a peak at $MW \approx 6700$ amu presumably due to an association of two NCs.

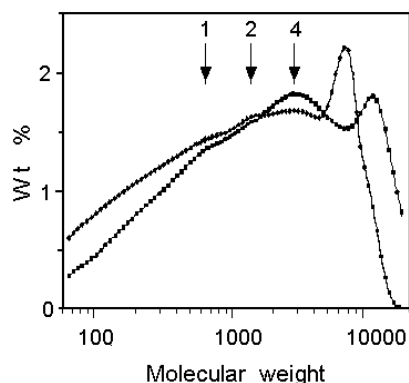


Fig. 6. Molecular weight distributions for asphaltens precipitated by *n*-pentane and *n*-heptane from five different crude oils (Vazquez and Mansoori, 2000).

An example of a one-peak MW distribution being transformed to a multimodal one was presented by Mozaffarian et al. (1997). The authors discuss the earlier data (Stout and Nicksic, 1968) for asphaltens from crudes collected at the wellhead before and after stimulation of the well with steam. Before stimulation, asphaltene MW distributions had a single maximum at ~ 2500 amu, which we may attribute to dimer pairs (NCs). One day after steam stimulation, the MW maximum shifted to ≤ 1600 amu (indicating the predominance of asphaltene dimers) and new less intense peaks appeared in the MW distribution. The broad maximum at $MW \approx 4600$ –4900 amu may be interpreted as due to such even-numbered aggregates as [NC + NC] or [NC + dimer]. Two weaker features at $MW \approx 6700$ –6900 and 8100–8300 amu may reflect the presence of such aggregates as [NC + NC + dimer] and [NC + NC + NC]. Finally, 200 days after steam stimulation, the MW distribution returned to its initial shape with a single maximum close to $MW \approx 2700$ –2600 amu, indicating predominance of nanocrystallites (dimer pairs).

Summarising, a variety of data obtained by numerous experimental methods indicate that asphaltenes of any source or origin may indeed be composed of similar monomers and oligomers with narrow distributions of structural properties. The predominant oligomers evidently are the even-numbered ones. These data are further supported by the similarity of aggregation stages in different types of solutions, as observed in our experiments.

4. Conclusions

The measurements of optical absorptivities reveal the common properties of asphaltene aggregation in toluene solutions of solid asphaltenes and a crude oil. Asphaltenes evidently form aggregate-free (molecular) solutions only at concentrations below 1–5 mg/l. The observed aggregation stages at higher concentrations are attributed to massive formation of even-numbered asphaltene aggregates. It is concluded that at asphaltene concentrations of about 10–20 mg/l dimers become the predominant species, while at concentrations of 90–100 mg/l, quasispherical dimer pairs are formed.

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