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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.

Keywords: Crude oil; Dispersion; Asphaltenes; Aggregation; Phase separation

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 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 ($m_{drop} = 10.8 \pm 0.4$ mg). As a standard procedure, the measurements began within 10-15 minutes 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 (22-25⁰C) and at ambient pressure.

2.2 Apparatus and procedure

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 $f_{ATT} = \exp(\epsilon DC)$ 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]).

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.

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 minutes 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].

The basic Rayleigh – Gans - Debye equation describing light scattering from dilute solutions is usually written [12] as :

$$K^*C/(I - I_0) = 1/M_{app} + 2A_2C + .. \quad (1)$$

where I is the intensity of scattering from a solution; I_0 is the intensity of scattering from pure solvent; M_{app} is the apparent mass-average molecular weight of the solute, A_2 is the second virial coefficient ; C is the solute concentration and K^* is the appropriate optical constant.

In non-aggregating dilute solutions A_2 is virtually constant and the plots of $C/(I - I_0)$ vs C (Debye plots) are expected to result in straight lines. Fig. 2 shows the respective plot of our SLS data. It is clear that that the straight line may be fitted to the data only in the limit of the highest dilutions, at $C < 40\text{-}50$ mg/L . The slope of this line gives a second virial coefficient for two-body interactions: $(A_2)_{DIL}$. The departure from a straight line is indicative of asphaltene aggregation, especially prominent for $C > 150\text{-}170$ mg/L. The strong (and varying) curvature of the experimental Debye plot suggests [12] the concentration dependence of the

virial coefficient. Hence, in the next approximation, we analyzed the data of Fig. 2 by fitting linear functions in a window of the width 40 mg/L, moved along the concentration axis by steps of 5 mg/L. The concentration dependence of “local” virial coefficients was smoothed to suppress high-frequency fluctuations. The results of this procedure are shown in Fig. 3.

In Fig. 3, the concentration-dependent virial coefficient A_2 is normalized to the above value of $(A_2)_{\text{DIL}}$. The peculiar behaviour of $A_2(C)$ may be interpreted taking into account the literature data for surfactant- and polymer-containing solutions. The role of virial coefficients in these aggregating molecular systems is often discussed by an analogy with phase transitions of simple fluids [13]. Namely, one defines regions dominated by either repulsive or attractive two-body interactions as corresponding to regions of a positive or negative A_2 , respectively. These two regions are separated by the specific point (e.g., the specific concentration), at which the second virial coefficient vanishes. This leads to a sharp onset of the solute’s aggregation. The critical (threshold) aggregation concentration (CAC) is expected to be somewhat below the above specific point.

Accordingly, the data of Fig. 3 we may interpret as an indication of a CAC and instability (phase transformation) of an asphaltene subsystem in oil/toluene solutions. The CAC is close to 50 mg/L, where A_2 decreases virtually to zero. The phase transformation evidently begins at about 100 mg/L, where A_2 starts to decrease again. This stage fully develops at 150 mg/L, where A_2 assumes a large negative value ($A_2 \approx - 3,3 \times (A_2)_{\text{DIL}}$). Such behaviour of virial coefficients is typical for structurally unstable systems [13,14] and suggests the onset of massive association which frequently results in a phase separation (demixing, coacervation) [15].

3.2. An apparent bi-fractional composition of petroleum asphaltenes

In the above discussion, the asphaltene (crude oil) solutions have been implicitly assumed to be binary systems, in accordance with contemporary models of asphaltene

flocculation/precipitation [16]. In binary models even complex crude oils are treated as mixtures of two pseudo-components, with asphaltenes as one component and the remainder of the oil as the other. Due to this simplification, the Flory-Huggins polymer theory can be applied to calculate the solubility and phase behaviour of asphaltenes. In terms of the binary model, the above “massive aggregation” at C close to 100-150 mg/L may be qualitatively interpreted as a phase separation into an asphaltene-poor lighter phase and a heavier, asphaltene-rich phase [16].

However, within the limits of the binary solubility model we failed to get a self-consistent explanation for a variety of our experimental results (including viscosity and NMR relaxation data, discussed below). On the other hand, most of our concentration dependencies closely resemble those frequently observed in ternary molecular systems, i.e. in solutions of colloid/polymer [17] or polymer/surfactant [18] mixtures. In particular, the peculiar abrupt changes of virial coefficients at low solute concentrations, like those in Fig. 3, are frequently attributed [17] to additional “multiple-body” attraction between the larger molecules of solute, induced by depletion action of the smaller solute molecules. In the limited range of concentrations the depletion forces become strong enough to induce a transient phase separation (in some cases, a transient gelation [18]). A transient gelation may be further facilitated by a propensity of the smaller solute molecules to adsorb at the larger ones. The necessary common feature of the above phase-separating systems is a strong asymmetry between two components of a solute [18]. In weakly interacting systems this asymmetry is with respect to molecular sizes of co-solutes, while for molecules of comparable dimensions one co-solute is frequently singled out by its strongly lyophobic properties. It should be noted that in some recent publications the observed extrema of virial coefficients are attributed solely to the specific non-DLVO lyophobic/lyophilic interactions [19].

By analogy, we may suggest that the common aggregation behaviour of asphaltenes in different solutions is also determined by their intrinsic asymmetrical bi-fractional

composition. Indeed, the existence of such fractions has been indicated by some recent experiments [20-23]. The asymmetry of two asphaltene fractions (denoted as A1 and A2 in Ref. 20) is manifested mainly by their strikingly different solubilities. The first fraction (A1) is extremely lyophobic and almost insoluble. In toluene at room temperature its solubility does not exceed 93 mg/L [20]. Apparently, aggregation of A1 molecules starts at concentrations as low as 6-10 mg/L, as indicated by surface tension measurements at 25 °C in quinoline solutions [23]. The solubility of the second asphaltene fraction (A2) is higher almost by three orders of magnitude (59 g/L in toluene [20]). The relative amounts of A1 and A2 in asphaltenes obtained by standard techniques (*n*-pentane or *n*-heptane precipitation) evidently depend on the type of the parent crude. Namely, in Ref. 22, 80% of precipitated asphaltenes (apparently A2 fraction) were reported to dissociate to monomeric state in CH₂Cl₂. The remaining undissociated 20% may be attributed to A1 aggregates. In Ref. 20, the relative amount of insoluble A1 asphaltenes in samples of various origin was between 48% and 70%. Asphaltenes with low solubility (A1) are more polar and hydrogen bonding [21]. This fraction has a lower H/C ratio (0.90 [20]) and higher N, V, Ni, and Fe contents [21] than the less polar and more soluble fraction of asphaltenes (A2). Finally, A1 asphaltenes evidently possess some properties of “chemical species” as they may be separated from other asphaltenes by means of a specific chemical reaction. Namely, as shown in Ref. 20, in cumene solutions only A1 asphaltenes form insoluble charge-transfer complexes with *p*-nitrophenol.

3.3 Viscosity of dilute asphaltene-containing solutions

Fig. 4 shows relative dynamic viscosity η_{rel} vs. asphaltene concentration C in toluene solutions of the crude oil. The three data sets are representative results obtained over a period of several months. In spite of quantitative discrepancies (discussed below), there is an overall qualitative agreement of all $\eta_{rel}(C)$ dependencies. Namely, there is a small initial increase of viscosity at C below ca. 10 mg/L, followed by a sharp drop of η_{rel} at higher concentrations. In

the interval of $C = 50\text{-}120$ mg/L the viscosities remain fairly constant and start to increase again at concentrations exceeding 150-170 mg/L. The hatching in Fig. 4 denotes the range of concentrations where we observed some persistent peculiarities in course of viscosity measurements. Namely, in some cases a “jerky” movement of the falling ball was registered, in others – a “poor visibility” or “smearing” of the ball boundaries. These peculiarities did not cause any noticeable increase of the scatter of experimental results, but are important for further discussion.

To our knowledge, concentration dependencies with a viscosity minimum in asphaltene or crude oil solutions have not been reported by other authors. On the other hand, this type of viscosity behaviour has been observed in a number of the above discussed ternary fluids, e.g. in polymer/surfactant/water mixtures [24]. In the relevant publications, the $\eta_{rel}(C)$ minimum is attributed to a transient phase separation (coacervation of a solute). A phase transition may commence with formation of a transient microphase gel, which effectively adsorbs at the viscometer's surfaces [24]. Such adsorption may be the reason for the peculiar character of our results in the shaded region of Fig. 4.

It is well-known [25] that quantitative analysis of viscosity data in strongly interacting/aggregating solutions, like those of asphaltenes, is always a challenge. Since Einstein derived the basic viscosity equation for the hard-sphere diluted suspension, many new models have been proposed [25] the majority of them being purely empirical and providing no information on the molecular processes in the system. The applicability of various colloidal viscosity models with respect to asphaltene aggregates in solutions has been analyzed in detail by Sheu et al. [25]. We have tested several of these models for interpretation of the results in Fig. 4 and found that the most informative one appears to be the Eiler empirical model which explicitly accounts for a maximum packing volume fraction of molecular aggregates ϕ_m :

$$\eta_{rel}(\phi) = [1 + k(\phi/\phi_m)/(1 - (\phi/\phi_m))]^2 \quad (2)$$

where ϕ is the volume fraction of the solute and the constant k is related to the intrinsic viscosity $[\eta]$: $k = [\eta]\phi_m/2$. It is useful [25] to re-write this formula as :

$$(\eta_{rel}^{1/2} - 1)/\phi = [\eta]/2 + (\eta_{rel}^{1/2} - 1)/\phi_m \quad (3)$$

Then the Eiler plot of a $(\eta_{rel}^{1/2} - 1)/\phi$ versus $(\eta_{rel}^{1/2} - 1)$ is expected to result in a straight line, its intercept and slope being determined by $[\eta]$ and ϕ_m .

To calculate the volume fractions of asphaltenes in solutions we used a frequently cited density of solid asphaltenes: $\rho = 1100$ g/L [25]. The respective Eiler plots for all $\eta_{rel}(C)$ data sets from Fig. 4 resulted in characteristic re-entrant α -shaped (γ -shaped) curves with the expected linear dependencies are present only for asphaltene concentrations exceeding 150-200 mg/L. The non-linear behaviour at lower concentrations, i.e. breakdown of the Eiler model, indicates that very dilute oil/toluene mixtures can not be regarded not as suspensions of stable (e.g., hard sphere) colloidal particles. As discussed above, the alternative model is that of evolving (aggregating) solution of strongly interacting molecular species. The abscissa μ at the turning points of each α -shaped curve is determined by the depth of the respective viscosity minimum in Fig. 4 : $\mu = (\eta_{rel}^{1/2})_{min} - 1$. We have found that the Eiler plots for all $\eta_{rel}(C)$ data sets may be reduced to a single universal α -shaped curve after re-scaling them by the respective values of μ (i.e by plotting $(\eta_{rel}^{1/2} - 1)/\phi\mu$ versus $(\eta_{rel}^{1/2} - 1)/\mu$). The corresponding re-scaled Eiler plot is shown in Fig. 5 (for clarity of presentation, we do not show the clusters of overlapping data points and some local deviations due to a fine secondary structure of the original $\eta_{rel}(C)$ dependencies). The possibility of a universal scaling suggests that the discrepancies between the data sets in Fig. 4 are not caused by random experimental errors/artifacts, but are determined by different parameters of certain common physical processes in the studied solutions. The precise nature of these processes is not clear, but some preliminary conclusions may be arrived at from the fact that the empirical scaling parameters μ are correlated with (inversely proportional to) the respective maximum packing volume fractions ϕ_m , evaluated from the linear parts of the unscaled Eiler plots. Namely, for a data set,

denoted by triangles in Fig. 6, $(\phi_m)_1 = 2.8 \times 10^{-4}$, $\mu_1 = -0.0106$, while for a data set, denoted by filled circles, $(\phi_m)_2 = 6.1 \times 10^{-4}$, $\mu_2 = -0.0042$. This gives a ratio $(\phi_m)_2/(\phi_m)_1 \approx 2.2$ in a fairly good agreement with $\mu_1/\mu_2 \approx 2.5$. Hence, scaling by an empirical parameter μ apparently is equivalent to scaling by a maximum packing volume fraction of colloidal particles, appearing in the system after a transient phase separation. We suggest further that the final value of ϕ_m for the colloidal state in each individual experiment was determined by the maximum concentration of strongly interacting asphaltene monomers (the degree of dissolution of the added oil drops) initially achieved in samples with asphaltene concentrations not exceeding 40-50 mg/L. In turn, the precise degree of oil dissolution may have depended on a number of experimental parameters which were not strictly controlled, i.e. on the height from which oil drops fell onto the solution's surface, on the precise manner of stirring the solution, on the time interval between consecutive changes of the sample's concentration, etc.

In more general terms, the above dependence on the "initial conditions" indicates that the individual colloidal properties of an asphaltene-containing petroleum fluid/mixture may be controlled by a specific path to its final conformation, i.e. by a specific sequence of aggregation, dissolution, etc. events. In this case, the final (observed) state of a molecular system may be determined not necessarily by a global free energy minimum (a pathway-independent thermodynamic control), but also by some local free energy minimum on a specific pathway (kinetic control).

Independent of the subsequent interpretation, the plot in Fig. 5 clearly defines several principally different states in the studied oil/toluene solutions. The linear fall from point A (asphaltene concentrations in different experiments from 5 to 15 mg/L) to point B (40-60 mg/L) in the further discussion we ascribe to a state of a "molecular solution" of strongly interacting asphaltene monomers. The almost vertical rise to point C (100-120 mg/L) corresponds to the region of a fine structure in $\eta_{rel}(C)$ dependencies, attributed to formation of simple asphaltene oligomers. The following stage, terminating close to a point D (140-210

mg/L), corresponds to a shaded interval of Fig. 4 and, according to the above arguments, may be attributed to a transient phase separation (coacervation). Finally, the linear rise from point D to point E (≈ 400 mg/L) and to higher concentrations is predicted by the Eiler model and hence should be attributed to a state of a colloidal suspension.

3.4 Correlation of viscosity with NMR relaxation time

A detailed description of NMR relaxation experiments was presented in Ref. 3. The dependencies of spin-spin relaxation time T_2 on asphaltene concentration had the shape, closely resembling that of the $\eta_{rel}(C)$ data. From the measured results, we numerically calculated the quantities $dT_2/d\eta$ in concentration intervals of a fixed width. In order to suppress high-frequency fluctuations and to reveal the general trends of T_2 - η correlation, the concentration dependence of $dT_2/d\eta$ was smoothed with a 5-point sliding data window. The results of this procedure are presented in Fig. 6. In very dilute “molecular solutions” ($C < 40$ - 60 mg/L) the relaxation time linearly increases with increasing viscosity, as indicated by a constant positive $dT_2/d\eta$. At higher concentrations this direct correlation becomes increasingly non-linear and, close to 100 mg/L, a discontinuity of $dT_2/d\eta$ is observed. In the presumed phase-separation regime (150-200 mg/L) $dT_2/d\eta$ becomes negative, indicating the onset of an inverse T_2 - η correlation, which persists at still higher asphaltene concentrations, in the presumed state of a colloidal suspension.

An inverse correlation between NMR relaxation time and viscosity is a conventionally assumed property of petroleum-based fluids. It has been repeatedly observed that T_2 decreases linearly with increasing viscosity on a log-log plot for crude oils [26]. The corresponding negative sign of $dT_2/d\eta$ is predicted by well-known “hydrodynamic” relaxation models [9]. Positive $dT_2/d\eta$ in Fig.6 indicates the breakdown of the hydrodynamic theory at low asphaltene concentrations. Earlier, the breakdown of the hydrodynamic theory was exhibited experimentally in Ref. 27 and attributed to specific molecular interactions. The origin of non-

hydrodynamic behaviour was also investigated by molecular dynamics simulations [28]. The results of these simulations show that positive values of $dT_2/d\eta$ (as well as an appearance of a local $\eta(C)$ minimum) are indicative that asphaltene–solvent interactions are weak compared both to interactions between asphaltenes and to interactions between solvent molecules. This situation is typical for solvophobic solutes, or “repulsive solutes” in the terminology of supercritical fluids [29].

3.5 Possible role of solvophobic effects in asphaltene-containing media

Asphaltenes were frequently classified as lyophobic species in crude oils and in common solvents (cf. a review in Ref. 30). In turn, an extremely low solubility of the above discussed A1 asphaltenes makes them the most lyophobic fraction of n-heptane (n-pentane) precipitants. We suggest that this property is the cause not only of a phase separation/coacervation, commencing at $C \approx 100\text{--}150$ mg/L, but also of anomalies observed at higher dilutions.

Typically, interactions and stability of lyophobic colloids and macromolecular solutions are treated in terms of Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory [31]. While appropriate for a wide variety of systems, the DLVO approach failed to account for some experimentally observed features of stability behaviour. Hence, other types of “non-DLVO” interactions have been put forth [15], one of the most important being the attractive hydrophobic force (hydrophobic effect). Later, it was realized that in this respect water is not unique and similar attractive interactions are likely to exist in many other solvents, hence the new term “lyophobic effect”. In more recent publications these non-DLVO interactions are most often described as “solvophobic effects” [32]. The characteristic feature of solvophobic interactions is the narrow concentration range over which aggregation/phase separation of solute occurs. At present, there is no satisfactory explanation of such “critical aggregation concentration” in terms of an atomistic physical mechanism.

Qualitatively, the attraction between solvophobes is usually explained as an entropic effect, attributed to the solute imparting structural perturbations to the surrounding molecular systems and changing their entropy relative to the bulk solvent. Accordingly, the solvophobic phase separation is treated in terms of "entropic" solubility limit. At low concentrations, the entropy of mixing causes the solute molecules to become individually dispersed in the solvent. When the concentration exceeds the critical limit, the mixing entropy term is overridden by the entropy change of the perturbed solvent, and phase separation occurs.

The macroscopic thermodynamic view is just a description of trends in bulk properties of solution; it does not explain solvophobic effect in microscopic molecular terms. The state-of-the-art understanding of the molecular nature of this effect is based on the results of computer simulations which, however, are not numerous. We have made a detailed literature analysis of theoretical/simulation studies of non-DLVO solutions but did not find any data on solvophobic solvents which may be directly compared to our experimental results. On the other hand, there are quite a number of papers providing theoretical explanation for the anomalies of virial coefficients, viscosity, relaxation time, etc. in solutions of solvophilic molecules. Regarding the solvophobic effect as a "mirror image" of the solvophilic one, the available publications may be implemented for interpretation of our experiments.

Firstly, maxima of the second virial coefficients in dilute protein solutions were explained by non-DLVO interactions of the "attractive" solvophilic solute [19]. In line with these theoretical arguments, minima of A_2 observed in Fig. 3, may be explained by the "repulsive" solvophobic properties of the studied asphaltenes.

Secondly, a well-defined local viscosity maximum have been observed in dilute aqueous solutions of 1,2-dimethoxyethane [33]. These measurements were interpreted (via molecular dynamics simulations) in terms of strong (attractive) perturbations of the solvent, induced by the solvophilic solute molecules. Namely, from a dynamic point of view, in solutions there appears a new kind of "perturbed" solvent molecules, confined in the solvation

shells. The molecules perturbed by a solvophilic solvent are characterized by longer relaxation times and lower translational/rotational diffusion coefficients, which explains the observed anomalous increase of viscosity [33].

By analogy, we may explain the viscosity anomalies observed in extremely diluted solutions of asphaltenes (Figs. 4-6) by the solvophobic effect, in other words, by the “repulsive” perturbations (“depletions”) of the solvent. Solvophobic interactions are most commonly regarded to be entropically-driven. However a useful molecular picture is that of an “attraction of a solute through repulsion (local depletion) of a solvent”. An example is the local solvent density depletion around the repulsive solute at supercritical conditions [29]. Depleted zones may be viewed as “anti-solvation shells”. The solute molecules have to escape from these zones in order to avoid being confined and thereby have their translational entropy lowered. Hence, the “repulsive” perturbations by solvophobic asphaltenes should effectively decrease relaxation times and increase diffusion coefficients of the perturbed solvent. At high dilutions, the overall dynamical features of a solution apparently are controlled by those of a solute. Additional A1 asphaltene monomers, which are strongly interacting and extremely solvophobic, form more and more extended depletion volumes. This increases the overall mobility of toluene, and results in a decrease of the solution’s viscosity η which correlates with the decrease of the NMR relaxation time T_2 (cf. Figs. 4 and 6). Such behaviour is terminated by massive aggregation of A1 asphaltenes. The solvophobic interactions may determine some specific structural properties of asphaltene aggregates. Namely, solvophobic effects have been invoked [34] in explaining π -stacking of molecules with large planar aromatic subunits, like those in asphaltenes. The phenomenon of π -stacking is incorporated in some well-known models of asphaltene aggregation [4] and the formation of stacked “face-to-face” aggregates in dilute asphaltene solutions was indicated by the blue shift of optical absorption bands in our recent experiments [2,3].

The depletion of the solvent density around a molecular aggregate was shown to increase with its size, which results in a much more attractive solvophobic force between the larger aggregates [32]. Hence, aggregation may provide conditions for an onset of a phase separation of asphaltenes. Note that in a phase separation region one may expect a crossover from the solvent-dominated direct (solvophobic) correlation to the solute-dominated inverse (hydrodynamic) correlation between viscosity and relaxation time (Fig. 6).

It should be also noted that no precipitation have been observed in the studied solutions. Hence, there is obviously some molecular mechanism of stabilizing asphaltene dispersions. The prevailing view is that asphaltenes are peptized and prevented from precipitation in the oil media by the resinous components [1]. In the studied dilute solutions there is evidently some other stabilizing agent, as our previous results [2,3] show the similarity of aggregation properties in resin-free solutions of solid asphaltenes and in resin-containing solutions of crude oils. Taking into account the above discussion and the aggregation model of Ref. 20, we suggest that the aggregates of A1 asphaltenes are stabilized by the more soluble A2 fraction. Being less solvophobic, A1 molecules do not form closely packed face-to-face structures. They are thought to adsorb at the A1 stacked aggregates in the edge-to-surface manner, and stretch their aliphatic groups outward to form a steric-stabilization shell (corona) around the A1 core [20]. The possibility of adsorption of asphaltenes on an insoluble asphaltene derivative also has been verified experimentally [35]. Summarizing, the A1-A2 core-shell (core-corona) structures are thought to be responsible for asphaltene colloidal stability, at least in the case of dilute solutions. On the other hand, the A2 asphaltenes may play a crucial role in the presumed transient gelation of the asphaltene-rich microphase. The above discussed natural abundance of A2 fraction is evidently close to that of A1 asphaltenes. Hence, in very dilute solutions apparently all A2 asphaltenes are bound in the core-corona structures. At higher concentrations, additional A1 aggregation should result in the decrease of the relative volume of the coronas/shells and in the appearance of free A2

molecules. In the asphaltene-rich coacervates these molecules may interact with the bound ones via the side aliphatic chains and “glue” the core-shell aggregates into extended gel-like structures.

4. Conclusions

By a variety of experimental techniques we have studied asphaltene dispersions in dilute toluene solutions of a crude oil. The discussion of experimental results and comparison with other published data strongly support the idea that asphaltenes are composed of two main fractions with principally different solubilities. One of these fractions is so solvophobic that even in dilute solutions it is on the edge of instability. It exhibits an onset of aggregation and an apparent phase separation (coacervation) at overall asphaltene concentrations close to 10-15 and to 100-150 mg/L, respectively. Presumably, one of the key factors that govern the aggregation processes is the solvent-mediated interaction between asphaltenes, determined by the solvophobic effect. The asphaltene colloidal particles are thought to have core-shell (core-corona) structures. Presumably, the cores are stacked aggregates of “insoluble” asphaltenes, while the stabilizing shells/coronas may be composed of asphaltene molecules with higher solubility.

Finally, it should be noted that after this article has been submitted to publication, there appeared a number of papers with independent proofs (by various experimental techniques) of onset of asphaltene aggregation at concentrations close or below 10 mg/L [36-38], as well as of a massive aggregation stage at concentrations of 50-150 mg/L ([39] and references therein).

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Figure captions

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

Fig. 2. A Debye plot of absorption-corrected SLS results. The solid line is linear dependence expected in case of a constant second virial coefficient.

Fig. 3. Normalized concentration-dependent second virial coefficient in oil/toluene solutions.

Fig. 4. Relative dynamic viscosity of dilute oil/toluene solutions. Three data sets were obtained in different experiments over the period of several months. The concentration range defined by hatching was attributed to a phase separation.

Fig. 5. Scaled Eiler plots for three viscosity data sets denoted by the same symbols as those in Fig. 4. The letters denote the consecutive characteristic states of solutions with increasing asphaltene concentration.

Fig. 6. Correlation of NMR relaxation times T_2 and dynamic viscosities η in oil/toluene solutions.

Figures.

Figure 1.

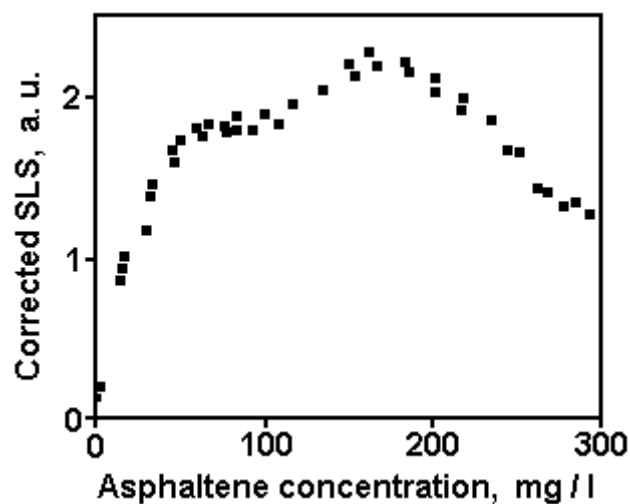


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Figure 2.

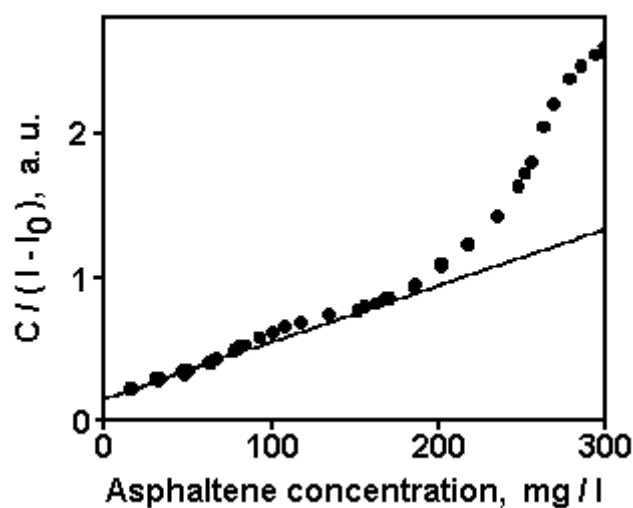


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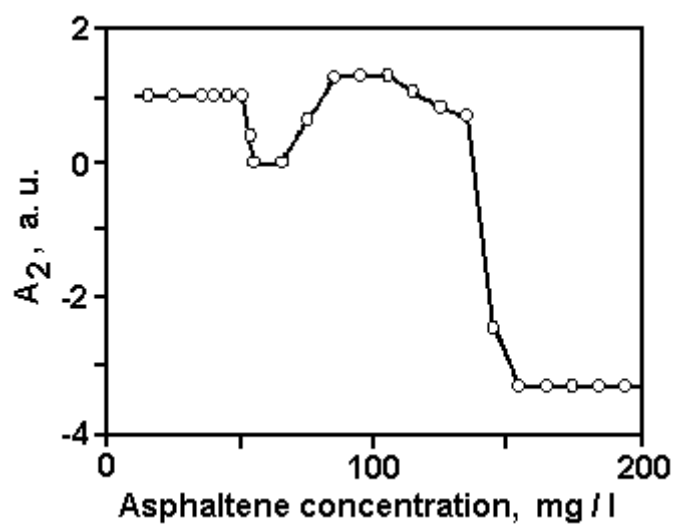
Figure 3.

Figure 3. Normalized concentration-dependent second virial coefficient in oil/toluene solutions.

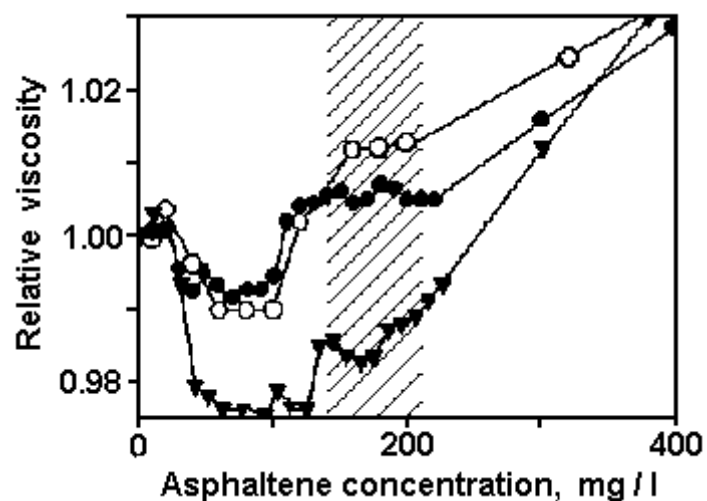
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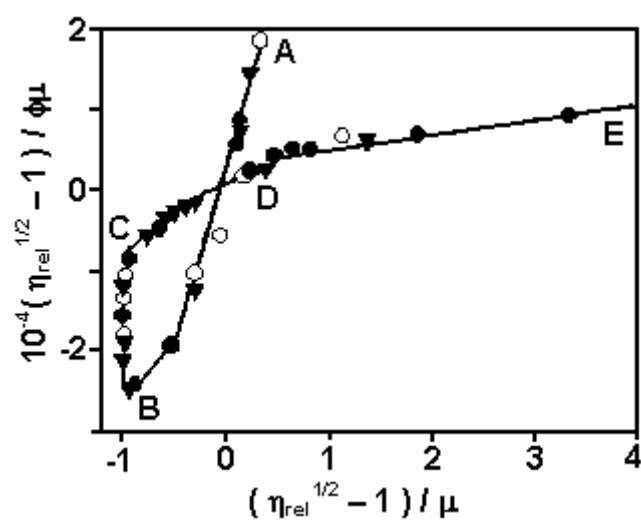
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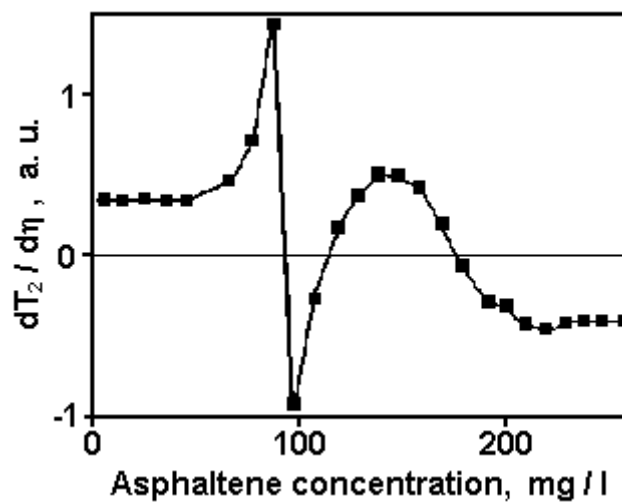
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