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Rheological evidence of structural phase transitions in asphaltene-containing petroleum fluids

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Abstract

The aim of this paper is to provide data on the rheological/structural properties of “synthetic oils”, composed of light hydrocarbons (toluene) and a heavy fraction, containing asphaltenes (vacuum residue, VR). Samples with asphaltene concentrations 20–85 g/l have been studied at temperatures 0–60 °C and shear rates up to 1500 1/s. The non-Newtonian flow curves were approximated by the Bingham and the Herschel–Bulkley models to determine the apparent yield stress and the shear-rate exponent as functions of the asphaltene concentration and the temperature. Sharp variations of these parameters were attributed to formation/destruction of extended ordered structures in asphaltene colloid suspensions. Structural changes were observed in the temperature range 20–30 °C, particularly important for industrial processes of reservoir development and pipeline transportation. A molecular model of the observed macroscopic effects takes into account possible first-order structural phase transitions in the nanometer-size resin/asphaltene colloid microparticles.

1. Introduction

Rheological parameters of petroleum fluids are very important for all processes where these fluids are transferred from one place to another. For example, description of petroleum migration in the source/reservoir rocks requires the viscosity of the migrating fluids (Werner et al., 1996). Petroleum viscosity is important in technological applications, such as the production processes of hydrocarbon reservoirs and the processes of petroleum refining. In the refining units, rheological properties of crude oils determine the head losses and, thus, the pressure within a unit. Fluid mechanics problems in the heavy petroleum industry frequently involve nonlinear rheological behaviour (Werner et al., 1998a,b; Pedersen and Rønningsen, 2000).

Despite the demand for oil viscosity/rheology data as a function of composition and external parameters, only a limited number are available, particularly, for very heavy fluids, rich in resins and asphaltenes. Most authors focus on the effect of only one parameter, usually either pressure or temperature, neglecting the effect of the others (Al-Besharah et al., 1987; Amin and Beg, 1993). It has been repeatedly stated that studying viscosities of fluids with heavy oil components requires close monitoring of the phase behaviour of the mixture (Werner et al., 1996). Such studies are important also because flow behaviour (rheology) of these fluids is enormously sensitive to structural transformations far too subtle to be detectable by other experimental techniques. Rheological characterisation often becomes the method of last resort, as have been demonstrated, e.g. in studies of polymer-containing fluids (Hussein and Williams, 1999; Janzen and Colby, 1999). Hence, rheometers/viscosimeters may be regarded as probes not only of the macroscopic flow parameters, but also of the subtle molecular-structure features.

Shear-induced structural evolution of nonlinear fluids is an extensively studied subject. Polymeric liquids typically shear-thin, branched polymers may exhibit shear thickening (Janzen and Colby, 1999). Colloidal suspensions in clays usually shear-thicken (van Kessel and Blom, 1998; Abend and Lagaly, 2000), solutions of surfactants can shear-thicken or shear-thin. In some suspensions, the flow-induced structural transformations are dramatic and have many features in common with equilibrium phase transitions (Annable et al., 1993; Wolthers et al., 1997; Mellema

and van den Ende, 1998). Less common is the use of viscosity measurements as a tool to investigate temperature-induced phase transitions. High sensitivity of such measurements has been demonstrated, e.g. in studies near the critical consolute point of two-component hydrocarbon fluid mixtures (Drozd-Rzoska, 2000).

2. Experimental

2.1. Samples

Experiments have been carried out on samples of “synthetic oils”—a convenient name frequently used for petroleum liquid mixtures with simplified composition (Werner et al., 1998a,b). The light hydrocarbon fractions of natural oils were represented by toluene. Vacuum residue (VR) obtained from natural heavy crudes represented the heavy oil fractions. These heavy crudes with comparatively high concentrations of resins and asphaltenes originated from the same basin in Western Siberia, Russia and have been processed at the Novoufimsk refinery. Some of the characterisation data for the VR component are given below.

Density at 20 °C	979 kg/m ³
Pour temperature	18 oC
Boiling point	342 oC
Liquid phase at 800 °C	86%
Asphaltenes	11 wt.%

There was no evidence for precipitation/sedimentation of solid material from any of our synthetic oils even after a storage period of 4–6 months at room temperature. Microscopic inspection of fluid samples did not reveal the presence of suspended solids or microemulsion droplets. Synthetic oils with the same VR component have been used in our previous studies, which provided experimental evidence for low-temperature phase transitions in asphaltene–resin colloid systems (Evdokimov and Eliseev, 1999; 2000a,b).

2.2. Apparatus and procedure

The effects of fluid composition have been studied in a Rheotest 2.1 Viscosimeter (MLW Prüfgerate- Werk Medingen, BRD) at room temperature (19–20 °C). The measurements were conducted in a two-cylinder cell at shear rates from 5 to 1500 1/s. The vacuum residue contents in synthetic oils varied from 24 to 87 wt.% (asphaltene concentrations from 23 to 92 g/l).

The temperature effects have been investigated at 5–60 °C, for shear rates up to 150 1/s, in a Brookfield Programmable DV-II+ Viscometer (Brookfield Eng. Labs., USA) equipped with temperature control. All synthetic oils had the same composition (~44 wt.% vacuum residue; ~40 g/l asphaltenes). For such low-viscosity samples, a YULA-15 Adapter with a concentric cylinder geometry had to be used. The inner cylinder diameter was 25.15 mm with the gaps of 1.23 mm.

All prepared VC/toluene mixtures were stored for 2 weeks at room temperature (19–20 oC) to eliminate possible short-time relaxation effects. Each rheological experiment has been performed on a new sample. In studies of temperature effects, the sample was introduced into the rheometer cell at room temperature (19–20 °C) and was given an individual thermal pretreatment before standard rheological tests. The sample preconditioning was conducted at rest for 1 h at a constant temperature (from 15 to 60 °C), followed by cooling to the lowest operating temperature (5 oC or 8 oC) at the rate of 1–1.5 oC min⁻¹.

At each operating temperature, the system was initially held at rest for 20 min. The tests began at the lowest shear rate and measurements continued with unidirectional cylinder rotation in an ascending rate order up to the maximum torque limit. At each shear rate, the torque and shear stress data were collected for 90–120 s and averaged. There was no evidence of thixotropic behaviour in the studied samples though certain stress transients were sometimes encountered when the tests continued from a rest state at the new operating temperature. It was found by experience that these transients passed within about 0.5 min in most cases. With the above procedure, the typical data reproducibility on different samples was within ±10%.

3. Results and discussion

3.1. The influence of asphaltene concentration

Samples with different VR/toluene contents were not subjected to thermal pretreatment and were prepared and studied at room temperature (20 °C), for shear rates up to 1500 1/s. In all samples, a measurable “shear thinning” (decrease of viscosity, η , with increasing shear rate, $\dot{\gamma}$) was registered, which is characteristic for pseudoplastic and viscoplastic materials (Barnes et al., 1997; Siginer et al., 1999), in particular, for suspensions of colloidal particles with sufficiently important attractive forces (Yziquel et al., 1999; Belloni, 2000).

Petroleum heavy crudes/residues have been repeatedly verified as suspensions of asphaltene colloids stabilised by resins (Yen and Chilingarian, 1994 and references therein; Mullins and Sheu, 1998; Wong and Yen, 2000). The smallest colloid particles evidently possess a diameter of 2–4 nm and may form clusters with dimensions 10–30 nm, which are frequently referred to as asphaltene “micelles”. Further asphaltene aggregation leads to formation of flocs and macrostructures responsible for various problems of heavy petroleum industry (Yen and Chilingarian, 1994; Mullins and Sheu, 1998). In view of the above information, rheological effects observed in our fluid samples were discussed in terms of asphaltene/resin colloidal suspensions. It is surprising, but the colloidal nature of asphaltenes is not given any attention in most experimental and theoretical studies of the heavy oil viscosity (Werner et al., 1998a,b and references therein). The experiments analysed in terms of asphaltene colloids are comparatively less common (Reerink, 1973; Storm and Sheu, 1993; Escobedo and Mansoori, 1995, 1997).

We have tested several rheological models to describe the observed shear thinning behaviour of the studied asphaltene suspensions. A simplest two-parameter power law model for pseudoplastic fluids was found to provide insufficient information for further analysis of concentration and temperature effects. Viscoplastic models were found to be more informative, although the starting yield stress was never registered in any of our samples. As a rule, the Herschel–Bulkley three-parameter viscoplastic model (Barnes et al., 1997; Siginer et al., 1999) was used to describe the measured dependencies of shear stress, σ , on shear rate, $\dot{\gamma}$:

$$\sigma = \sigma_e + \alpha \dot{\gamma}^m \quad (1)$$

where σ_e is the apparent yield stress and the other two parameters are the constant factor, α , and the shear rate exponent, m .

As discussed below, the shear rate exponent was found to depend on the magnitude of the shear rate and on the fluid’s temperature (cf. Section 3.2.), but in all studied cases m was close enough to unity. Thus, in the first approximation, the effects of asphaltene concentration on the apparent yield stress σ_e were analysed with a two-parameter model for a Bingham plastic fluid (Barnes et al., 1997):

$$\sigma = \sigma_e + \eta_p \dot{\gamma} \quad (1)$$

where the constant, η_p , usually is referred to as the plastic viscosity.

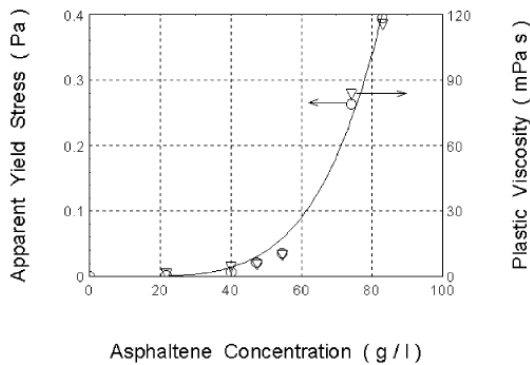


Fig. 1. Plots of the apparent yield stress, σ_e (circles), and the plastic viscosity, η_p (triangles), vs. asphaltene concentration, c_a , in “synthetic oils”. The solid line is the power law fit to both plots with a power of $x=4.5$.

Fig. 1 shows the values of the apparent yield stress and the plastic viscosity obtained by fitting Eq. (2) to the experimental $\sigma(\dot{\gamma})$ dependencies. One can recognise from these results that the liquid’s asphaltene concentration, c_a , is a deciding factor for its rheological behaviour. Both sets of

data in Fig. 1 may be reasonably well described by a single smooth power law function $\sim(c_a)^x$ with a concentration exponent, x , of 4.5 ± 0.5 . The observed strong dependence of σ_e and η_p on asphaltene concentration may be viewed as a consequence of aggregation of asphaltene colloid particles. By definition, plastic viscosity should be more sensitive to changes of the sizes/shapes of colloid aggregates, which affect their interactions with the suspending medium. On the other hand, the presence of the apparent yield stress indicates that interacting aggregates form a certain microstructure (network) and the value of σ_e characterise the forces needed to break down this microstructure.

The observed smooth power law dependence implies that there are no “critical concentrations” in the studied c_a range. Deviation from smooth concentration dependencies of kinematic viscosity has been interpreted as indicative of asphaltene flocculation/aggregation in an Isthmus crude with $\approx 40\text{--}42$ vol.% of various solvents, including toluene (Escobedo and Mansoori, 1995; 1997). The original crude contained 1.3 wt.% asphaltenes; hence, the “critical concentration” of asphaltenes in the solutions may be evaluated as not exceeding 10 g/l, which is well below the concentration range in our experiments.

Direct measurements of the volumes, V_a , of asphaltene colloid particles have been recently reported for various concentrations of asphaltenes in mixtures of the heavy distillation residue (>450 °C) with the light hydrocarbon fraction (<300 °C) of the same crude oil (Syunyaev et al., 2000). Methods of fluorescence polarisation spectroscopy have been used, which were selectively sensitive to asphaltenes. In Fig. 2, these V_a results are compared with our σ_e data from Fig. 1. For convenience, the particle volumes and the apparent yield stresses were normalized to their respective values at $c_a \approx 40$ g/l (note the double-log scale in Fig. 2). It can be seen that for moderate to high asphaltene concentrations, the normalised data for different fluid systems collapse to the same power-law dependence. Just below the concentration range studied in this paper, there is an abrupt change of a power value at $c_a \approx 20$ g/l, which has been interpreted as some “critical concentration of aggregation) (Syunyaev et al., 2000).

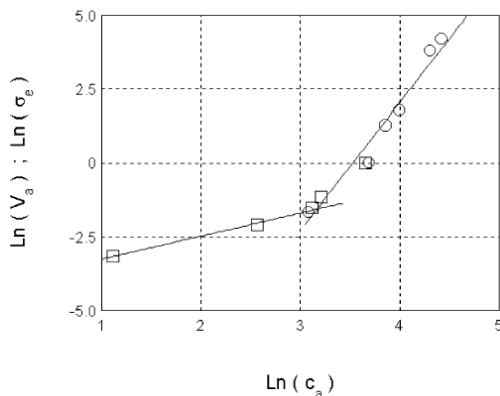


Fig. 2. Dependencies on asphaltene concentration, c_a (g/l), of suspension parameters, normalised to their values at $c_a \approx 40$ g/l. (1) Apparent yield stress, σ_e , from Fig. 1 (circles). (2) Average volume of asphaltene colloid particles, V_a (squares), (Syunyaev et al., 2000).

3.2. The influence of temperature

The temperature effects have been studied at shear rates up to 150 1/s for fluid samples with the same asphaltene concentration of 40.1 g/l. Each flow curve has been analysed using a two-step procedure. At the first step, the Bingham model (Eq. (2)) has been applied in the whole range of $\dot{\gamma}$ to obtain the apparent yield stress, σ_e . Then the Herschel–Bulkley model (Eq. (1)) was used to study possible variations of the shear rate exponent, m . At this step the calculated σ_e value was subtracted from the measured shear stresses, σ , and the differences plotted vs. the shear rates, $\dot{\gamma}$, in a double-log scale, as shown in Fig. 3. It can be seen that a single-exponent model may be applied to the measured results only as a crude approximation—there is a small, but clearly detectable and reproducible, change of the exponent value with increasing $\dot{\gamma}$. In such conditions, the concept of a constant plastic viscosity is no longer applicable; hence, for further analysis, two exponents, m_{low} and m_{high} , were used to characterise the measured flow curves in the ranges of $\dot{\gamma} < 45$ 1/s and $\dot{\gamma} > 45$ 1/s, respectively.

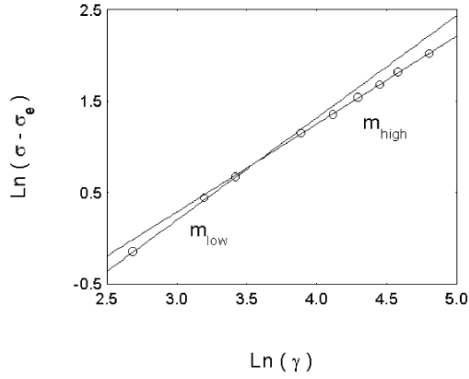


Fig. 3. The Herschel–Bulkley shear rate exponents, m_{low} and m_{high} , at low and high shear rates, $\dot{\gamma}$ (1/s), as determined from the differences of the measured shear stresses, σ (Pa), and the calculated apparent yield stress, σ_e (Pa).

Two types of temperature effects have been observed in our studies. Firstly, the rheological parameters were dependent on the in situ temperature, T_{flow} maintained in course of flow measurements. Secondly, large effects were due to changes of the fluid pretreatment temperature, T_{treat} (cf. Section 2.2).

3.2.1. Effects of in situ temperature

Figs. 4 and 5 show the temperature dependencies of the shear rate exponents, m_{low} and m_{high} , and the apparent yield stress, σ_e , for samples mixed and pretreated at room temperature ($T_{treat}=19$ °C) and samples pretreated at $T_{treat}=36$ °C (all data sets are averaged over several samples.. It is still usually assumed that when heated above their pour point, even heavy crude oils and processed petroleum fluids, despite their enormous compositional complexity, behave like simple liquids with their parameters following smooth temperature dependencies described by Arrhenius-type equations with a constant activation energy, U (Werner et al., 1998a,b; Pedersen and Rønningsen, 2000). In the special studies of asphaltene suspensions, such activation energy is interpreted as an energy of association of asphaltenes (Tynan and Yen, 1969; Shibata et al., 1978; Wong and Yen, 2000). The data of Figs. 4 and 5 prove that sufficiently careful analysis reveals non-smooth temperature dependencies already in comparatively simple asphaltene-containing fluids. The experimental results indicate the presence of the temperature range, presumably associated with some structural phase transformations in the asphaltene/resin suspensions and defined by the lower and the upper specific temperatures $T_1 \approx 19\text{--}20$ °C and $T_2 \approx 26\text{--}28$ °C. 1 2

In the lower-temperature phase, at $T_{flow} \leq T_1$, the current shear-rate exponents remain fairly constant (Fig. 4); however, the relationship between m_{low} and m_{high} depend on the pretreatment history of the sample. In samples mixed and pretreated at $T_{treat}=19$ °C, $m_{low} \approx m_{high} \approx 1$, i.e. the fluid shows a Bingham-type behaviour with a constant plastic viscosity, η_p , which implies that the suspension's microstructure is insensitive to the increase of mechanical energy introduced into the fluid system. In samples pretreated at $T_{treat}=36$ °C, $m_{low} > 1$ is notably larger than $m_{high} < 1$. In terms of the widely used two-parameter Bingham model (Eq. (1)), the larger-than-unity Herschel–Bulkley exponents in Fig. 4 correspond to the increase of the Bingham “plastic viscosity”, $\eta_p = (\sigma - \sigma_e) / \dot{\gamma}$, with increasing shear rate, $\dot{\gamma}$, i.e. to “plastic shear thickening” (flow-induced buildup of the suspension's structure). Accordingly, $m < 1$ corresponds to “plastic shear thinning” (flow-induced structural breakup).

In the phase-transition temperature interval $T_1 < T_{flow} < T_2$, the studied fluids typically show the Bingham-type behaviour ($m_{low} \approx m_{high} \approx 1$) independent on their pretreatment history.

The data of Fig. 4 show that in the higher-temperature phase ($T_{flow} \geq T_2$), the shear-rate exponents again start to deviate from unity. The manner of such deviation is qualitatively the same for all T_{treat} - in this phase, m_{high} is always greater than m_{low} , which implies that at higher shear rates, structural build-up effects dominate over the flow-induced breakup of the suspension's structure.

The decrease of the apparent yield stress in the lower-temperature phase (Fig. 5) may be attributed to a gradual destruction of colloid “network” bonds with increasing thermal energy. At

temperatures $T_{\text{flow}}=8\text{--}18\text{ }^{\circ}\text{C}$, the Arrhenius association energy for this phase is close to $U=10$ kcal/mol (cf. Fig. 9 for more details). The transition to the higher-temperature phase (at $T_{\text{flow}}>T_2$) is manifested by the virtual disappearance of the apparent yield stress in all samples, independent of the manner of their pretreatment. The Arrhenius association energy in the phase transition region ($T_{\text{flow}}=20\text{--}28\text{ }^{\circ}\text{C}$) increases (typically to about $U=30$ kcal/mol in preheated samples).

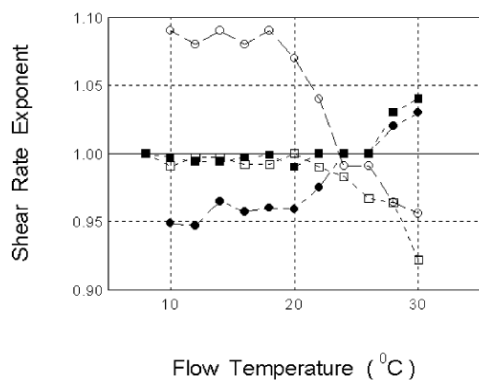


Fig. 4. Effects of temperature, maintained during the flow measurements, on the Herschel–Bulkley shear rate exponents, m_{low} (open symbols) and m_{high} (filled symbols), of “synthetic oils” pretreated at $19\text{ }^{\circ}\text{C}$ (squares) and at $36\text{ }^{\circ}\text{C}$ (circles).

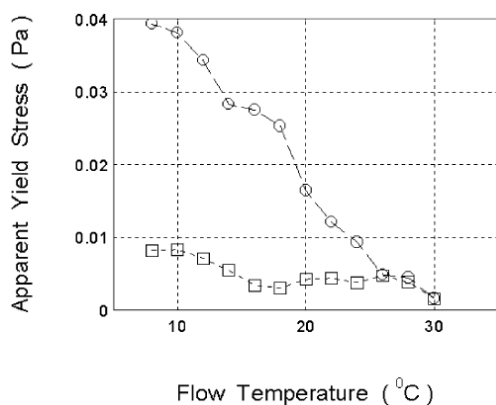


Fig. 5. Effects of temperature, maintained during the flow measurements, on the apparent yield stresses of “synthetic oils” pretreated at $19\text{ }^{\circ}\text{C}$ (squares) and at $36\text{ }^{\circ}\text{C}$ (circles).

It should be noted that the above association energies are obtained by the data analysis which from the start assumes the existence of different suspension phases in specific temperature intervals. If “in the first approximation” a single Arrhenius plot is fitted to the whole measured $\sigma_e(T)$ dependence (i.e. no phase transition is implied), then the “average” association energies for our experimental conditions fall typically into a range of $U=17\text{--}20$ kcal/mol (cf. Fig. 9). This is close to the range of $14\text{--}20$ kcal/mol determined earlier for a number of petroleum asphaltenes (Tynan and Yen, 1969; Shibata et al., 1978; Wong and Yen, 2000). For example, at $T=45\text{--}100\text{ }^{\circ}\text{C}$ (which is just above our temperature range), the average association energy of the Boscan asphaltene was found to be 17.4 kcal/mol (Wong and Yen, 2000).

The above results may be again compared with the direct measurements of asphaltene particle volumes in mixtures of a heavy oil residue with a light distillate (Syunyaev et al., 2000). In this paper, the authors stated that “temperature dependence for . . . mixture demonstrates existence of maximal value of asphaltene particle sizes . . . in temperature experiments from $20\text{ }^{\circ}\text{C}$ to $65\text{ }^{\circ}\text{C}$ ”. By kind permission of R.Z. Syunyaev, we present in Fig. 6 his original data referred to in this citation. The results for different mixtures are normalised to their respective maximum values. Comparison of the results of Figs. 4–6 confirms the above conclusion that the rheologically observed phase transformations are related to changes in the volumes of asphaltene colloid particles. The data of R.Z. Syunyaev show that for our asphaltene concentration of ~ 40 g/l, the phase transformation may be accompanied by a volume increase of approximately 60%, from $150 \cdot 10^{-27}$ to $240 \cdot 10^{-27}$ m^3 . For spherical particles, it would imply the increase of their radii from 3.3 to 3.9 nm. Evidently, such phase transition does not involve clustering/destruction of complex

colloid aggregates. More probable are some changes in individual colloids, e.g. in the layers of resin molecules adsorbed at asphaltene particles.

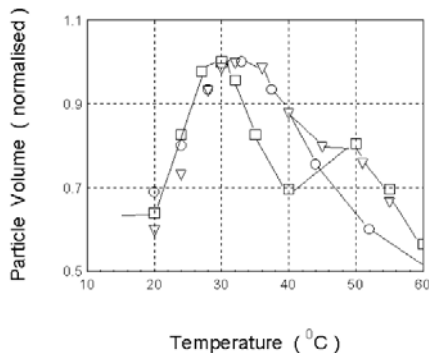


Fig. 6. Effects of temperature on the average volume of asphaltene colloid particles in mixtures of a heavy oil residue with a light distillate. Asphaltene concentrations: 23 g/l (circles), 28 g/l (triangles) and 36 g/l (squares). (Data of R.Z. Syunyaev).

This comparison of results from different laboratories as well as our earlier experiments (Evdokimov and Eliseev, 1999, 2000a,b) indicate that the absolute values of the transition temperatures appear to be almost insensitive not only to variations of asphaltene concentration, but to the origin of these asphaltenes (native crudes) and to the exact composition of the light hydrocarbon fraction of the studied fluid. In support of this conclusion, we have obtained recently some additional data which will be presented in a separate publication.

To conclude this section, it should be noted that measurements of 1% and 5% asphaltene solutions in toluene have indicated that the radius of the asphaltene “micelles” may stay constant at temperatures from 25 to 100 °C (Sheu et al., 1992). No destruction of micelles has been detected after heating to 90 °C of a crude/toluene mixture with 0.5% asphaltenes (Galtsev et al., 1995). On the other hand, dissociation of asphaltene micelles has been observed in a 0.4% asphaltene/tetrahydrofuran solution at 20 °C (Tynan and Yen, 1969). Such discrepancy of the published data should be the subject of a more detailed analysis.

3.2.2. Effects of pretreatment temperature

Some effects of the thermal treatment prior to rheological measurements can be deduced already from the data of Figs. 4 and 5. Firstly, after heating at $T_{\text{treat}}=36$ °C, the apparent yield stress in the treat lower-temperature phase strongly increases (Fig. 5), which may be attributed to the development of the suspension’s network structure. Secondly, this structure becomes more affected by the flow, as indicated by a notable departure from the Bingham shear-rate exponent, $m=1$, at $T_{\text{flow}}=8-20$ °C (Fig. 4). Qualitatively similar effects have been observed for other pretreatment temperatures up to 55 °C.

Further analysis indicated that the observed phase transition is evidently not of a flow-induced type and it may be initiated merely by thermal treatment of the asphaltene-containing fluid. To test this conclusion, a special experiment has been conducted to evaluate the influence of mechanical agitation. In this study, pretreatment of the sample at 36 °C and subsequent cooling to 8 °C was not conducted at rest, but in conditions of continuous flow at a shear rate of 122 1/s. The results proved that that possible fluid effects are only of secondary importance. As compared to data of Figs. 4 and 5, the apparent yield stresses slightly decreased (not more than by 10-15%), the low-temperature shear exponents, m_{high} and m_{low} , remained practically on the same level, transition temperatures, T_1 and T_2 , decreased by 2–3 °C.

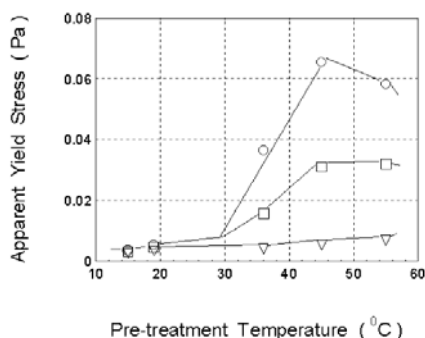


Fig. 7. Effects of temperature, maintained during 1 h thermal pretreatment of “synthetic oils”, on the apparent yield stress in subsequent flow measurements at temperatures: 10 °C (circles), 20 °C (squares) and 30 °C (triangles).

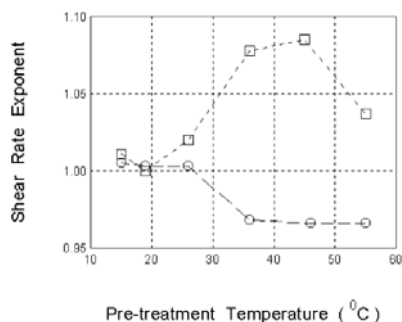


Fig. 8. Effects of temperature, maintained during 1 h thermal pretreatment of “synthetic oils”, on the Herschel–Bulkley shear rate exponents, m_{low} (squares) and m_{high} (circles), in subsequent flow measurements at 18 °C.

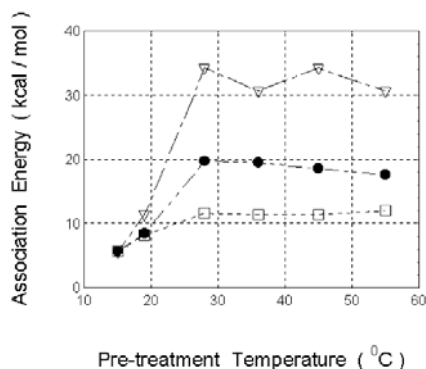


Fig. 9. Effects of the thermal pretreatment on asphaltene association energies, measured in specific temperature intervals of 8–18 °C (squares) and 20–28 °C (triangles). Filled circles denote the “average” association energies for flow measurements at 8–30 °C.

The dependencies of some fluid parameters on the pretreatment temperature, T_{treat} , are shown in Figs. 7–9 and all of them demonstrate a step-like behaviour, indicative of a phase transition. In particular, the apparent yield stress measured at any T_{flow} , notably increases in samples, preheated to temperatures exceeding the above cited specific value of 26–28 °C (Fig. 7). This increase is the more prominent the lower is the flow temperature. Even more sharp are step-like variations of the shear-rate exponents induced by the phase transformation, as shown in Fig. 8 for $T_{flow}=18$ °C. Finally, as shown in Fig. 9, preheating to temperatures above the phase transition region leads to an increase of Arrhenius association energies. Such increase is observed already for average values (cf. Section 3.2.1.) of U , denoted by filled circles in Fig. 9, and this effect becomes much clearer if association energies are determined within the phase transition region (open triangles).

An overview of the above experimental results leads to an obvious question about the observed structural anomalies: Why have they not been reported before? One might expect that rheology of heavy petroleum fluids would have received abundant experimental attention over the years. Indeed, the literature contains many examples of such work, including data obtained by different methods, from a variety of instruments, for wide ranges of temperatures, shear rates and asphaltene concentrations. We suspect that the structural transitions may have been overlooked for several reasons. Primarily, they are rather subtle effects and do not lead to the obvious “peaks”, “drops”, etc., of the commonly investigated fluid characteristics (such as viscosity, density, etc.).

The sharp anomalies are revealed only for certain parameters (activation energies, power-law exponents) of the closely followed dependencies on external experimental conditions. It is still customary to study thermal effects with temperature steps of several tens of degrees, so that any narrow anomaly regions would remain unnoticed. For example, the above-cited asphaltene association energy of 17.4 kcal/mol (Wong and Yen, 2000) was deduced on the basis of only three measurements at 45, 60 and 100 °C, respectively. Furthermore, earlier structure-sensitive experiments with asphaltenes have been conducted mainly at temperatures significantly higher than those in our study, typically close to 100 °C. The data of Fig. 6 indicate, however, that the discussed phase transformation may be of a transient type and its effects may quickly level off above 60–70 °C.

3.3. Some model considerations

Presently, we lack a credible understanding of any of the driving mechanisms of the observed temperature-induced structural transitions. The above discussion suggests that such understanding could be achieved by further developing of molecular-level models describing asphaltene-containing petroleum fluids as evolving colloid systems.

The concept that asphaltene molecules form colloidal systems is credited to Nellensteyn (1924). The first consistent model of asphaltene colloid particles has been introduced by Yen and is being further specified (Yen et al., 1961; Wong and Yen, 2000). It has been repeatedly proven that the rheological behaviour of any colloidal suspension is determined by the nature and magnitude of the colloid–colloid and the colloid–solvent interactions (Siginer et al., 1999; Yziquel et al., 1999; Belloni, 2000). In particular, the stability of the asphaltene suspension with respect to irreversible coagulation or reversible aggregation and phase transition (and, consequently, its rheology) is controlled primarily by such solvent components as petroleum resins (Koots and Speight, 1975; Lian et al., 1994).

The simplest molecular-level models of suspensions use the hard-core potential for direct interaction of bare colloid particles. The solvent molecules add two new contributions to the effective colloid–colloid potential. At larger distances, it is a depletion attraction due to solvent concentration/pressure gradients in the interstitial region between colloids. When the colloid–solvent attraction is present, the main factor at short distances is a so-called “steric” repulsion. It is due to an adsorbed solvent layer around each colloid particle, which can be viewed as a “hard shell”, preventing the particles from coming into true contact.

This steric effect of resin molecules is commonly regarded as being responsible for stabilisation of colloidal suspensions of large asphaltene clusters (Mansoori, 1997). Irreversible flocculation of asphaltene particles out of the solution is caused by migration of resin molecules from the asphaltene surfaces, which may be due to the decrease of resin concentration in the fluid phase. If resin concentration is sufficiently high, an asphaltene suspension is believed to remain stable regardless of how much the fluid is agitated, heated or pressurised (Lichaa, 1977).

On the other hand, some stable asphaltene suspensions were shown to consist of comparatively small micelles with narrow size distributions. The structure of such colloid systems is governed by reversible self-association processes in which resins are believed to play a minor role or no role at all (Leontaritis and Mansoori, 1988; Park and Mansoori, 1988). Despite the experimental evidence on the “micellisation” of asphaltenes, little theoretical and modelling research has been performed to explain and quantify this phenomenon (Mansoori, 1997).

Obviously, self-association of colloids cannot be described in terms of the hard-core potential, which implies that colloid particles are formed from an inert, structureless material. In reality, colloids are made of polar and polarisable molecules carrying electronic dipoles. The averaged interactions between all dipoles define the van der Waals (dispersion) forces (Israelachvili, 1991), which are attractive and tend to destabilise colloidal suspensions towards irreversible coagulation. In the microscopic description, the inclusion of this interaction would require to consider both colloids and solvent molecules as moving dipolar, polarisable particles and to average the multibody interactions over the dipole fluctuations and solvent spatial configurations. Above all, the solvent layer near the colloidal surface may be affected by surface–solvent dipole–dipole van der Waals coupling. The consistent description of all these miscellaneous effects in colloid suspensions is a formidable task and still forms a future challenge for theoreticians.

In a simplified “mesoscopic” approach a colloid particle (together with an adsorbed solvent “shell”) may be regarded as a single structural entity carrying a permanent dipole. The dipole nature of asphaltene micelles has been identified in asphaltene/toluene gel systems (Sheu et al., 1994) and clustering of micelles has been attributed to dipole–dipole interactions (Ensley, 1975). Dipolar fluids and their microstructural properties have been the subject of renewed interest in recent years. New theoretical models (Teixeira et al., 2000; Telo da Gama and Tavares, 2000) revealed behaviour not predicted by earlier theories: formation of chain-like aggregates and the appearance of an ordered fluid phase (network of aggregates). Models of aggregation of dipolar asphaltene

“molecular nanoclusters” (particles of sub-“micellar” size) indicate the energetical preference of rod-like and ring-like aggregates as compared to three-dimensional quasi-spherical colloid particles (Evdokimov et al., 2001).

In macroscopic models, the existence of some ordered phase is not deduced from the molecular “first principles”, but is frequently postulated. The coexistence of two phases under flow is implied in the viscosity models of ordering suspensions (van der Vorst et al., 1997, 1998). The ordered structure of the suspension is assumed to be broken down under shear flow into domains (crystallites) of ordered phase suspended in a disordered fluid phase. The presence of the ordered phase may be proved, for example, by the observation of an apparent yield stress. For example, the results of Figs. 5 and 7 show the presence of a measurable yield stress in our synthetic oils at temperatures up to 26–28 °C, indicating high thermal stability of some “ordered domains” which may be still present in these samples far above their pour point. An existence of a yield stress (ordered structures) at temperatures at least 100 °C higher than the solid–liquid transition point has been demonstrated recently in liquid polymers (Hussein and Williams, 1999). How the ordered regions are organised is still an open question. Some new ideas may be obtained from a microrheological model of weakly (i.e. reversibly) aggregating dispersions which has been developed and experimentally verified in the last few years (Potanin et al., 1995; Wolthers et al., 1996). In this model, the macroflow viscosity and elasticity are related to structures formed by fractal colloid aggregates. Fractal concepts have been used in models of asphaltene deposition (Janardhan and Mansoori, 1993; Mansoori, 1997) and the existence of fractal asphaltene aggregates was clearly illustrated by atomic force micrography (Toulhoat et al., 1994).

On the basis of the above discussion, we propose a probable schematic picture of different phases which may exist in our synthetic oils.

The first suspension phase (A) shows signs of being equilibrium at temperatures below 18–20 °C. It is observed in thermally untreated samples, which exhibit a Bingham-type rheology (fairly close to Newtonian). The smaller volumes of colloid particles and lower association energies are indicative of a “closely packed” (energetically most favourable) configuration of the “inert hard shell” of resins adsorbed at the surface of an asphaltene “kernel”. Association of colloid particles due to the kernel–kernel attraction (e.g. of dipolar nature) is limited by the steric action of these shells.

The second phase (B) may be regarded as “quasi-equilibrium” at temperatures just above 28–30 °C. In this phase the resin shells supposedly become “fluffy”, so that the apparent volumes of colloid particles grow. The behaviour of association energies indicates that these fluffy shells are also more “sticky” as compared to the “hard” ones. The appearance of the additional (shell–shell) attraction may be the result both of desorption of resins from the shell and of adsorption of other solvent molecules. The fluffy composite shells are weakly bound and are thermally destroyed at elevated temperatures.

By cooling an asphaltene suspension, some sticky shells may be temporarily conserved at lower temperatures. In conditions of decreased thermal movement, interparticle attraction leads to the formation of extended ordered microstructures and the relative volume of ordered domains increases with decreasing temperature. This suspension phase (C) is intrinsically nonequilibrium and, as compared to the phase (A) under the same experimental conditions, shows a distinct apparent yield stress and is characterised by a threefold increase of the association energy. At temperatures below 18–20 °C, phase (C) is evidently metastable and rather long-lived, the ordered structures are only partially broken in a shear flow (as indicated by small changes of the shear-rate exponent). However, this nonequilibrium phase is easily destroyed by reheating the sample to temperatures above the phase transition range (e.g. to 28–30 °C or higher).

Finally, there should be a certain primary molecular mechanism, which triggers the chain of various secondary effects of the discussed phase transition. As has been pointed in Section 3.2.2., the phase transition temperature is practically insensitive to composition of the “solvent” (light hydrocarbon fluid). Hence, it should be determined by some basic process in the asphaltene–resin subsystem, e.g. at the shell/kernel interface, effectively shielded from the influence of solvent

molecules. Hypothetically, the “trigger” action may be caused by the phase transition between closely packed and loosely bound structures in the shell. Such first-order structural transitions have been observed at temperatures 20–35 °C in adsorbed layers of heavy dipolar organic molecules (fatty acids, phospholipids, etc.) (Iwamoto et al., 1996; Kaganer et al., 1999). A measurable increase of the effective volumes of colloid particles in drilling muds was attributed to transition in adsorbed surfactant shells from a compact structure to a fluffy one (Allahverdieva and Evdokimov, 1991). Another possible “trigger mechanism” is the change of the surface energy of asphaltene kernels due to phase transformation of their inner molecular structure. The basic asphaltene kernel is assumed to be a “crystallite” consisting of five to six condensed aromatic layers (Wong and Yen, 2000 and references therein) and stacking structures of such layers are known to have different polymorphic forms (Glowka et al., 1999).

4. Conclusions

We have studied the nonlinear rheology of model heavy petroleum fluids. Our experiments prove that rheological parameters of such fluids are determined primarily by their asphaltene/resin colloid subsystem. When present in sufficiently high concentrations, asphaltene microparticles change the flow properties to viscoelastic non-Newtonian behaviour with an apparent yield stress and a shear-rate exponent depending on the experimental conditions, in particular, on temperature. Observed temperature effects may be subdivided in two categories: (1) the effects of in situ temperature in course of flow measurements; (2) the influence of the thermal treatment of the fluid before rheological tests. Both types of effects indicate the existence of a structural phase transition in the temperature range 20–28 °C. The fact that this temperature range is commonly used in industrial applications makes such discovery particularly important. The observed rheological effects may be attributed to generation/destruction of domains of an ordered phase suspended in a disordered fluid. These macroscopic effects may be triggered on a molecular level by first-order phase transitions in nanosize asphaltene kernels or in the surrounding resin “cores”.

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