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**Initial stages of asphaltene aggregation in dilute crude oil solutions:
studies of viscosity and NMR relaxation**

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Abstract

In crude oil – toluene solutions dynamic viscosity η and spin-spin relaxation time T_2 were measured as functions of asphaltene concentration C in the range of 10-300 mg/l. The results were supplemented by studies of optical absorption. Extrema in the measured concentration dependencies are attributed to a transient predominance of specific asphaltene aggregates – from dimers to stacked molecular nanoclusters (MNCs) of four monomers. The strikingly non-ideal properties of solutions with C below 150-170 mg/l are attributed to the strong interactions between asphaltene species. At higher C the solution properties are evidently determined by the weaker interacting MNCs and the concentration effects are closer to those in ideal fluid mixtures. The observed re-entrant $\eta(T_2)$ behaviour in asphaltene solutions hypothetically has the same origin as in supercooled or demixing molecular systems, where anomalous structural and dynamical features are often explained by emerging heterogeneity due to transient spontaneous clustering.

Keywords: Asphaltenes; Aggregation; Crude oil; Phase transition; Re-entrance

1. Introduction

Asphaltene aggregation is a phenomenon of considerable importance for petroleum industry. The increased aggregation is the cause of enhanced oil viscosity, undesirable stabilisation of water/oil emulsions, flock formation, low solubility and precipitation of asphaltenes, etc. As a consequence, significant difficulties may arise in the production, transportation and processing of crude oil. Despite the impact of asphaltenes in many technological spheres, some of their most fundamental properties have remained unresolved. Studies of crude oil solutions, particularly in aromatic solvents, such as toluene, could give important information regarding the concentration at which the aggregation begins and the manner of asphaltene-asphaltene interactions in the presence of other crude oil components.

Association of asphaltenes has been the subject of a number of studies, basically focusing on the apparent “micellisation” of asphaltenes (for earlier works cf. [1]). The methods employed have been calorimetry [2], measurements of surface tension [3], of viscosity [4,5] small-angle neutron scattering [6], X-ray diffraction [7,8], optical fluorescence [9], nonlinear optical [10] and thermo-optical [11] effects, etc. The measured “critical micelle concentrations” (CMCs) for asphaltenes are in the range 2-18 g/l, depending on a solvent. According to the definitions of a CMC [12], below this concentration asphaltenes in solution should exist in a molecular state, and “micelle” formation occurs only above the CMC. Despite of all the experimental evidence, the process of asphaltene aggregation is still not well-characterised and it is not clear whether one should consider asphaltenes in a solvent below the measured CMC either as a true molecular solution or as a dispersion of smaller molecular associates such as dimers, trimers, etc. [1,11].

It is well-known, though, that in organic solvents, e.g. in an oil medium, aggregation occurs by mechanisms different from those for micellisation in water [12]. For instance, a stepwise mechanism is more likely [11,13] where dimers, trimers and higher aggregates are consecutively formed as the asphaltene concentration is increased. The possibility of asphaltene aggregation below the conventional CMC has been investigated in our recent study [13]. We have measured the near-UV/Vis optical absorption in dilute toluene solutions of crude oils and of solid asphaltenes and obtained evidence in favour of a stepwise aggregation with aggregation stages determined almost entirely by the net concentration of asphaltenes in any solution. In particular, an increase of asphaltene concentration caused a blue shift of the Soret absorption band of porphyrin-type asphaltene chromophores, indicative that molecular aggregates are of the stacked (face-to-face) type. We concluded that molecular solutions are possible only for asphaltene concentrations below 1-2 mg/l. The most prominent of the observed aggregation stages, at concentrations of about 100 mg/l, we attributed to formation of stable asphaltene 4-mers (dimer pairs). It should be noted that the stacked four-membered asphaltene aggregates had been singled out in the aggregation model developed by T.F. Yen [1,8], who defined them as nano-sized “crystallites”. In line with a contemporary terminology in such fields as supramolecular science and nanotechnology, we have introduced [5,13] for a Yen’s “crystallite” the term “molecular nanocluster” (MNC).

In the present paper we report additional optical results and discuss new properties of asphaltene aggregation, revealed by measurements of NMR relaxation time T_2 and of dynamic viscosity η in dilute crude oil solutions in toluene. Knowledge of these properties is important in the characterisation of petroleum reservoirs by NMR well logging and in prediction of production performance. In addition, existing

theories show that a comparative study of η and T_2 may provide new information on the intermolecular interactions [14,15]. The new experimental results indicate that the properties of solutions may be affected not only by formation of particular asphaltene aggregates, but also by the phase changes of the solution as a whole.

2. Experimental

2.1. Samples

The virgin crude oil was collected from a well-head at Romashkinskoye reservoir (Tatarstan) and after water separation had a density of 895 g/l, contained ~3.5 wt. % asphaltenes, ~20 wt. % resins, ~0.3 wt. % waxes. The obtained crude was stored in the dark, in air. As a solvent, a “chemically pure” grade toluene was used. Each optical measurement was performed on a new solution. In NMR and in viscosity experiments, the concentration of the sample was changed by means of consecutive additions to pure toluene (25-40 ml) of calibrated oil drops ($m_{drop}=10.8\pm 0.4$ mg).

2.2 Apparatus and procedure

The optical absorption at $\lambda=315-750$ nm have been studied with a spectrometer, equipped with a set of light filters (KFK-2 Photocolorimeter [13]). The optical cuvetts had the path length of 5.07 mm which predetermined the studied range of asphaltene concentrations in oil solutions (~110 samples): from 5.1 mg/l to 1.3 g/l. The absorptivities (extinction coefficients) ε in units of cm^2 per mg of asphaltenes were calculated from the measured light intensities by using a Beer-Lambert's law.

NMR relaxation time studies were performed on a low field NMR-08-RS Relaxometer (KGU, Kazan) with a permanent magnet and a ^1H frequency of 4.6 MHz. A Carr-Purcell-Meiboom-Gill pulse sequence was used to measure the spin-

spin relaxation time T_2 . 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, the measurements were started within 30 seconds and repeated with an interval of approximately 1 minute. The initial (one to three) decay curves were always biexponential. The fast relaxing component was attributed to non-dissolved oil, while the slower relaxation was close to that in pure toluene. After 3-5 minutes the biexponential behaviour was no longer evident, so the results were approximated by a single exponential decay with an “apparent” relaxation time T_2 . As a standard procedure, each solution was characterised by the value of T_2 measured 10 minutes after the change of concentration.

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 homogenise 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 (mostly 0.03-0.6 wt. % of oil) density variations were less than a scatter of experimental results. Hence, in calculations of the dynamic viscosity η we used the density of solution ρ , determined from the additivity law:

$$\rho = (1-z)\rho_T + z\rho_O \quad (1)$$

where z is the mass fraction of oil, ρ_T and ρ_O – the densities of pure toluene and of the crude oil, respectively.

All studies of crude oil/toluene solutions were performed at room temperature and at ambient pressure.

3. Results

3.1. Studies of optical absorption

In Fig. 1 we present a typical plot of 540 nm absorptivity ε vs. asphaltene concentration C in crude oil solutions in toluene. In very dilute solutions, for $C < 120$ -150 mg/l there is an overall *decrease* of ε with increasing concentration (the details are shown at the insert at Fig.1). In solutions with higher asphaltene content the measured $\varepsilon(C)$ dependence qualitatively changes – absorptivity *increases* with a diminishing rate. A simple Beer's law ($\varepsilon = \text{const}$) is fulfilled at concentrations higher than 700-750 mg/l. It is well-known that sharp deviations from the Beer's law are caused primarily by phenomena of molecular aggregation. Hence, an observed change from a decrease to an increase of ε with growing asphaltene content may be attributed to a process of massive aggregation of asphaltene species. Accordingly, the well-defined extrema of $\varepsilon(C)$ we attribute to a transient predominance of specific molecular aggregates. Namely, taking into account the existing models of asphaltene aggregation [1,8] and the results of our previous studies [13], we attribute the extrema just above 90-100 mg/l to stable molecular nanoclusters of four stacked asphaltene monomers (cf. Introduction), and the $\varepsilon(C)$ structure at 10-25 mg/l – to stacked (face to face) asphaltene dimers.

3.2. Reproducibility of the aggregation-sensitive features in NMR and viscosity studies

All measured dependencies of T_2 and of η on asphaltene concentration in crude oil solutions revealed the presence of non-monotonic features, resembling those in Fig. 1. The specific concentrations, defined by the extrema of these dependencies, were fairly well-reproduced in all experiments over a period of about three months.

However, the magnitude of the T_2 and η variations (i.e. the exact shapes of $T_2(C)$ and $\eta(C)$ curves) could notably change from one experiment to another. As an example, Fig. 2 shows the effects of asphaltene concentration on relative relaxation times (with respect to pure toluene) measured at 24⁰C in two consecutive days. A double peak close to 100 mg/l is present in both sets of results, but the changes of its shape and intensity are clearly seen. The discrepancies between different experiments apparently were due to some uncontrollable parameters, hypothetically to outside weather conditions (atmospheric pressure, humidity, magnetic field), to temporal/thermal history of the stored crude oil, etc. These discrepancies were of relatively minor importance for the analysis of asphaltene aggregation stages, determined from reproducible peak positions. On the other hand, additional information could be obtained from quantitative comparison of relaxation times and dynamic viscosities. In view of the influence of uncontrollable parameters, such comparison required special “parallel” NMR and viscosity experiments with the same samples, conducted at the same time and at the same location.

3.3. “Parallel” NMR and viscosity experiments

All “parallel” experiments have been conducted in a room free from other working equipment and typically lasted from 3 to 5 hours. The results of one of such experiments (T=23⁰C) are presented in Fig. 3 and Fig. 4.

Fig. 3 shows the dependence of the dynamic viscosity η on the asphaltene concentration C in crude oil/toluene solutions. At $C > 150$ -200 mg/l there is a “routine” monotonic increase of η with increasing C . At lower concentrations, apart from local extrema indicative of asphaltene aggregation (cf. Fig. 1), the notable feature of the measured dependence is an overall initial *decrease* of viscosity with the increasing

content of a more viscous component (crude oil). To our knowledge, this is the first reported case of such unusual viscosity behaviour in crude oil (asphaltene) solutions. In Section 4.1 we attribute the $\eta(C)$ decrease to strong intermolecular forces between asphaltene species in the “molecular solution” liquid phase (at C below ≈ 100 mg/l). The local $\eta(C)$ structure may be attributed, in accordance with Fig.1, to transient stages of asphaltene aggregation/clustering. The transient spontaneous clustering is presumably a finite-concentration effect and is governed by a competition between energy gained and entropy lost in cluster formation. The transient asphaltene aggregates are believed to be loosely-bound and may contain entrapped solvent molecules. There is a good overall agreement between the aggregation stages revealed by the optical and by the viscosity studies. Namely, the isolated $\eta(C)$ maximum at $C \approx 15-20$ mg/l was well-reproduced in all experiments (cf. Fig. 2) and is only slightly shifted from the position ($C \approx 12-16$ mg/l) of the major maximum of optical absorptivity in Fig. 1.

Fig. 4 shows the effects of an asphaltene concentration C in the studied crude oil/toluene solutions on the measured relaxation times T_2 . The above discussed asphaltene aggregation stages are again revealed by non-monotonic features of the $T_2(C)$ curve, closely resembling those observed in optical studies (cf. Fig. 1). A comparison with the “parallel” viscosity results in Fig. 3 shows that for concentrations below 150-180 mg/l there are *in-phase* variations of η and T_2 . Such in-phase behaviour is unexpected in the framework of the conventional NMR relaxation models, which predict that the relaxation time should be *inversely* related to η (cf. Section 4.2). In our experiments, the predicted inverse (out-of-phase) relationship of the data in Fig. 3 and in Fig. 4 was observed only at comparatively high asphaltene concentrations, where η increased and T_2 decreased with increasing C .

3.4. Correlation of NMR relaxation time and dynamic viscosity

To test the predictions of relaxation models for composite fluids, the relaxation time is habitually plotted not versus the fluid's composition, but as a function of some principal model parameter, such as the dynamic viscosity [14,15]. Such plot of our “parallel” experimental results from Figs. 3,4 is shown in Fig. 5. For a convenience of presentation, the measured T_2 and η are normalised to their respective values in pure toluene. In the figure, the capital letters “A” to “E” denote the consecutive specific states at the $T_2(\eta)$ “trajectory”, observed in the crude oil solutions with increasing asphaltene concentration (point “A” corresponds to pure toluene). The concentration increases along the path defined by arrows.

The $T_2(\eta)$ trajectory in Fig. 5 has a complex shape, sometimes referred to as the re-entrant behaviour of the relaxation time [14]. In discussions of experimental or simulated results [14] the term “re-entrance” is frequently employed just to define a situation, when different relaxation times are observed in solutions of the same viscosity. However, in the theories of phase transitions and critical phenomena [16,17] this term is much more meaningful. In particular, it may define a case, where a relatively small increase of a system's thermodynamical parameter induces a phase transition towards a new state, whereas a further increase of the same parameter drives the system back to its initial state through a “re-entrant” phase transition. As shown in the following discussion, various liquid phases may be identified by their strikingly different $T_2(\eta)$ dependencies in Fig. 5.

4. Discussion

The literature analysis shows that experimentally verifiable viscosity and relaxation models have been developed only for the simplest molecular systems, i.e. for binary mixtures (solutions). Hence, for the purpose of further discussion, we will regard the studied mixtures of toluene with the multicomponent crude oil as binary solutions of asphaltenes in a solvent composed of lighter “hydrocarbon” molecules. This assumption is supported by our earlier observations [13] of similarity of asphaltene aggregation in solutions of solid asphaltenes and of the parent crude oils.

4.1. Non-ideal composition dependence of viscosity

It is well known that in a real binary liquid mixture its viscosity η may be different from its predicted ideal value η_{id} given by the linear additivity law [18]:

$$\eta_{id} = x_A \eta_A + x_B \eta_B, \quad (2)$$

or by the logarithmic law [19]:

$$\ln(\eta_{id}) = x_A \ln(\eta_A) + x_B \ln(\eta_B) \quad (3)$$

where x_A and x_B are the mole fractions and η_A and η_B are the viscosities of the corresponding single component liquids.

Positive deviations from the ideal laws for viscosity (i.e. $\eta > \eta_{id}$) have been reported for various liquid mixtures [20,21]. Our results in Fig. 3 present a rare case of negative deviations from the ideal viscosity behaviour.

Quantitative explanation of the observed effects may be obtained from some simple thermodynamic arguments. In particular, the strength of the intermolecular forces affects the shape of the concentration dependence of the mixture's free energy F [22]. For fully miscible binary mixtures the (negative) interaction energies are dominated by the thermal energy, and the $F(x)$ dependence is convex (has a single

broad minimum). In this case, the dependencies of density, viscosity, etc. on concentration are either ideal, or show positive deviation from the ideal laws.

The observed negative deviations from the ideal viscosity seem to be accounted for by non-convex $F(x)$ dependencies in mixtures, where the interaction energies exceed the thermal energy. In this case the $F(x)$ function has a shape of a double well potential (a broad maximum flanked by shallow minima at x close to 0 and to 1). This manner of the free energy dependence allows for the separation of two phases with different concentrations, i.e. for a gap of miscibility [16,18]. The multiple extrema of the free energy are also believed to be the cause of strong heterogeneity and transient clustering in molecular systems, e.g. in supercooled liquids [23,24]. The exact shape of $F(x)$ and the manner of deviations of η from η_{id} depends on the relation of various interaction energies. In the context of our studies, a local viscosity minimum (Fig. 3) may be expected if the asphaltene-solvent interactions are weaker than both the asphaltene-asphaltene and the solvent-solvent interactions.

The above conclusions are supported by the detailed analytical calculations and molecular dynamics simulations presented in [14]. To calculate the viscosities, the authors introduced a model which directly accounts for interactions (described by the Lennard–Jones 12-6 potential) in the binary liquid mixtures. The results of [14] show that, depending on the relative strengths of interactions, there can exist different types of viscosity behaviour. In particular, our results, i.e. a viscosity minimum in dilute solutions of asphaltenes, seem to be described by a model of [14] in the assumption of weak asphaltene–solvent interactions (with a shallow potential well of a relative depth $\varepsilon_{AS}=0.3$), while assumed interactions between asphaltenes ($\varepsilon_{AA} = 1.0$) are notably stronger than those between solvent molecules ($\varepsilon_{SS} = 0.5$).

4.2. Re-entrant relaxation in crude oil solutions

There is a conventionally assumed inverse correlation between NMR relaxation time and viscosity for petroleum-based fluids. It has been observed that T_2 decreases linearly with increasing viscosity on a log-log plot for crude oils ([25] and references therein), for pure alkanes and alkane mixtures [26].

Some works show that the dominant relaxation mechanism for liquid hydrocarbons is through dipole-dipole interactions [27,28]. In this case, the NMR relaxation times are expected to be proportional to the rotational diffusion coefficient D_R , which is given by the well-known Debye–Stokes–Einstein relation [28]:

$$D_R = k_B T / (8\pi\eta a) \quad (4)$$

where $k_B T$ is the Boltzmann constant times the temperature, η is the viscosity of the liquid and a is the radius of the molecule. In this “hydrodynamic” model the spin-lattice and the spin-spin relaxation times are given by:

$$T_1 \approx T_2 \propto \eta^{-1} \quad (5)$$

Thus, according to the hydrodynamic theory, the viscosity is a unique determinant of the rotational relaxation time.

The breakdown of the hydrodynamic theory was exhibited in [15] by measurements of different relaxation times in solutions at the same viscosity but at different compositions. This re-entrant behaviour of the relaxation time has been qualitatively attributed to the specific molecular interactions [15]. Later, the origin of such re-entrance have been investigated in [14] by molecular dynamics simulations. The re-entrant relaxation behaviour was found in the same binary systems which have shown non-ideal viscosity dependence (cf. Section 4.1). The important results of the simulations were that the non-ideality in viscosity alone cannot explain re-entrance, and that the relaxation time depends more on the composition of the mixture. In

particular, re-entrance may be expected in heterogeneous mixtures with fluctuations of the system's composition induced, e.g. by the transient clustering of the strongly interacting component. In terms of the molecular systems, investigated in our studies, the results of [14] indicate that the re-entrance of the NMR relaxation time T_2 (Fig. 5) may be due to the transient processes of asphaltene aggregation.

4.3. Possible phase transitions in asphaltene-containing fluids

Among the systems exhibiting the phenomenon of re-entrance are the binary mixtures that show a closed-loop phase diagram (temperature versus concentration graph) [29]. In these systems the two liquids are completely miscible outside the loop and immiscible (splitting into two liquid layers) within the loop. Some of the models attribute the onset of the demixing phenomenon to the appearance of transient molecular complexes, i.e. to local inhomogeneities in the macroscopically homogeneous mixture. Recent experiments [30] show that in such mixtures there is a sizeable attractive interaction between the solute molecules even at the lowest concentrations, where no macroscopic phase segregation is observed.

The known properties of demixing fluids (e.g. re-entrance, strong intermolecular interaction, molecular aggregation, phase transformation) resemble some of those observed in our studies. Hence, our experimental results of Figs.1-5 may be regarded as indicative of the following scenario of the phase behaviour in the studied fluids.

At the lowest asphaltene concentrations ($T_2(\eta)$ trajectory between the points "A" and "C" in Fig.5) the solutions are fairly homogenous and their non-ideal properties are governed by strong interactions between asphaltene monomers. The dynamic viscosity and the NMR relaxation time in this liquid phase synchronously

decrease with increasing asphaltene content. The simplest asphaltene aggregates (dimers) appear at $C \geq 10$ mg/l, hence the local extrema at concentration dependencies in Figs.1-4 and the distortion of the $T_2(\eta)$ trajectory at the point “B” in Fig.5.

For concentrations above 90-100 mg/l the fluid properties are apparently dominated by transient clustering of asphaltenes (cf. trajectory loops in Fig. 5), the solution becomes inhomogeneous and starts to demix into an asphaltene-rich phase and a hydrocarbon-rich phase. However, no macroscopic phase separation follows, owing to the strongly non-equilibrium character of an asphaltene-rich phase (which may be described as a supersaturated or as a supercooled asphaltene solution). Hence, the emerging local regions of this phase quickly relax not by coalescence into a continuous bulk phase, but by a process of exothermic “nanocrystallisation” - formation of asphaltene molecular nanoclusters (MNC’s), weakly interacting with each other as compared to asphaltene monomers. As a result, in spite of the evident pre-demixing behaviour, the closed two-phase loop at the phase diagrams may never be detected in asphaltene solutions. However, the observed re-entrance apparently is closely related to the (potential) demixing phenomenon, as with the increasing asphaltene concentration the initially homogenous solution passes through a heterogeneous pre-demixing state and again returns to a homogenous phase at $C \approx 150$ mg/l. In Fig.5 this liquid phase commences at the state “D” and continues through the state “E” to higher asphaltene concentrations, uninterrupted by any major aggregation stages. As compared a to dilute solution, the properties of this phase are closer to those of ideal binary mixtures with non-interacting components and it may be described as a solution of asphaltene MNC’s or as a nanocolloid system. In this phase, the relaxation time T_2 is inversely proportional to viscosity, in line with the previously reported studies of petroleum-based fluids (cf. Section 4.2).

Summing up, our experimental results indicate the possible existence of different phases in dilute crude oil (asphaltene) solutions. A major phase transition (at 23⁰C) occurs at the asphaltene concentration somewhat below 150 mg/l. This transition point evidently belongs to a well-defined boundary line on the phase diagram of asphaltene-containing fluids. One more boundary may be defined by the conventionally cited asphaltene “CMC” (cf. Introduction). However, the existing experimental evidence is still not sufficient to answer the question, whether a true phase transition takes place at “CMC”, or the observed specific features are just apparent effects of some gradual aggregation process.

5. Conclusions

Based on the results of the optical, viscosity and NMR relaxation studies, it can be concluded that the molecular aggregation in crude oil solutions is a stepwise process, eventually leading to a phase transformation of a liquid. Local extrema in the measured concentration dependencies we attribute to a transient predominance of asphaltene aggregates from dimers to molecular nanoclusters (MNC's) of four stacked monomers. The dilute solutions in toluene (asphaltene concentrations below 100-150 mg/l) show peculiar non-ideal concentration dependencies resulting in an apparent re-entrant transition to a MNC-dominated fluid phase with the properties closer to those in ideal mixtures. The model discussion indicates that the key to the nonideality of the solutions belongs to the strong interactions between the non-associated asphaltene molecules even in the presence of very low levels of asphaltenes. The solution behaviour cannot be fully captured by using only the “static” models of the possible structures of asphaltene aggregates. The studied solutions show complex dynamic properties found in supercooled or demixing molecular systems, where transient

spontaneous clustering is often invoked in order to explain anomalous structural and dynamical features. We believe that the present study may provide further insight into the formation, stability and dynamic properties of molecular aggregates in crude oils, as well as in other asphaltene-containing industrial fluids.

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FIGURES

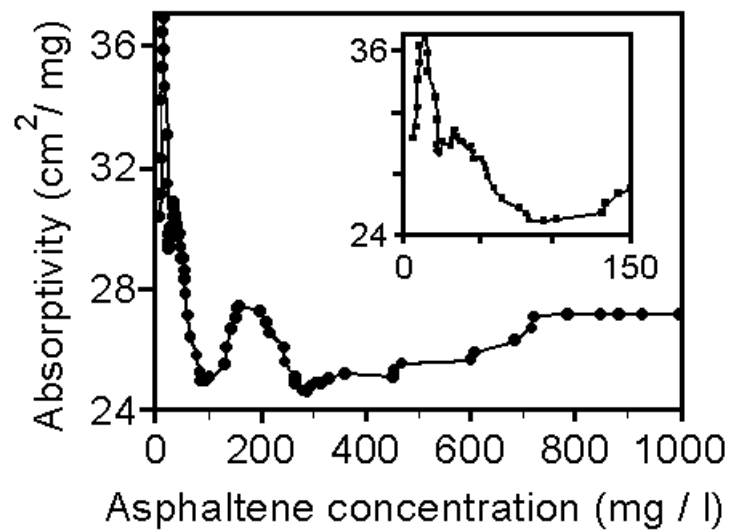


Fig. 1. Optical absorptivity of asphaltenes at 540 nm ε as a function of asphaltene concentration C in crude oil/toluene solutions.

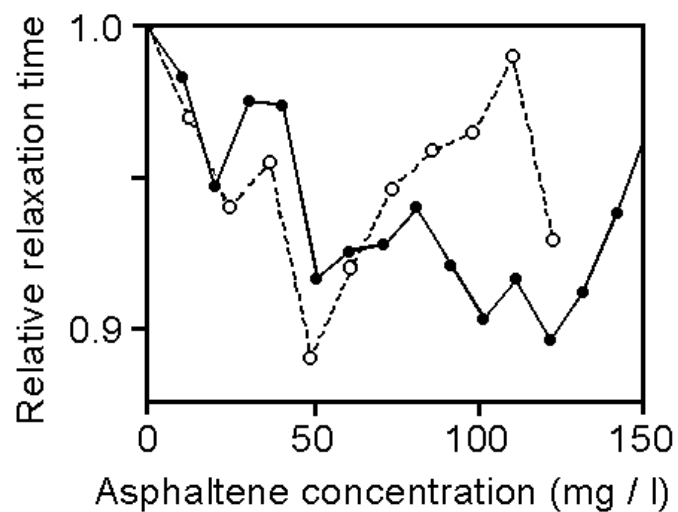


Fig. 2. Effects of asphaltene concentration in crude oil/toluene solutions on relative spin-spin relaxation times T_2 . The filled and the open circles denote the data sets obtained in two consecutive working days.

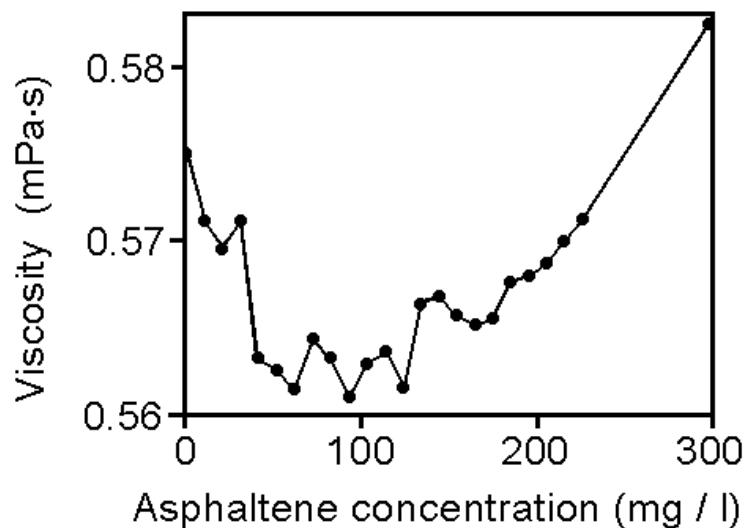


Fig. 3. Dynamic viscosity of crude oil-toluene solutions η as a function of asphaltene concentration C . The data set was obtained in an experiment “parallel” with the NMR studies, presented in Fig. 4.

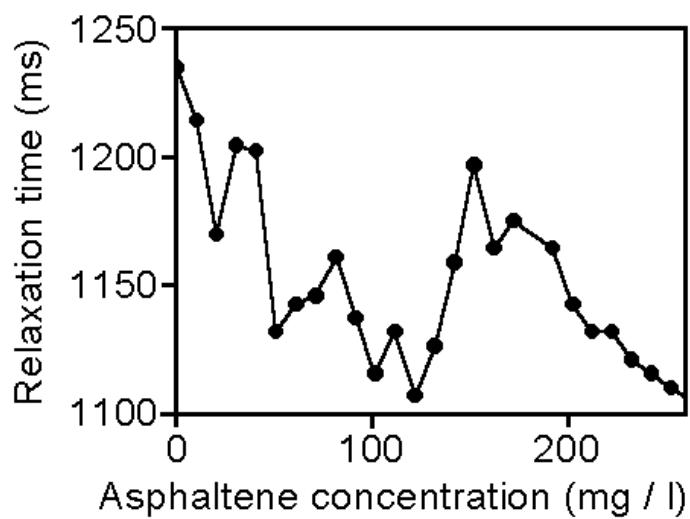


Fig. 4. NMR spin-spin relaxation time in crude oil-toluene solutions T_2 as a function of asphaltene concentration C . The data set was obtained in an experiment “parallel” with the viscosity studies, presented in Fig. 3.

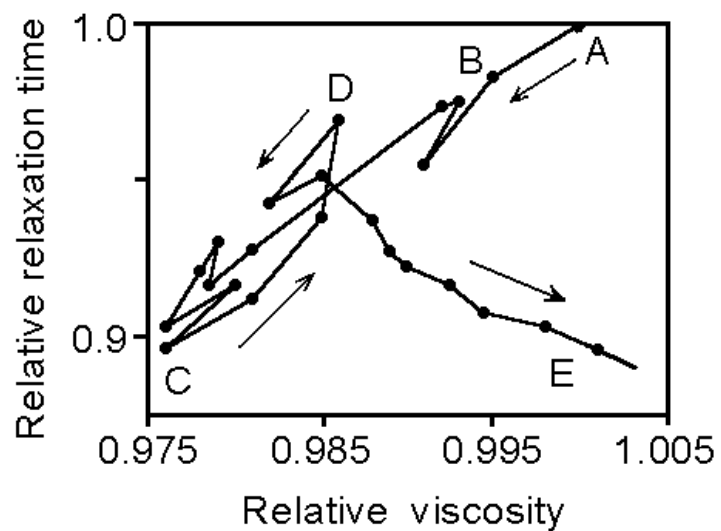


Fig. 5. NMR relaxation time T_2 as a function of viscosity η of crude oil solutions. The experimental data are those shown in Figs. 3,4. Both parameters are normalised to their respective values in toluene. Asphaltene concentration increases along the path indicated by arrows (point “A” – pure toluene).