

Asphaltene dispersions in dilute oil solutions

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Abstract

By measurements of static light scattering, optical absorption, dynamic viscosity and NMR relaxation we have studied formation of asphaltene dispersions in oil/toluene solutions with asphaltene concentrations from 1.6 to 400 mg/L. The observed threshold concentration for self-assembly of asphaltene monomers is below 10 mg/L, almost three orders of magnitude lower than the frequently reported ‘critical concentrations’ of asphaltene aggregation. The specific behaviour of the measured parameters at concentrations close to 100–150 mg/L we attribute to a phase separation. The discussion of the results suggests the existence of a solvophobic asphaltene subfraction singled out by its extremely low solubility. Hence, aggregation of asphaltenes appears to be controlled by solvent-mediated attraction, determined by the solvophobic effect. ‘Insoluble’ asphaltenes are thought to form the stacked cores of colloidal particles while the more soluble asphaltene fraction may provide surrounding stabilizing shells/coronas.

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1. Introduction

Asphaltenes constitute an important dispersed phase of crude oils, petroleum residues, bitumens as well as of processed fuels [1]. Asphaltenes are regarded to be polar species, formed by condensed polyaromatic structures, containing alkyl chains, heteroatoms (such as O, S and N) and some metals. The tendency of asphaltenes to self-aggregate distinguishes them from other oil constituents. Asphaltene aggregation is the cause of complex non-linear effects in such phenomena as adsorption at solid surfaces, precipitation, fluid’s rheology, emulsion stability, etc. Despite the impact of asphaltenes in many technological and economic spheres, some of their fundamental molecular properties have remained unresolved. Hence, of primary importance are experiments, which may reveal new details of dispersion formation, especially at its initial stages of appearance of the simplest molecular aggregates. A majority of previous aggregation studies have been conducted mostly with solutions of solid asphaltenes precipitated from original crudes, but not with asphaltenes in a native oil media. Some authors point out that

the precipitation techniques may provide an excessively strong interference into the delicate molecular organization of asphaltene associates, leading to their irreversible transformation, so that the supramolecular architecture in solutions of the precipitated material may be different from that in native crude. Consequently, studies of aggregation in crude oil solutions may supply valuable information regarding the manner of asphaltene–asphaltene interactions in the presence of other crude oil components.

Association of asphaltenes in solutions has been the subject of a number of studies, (cf. references in [2,3] and discussion of earlier publications in [4]). The reported specific concentrations of aggregation were typically in the range 2–18 g/L, depending on a solvent. Despite numerous experimental/theoretical studies, a complete picture of the molecular mechanism of asphaltene aggregation still remains elusive. At concentrations below ~ 1 g/L asphaltene monomers are usually assumed to be predominant species in liquid media [5,6]. However, a possibility of asphaltene aggregation at lower concentrations has been suggested in some publications [4,7] and has been investigated in our recent experiments [2,3]. Studies of optical absorption and dynamical properties in dilute toluene solutions of crude oils and of solid asphaltenes provided evidence of a stepwise aggregation with aggregation stages determined almost entirely by the net concentration of asphaltenes in any solution. These studies have shown that molecular solutions are possible only for asphaltene

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concentrations below 1–2 mg/L, while individual aggregation stages, at concentrations up to about 100 mg/L, may be attributed to formation of various asphaltene oligomers. A comparative evaluation of results obtained by different experimental techniques [3], indicated a possibility of a transient phase separation (coacervation) in solutions with asphaltene concentrations \approx 150–170 mg/L.

In this paper, we present several new contributions which include measurements of light scattering and viscosity in toluene solutions of a Tatarstan crude oil. These data are supplemented by some new results on NMR relaxation.

2. Experimental

2.1. Samples

The virgin crude oil was collected directly from a well-head at Romashkinskoye reservoir (Tatarstan, Russia), had a density of 895 g/L, contained ca. 3.5 wt% asphaltenes, 20 wt% resins, 0.3 wt% waxes. Oil samples were stored in the dark, in air. As a solvent, a ‘chemically pure’ grade toluene was used. In each experiment, oil/asphaltene concentration in a single sample was increased by means of consecutive additions to pure toluene (25–40 mL) of pre-calibrated oil drops ($m_{\text{drop}} = 10.8 \pm 0.4$ mg). As a standard procedure, the measurements began within 10–15 min after each oil addition, though the oil dissolution rate (observed by the changes of the measured parameter) was found to depend on the current concentration of the solution. All studies were performed at room temperature (22–25 °C) and at ambient pressure.

2.2. Apparatus and procedure

2.2.1. Static light scattering measurements

Dependencies of the SLS intensity on asphaltene concentration in solutions were studied at 90° geometry in a photon correlation spectrometer (PhotoCor Instruments) [2]. The light source was a He–Ne laser (633 nm, 5 mW), scattered intensity was monitored with a low-noise photo multiplier operating in a photon counting mode (data accumulation times were in the range 1–10 s). The data had to be corrected for optical absorptivity of solutions, owing to a large molecular extinction of asphaltenes [8]. In the studied range of asphaltene concentrations C , a significant increase of optical absorption could be detected by visual inspection of solutions. The resulting optical attenuation of the SLS intensity was taken into account by the introduction of a factor $f_{\text{ATT}} = \exp(\epsilon DC)$ where $\epsilon(C)$ is an extinction coefficient (absorptivity) and $D = 2$ cm is a diameter of a scattering cell. The absorptivity values have been determined in a spectrometer, equipped with a set of light filters (KFK-2 Photocolorimeter [2]).

2.2.2. Viscosity measurements

Dynamic viscosities of solutions were measured in a Hoppler-type viscometer. Oil drops were introduced into the viscometer’s tube, so that one or two revolutions of

the viscometer were needed to homogenize the liquid. The ball falling times (42–52 s) were collected during the following 4–10 revolutions and averaged. A series of measurement were performed to determine the solution densities, required in the Hoppler technique. In the employed dilute solutions density variations were less than a scatter of experimental results. Hence, in calculations of the dynamic viscosity we used the density of oil–toluene solution, determined from the ideal additivity law.

2.2.3. Measurements of NMR relaxation time

The studies were performed in a low field NMR-08-RS Relaxometer (KGU, Kazan) with a permanent magnet and a ^1H frequency of 4.6 MHz [3]. A Carr–Purcell–Meiboom–Gill pulse sequence was used to measure the spin–spin relaxation time T_2 [9]. About 100 FID accumulations were collected in one measurement. After each change of concentration (i.e. an introduction of a new oil drop into the sample), the solution was stirred and the value of T_2 was measured 10 min after the change of concentration.

3. Results and discussion

3.1. SLS data, virial coefficient

Fig. 1 shows the effects of asphaltene concentration in oil/toluene solutions on SLS intensity (corrected for optical absorptivity). Non-monotonous behaviour of the scattering intensity is clearly observed at concentrations below ca. 200 mg/L. Maxima of SLS intensity in surfactant-containing petroleum fluids are routinely attributed to massive formation of molecular aggregates [10]. Hence, the SLS data of Fig. 1 may be regarded as an additional experimental verification of asphaltene aggregation in highly diluted solutions, reported in Refs. [2,3]. Moreover, SLS peaking may serve as an indication of a liquid–liquid boundary in phase-separating (coacervating) solutions [11].

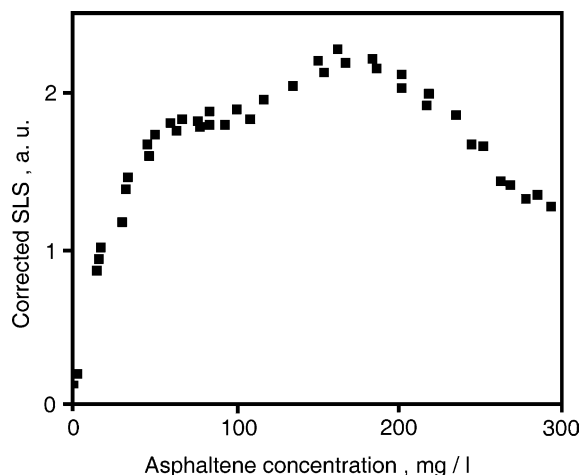


Fig. 1. Static light scattering intensity (corrected for absorption) vs. asphaltene concentration in dilute toluene solutions of the crude oil.

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