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Effect of asphaltenes on the thermal properties of emulsions  
encountered in oil recovery operations

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**Abstract**

Fabrication temperature of crude oil and bitumen emulsions was found to produce a very strong impact on dynamic viscosities  $\eta$  and activation energies of a viscous flow  $E_{act}$ . An anomalous increase of both  $\eta$  and  $E_{act}$  was observed in emulsions, fabricated at 36 °C, while fabrication at 45 °C improved the flow properties. The narrow critical range of thermally-induced anomalies extends from  $\approx 30$  °C to  $\approx 42$  °C, as revealed by studies of a matrix crude oil. At room temperature the materials retained a long-term memory of fabrication conditions. We suggest that the anomalous thermal effects are triggered by a structural phase transition in the asphaltene/resin molecular subsystem. Below the wax appearance temperature structurally modified asphaltene particles evidently act as cementing species in extended networks of wax crystals.

*Keywords:* Asphaltenes; Emulsions; Crude oil; Bitumen; Viscosity

## 1. Introduction

The factors contributing to the rheological parameters and to the colloid structure of petroleum emulsions is a problem of great concern and economic importance to the oil companies in the production of oil from underground reservoirs [1-5]. Crude oils recovered by water flooding are invariably accompanied by water. Water-in-crude oil emulsions are usually produced by the shear action and the pressure gradient drop in the well-head chokes and valves and in the production pipelines. Bitumen emulsions are injected into oil reservoirs for profile control by reduction of water permeability. A considerable effort has been made to study the physical, chemical [6,7] or engineering [8,9] aspects of the petroleum emulsions' preparation and their stability. Yet, comparatively few works deal with rheological behaviour of emulsions at varying temperature conditions. There is a high industrial demand for viscosity data for petroleum emulsions, particularly for those with very heavy oil components, rich in resins and asphaltenes. E.g., viscosity values and their temperature dependencies may be used to predict the stability of emulsions in course of water flooding, during pipeline transportation, in spilled oil layers, etc [2]. Moreover, viscosity measurements offer means to determine the inner structure of emulsions and provide evidence of the technologically important structural changes.

Recently, we have shown that the dynamic viscosity of petroleum fluids may be sensitive to structural transformations which often are too subtle to be detectable by other experimental techniques [10,11]. Hence, in this study we regard a viscometer as a probe not only of the macroscopic flow parameters but also of the molecular-structure features of petroleum emulsions. The preliminary results of this study have been reported at the 3d World Congress on Emulsion, Lyon 2002.

## 2. Experimental

### 2.1. Samples

The studied emulsions were the ones encountered in oil recovery operations at the Romashkinskoje reservoir, Tatarstan, Russia and have been provided by the TATNEFT oil company. The water/crude oil samples (25 vol. % of the emulsified reservoir water) were obtained directly from the oil-production well. The water-free oil phase contained 3.5 wt. % asphaltenes, 1.6 wt. % waxes, 22 wt. % resins, as reported by the provider. During prolonged laboratory storage at room temperature, oil and water phases separated from the samples by gravity. A visual inspection did not reveal the presence between the separated phases of any noticeable interfacial layer which may have contain some important emulsion stabilisers. Hence, the studied w/o emulsions (prepared by re-mixing the separated phases at the initial v/v ratio) were regarded as representative of the initial emulsions from the well.

The bitumen emulsions, utilised for the control of water flooding, were prepared from the “HIMEKO” concentrate (HIMEKO Co., Moscow) which contains 50 vol. % of bitumen (pavement grade), 40 vol. % of water and 10 vol. % of stabiliser ( $\text{CaCl}_2$ ), acid (HCl), various unspecified surfactants, dispersants and modifiers. As recommended by the producer, ready-to-use industrial bitumen emulsions were prepared by 1/1 dilution of the concentrate with the separately provided “KORE” solvent (hydrocarbon rectification residues).

### 2.2 Apparatus and procedure

The effect of fabrication temperature on rheology of all samples have been investigated at flow temperatures of  $8\text{ }^{\circ}\text{C}$ - $30\text{ }^{\circ}\text{C}$  , for shear rates up to  $150\text{ s}^{-1}$  , in a Brookfield Programmable DV-II+ Viscometer (Brookfield Eng. Labs., Inc., USA),

equipped with a YULA-15 Adapter with a concentric cylinder geometry. The inner cylinder diameter was 25.15 mm with the gaps of 1.23 mm. Each rheological experiment has been performed with a freshly prepared sample.

In studies of water/oil emulsions, two gravitationally separated phases were introduced into the viscometer's cell at the volume ratio of 1/3, equal to that in the production well (25% v/v of water). The bitumen concentrates were diluted in the viscometer's cell by adding an equal volume of the industrial dilutant so that studied emulsions contained 25 % v/v of bitumen and 20% v/v of water. Each emulsion was mixed for 1 hour at conditions close to a maximum viscometer's torque (shear stresses  $\approx 0.7-0.8 \text{ N/m}^2$ ), at a fixed fabrication temperature  $T_F$  in the range from 20 °C to 60 °C. Under constant mixing, each sample was cooled to the lowest measurement (flow) temperature (8-10 °C) at the rate of 1-1,5 °C per minute.

At each measurement (flow) temperature, the system was initially maintained at a constant shear rate for 20 min. The tests began at the highest shear rate and measurements continued with unidirectional cylinder rotation in a descending-rate order down to 0.1-0.2 s<sup>-1</sup>. At each shear rate the torque and shear stress data were collected for 90-120 s and averaged. Before changing to the next measurement temperature (by 2 °C steps, up to 30 °C), the shear rate was increased to its initial value. With the above procedure, the typical duration of one experiment was about 6 hours.

### **3. Results**

#### *3.1. Shear stress dependencies of viscosity*

For a majority of the studied samples the measured flow curves (viscosity vs. shear stress) exhibited a more or less pronounced shear-thinning (i.e. non-Newtonian)

behaviour, indicating the presence of some extended molecular structures destroyed by increasing mechanical load. As a measure of temperature-induced effects in all samples, we have used the viscosity value at a common shear stress of  $\sigma=0.7$  Pa, i.e. at flow conditions closest to Newtonian.

The results presented in Fig.1 were obtained at the flow temperature of  $16\text{ }^{\circ}\text{C}$  and show that for crude oil emulsions fabricated at room temperature ( $T_F=24\text{ }^{\circ}\text{C}$ ) shear thinning is comparatively small and the flow curve may be regarded as approximately Newtonian in the entire studied range of shear stresses  $\sigma$ , from 0.1 to 0.8 Pa. Such quasi-Newtonian behaviour is retained in emulsions, fabricated at sufficiently high temperatures ( $T_F=45\text{ }^{\circ}\text{C}$  in Fig.1). The most noticeable effect of high-temperature fabrication is a substantial reduction of the dynamic viscosity in crude oil emulsions. It was observed, however, that the effects of increasing the fabrication temperature are not straightforward. Severe anomalies of viscosity were observed at a certain interval of fabrication temperature, which in the following we will refer to as a “critical” range. Namely, in emulsions, fabricated in the “critical” range of  $T_F$ , from  $28\text{-}30\text{ }^{\circ}\text{C}$  to  $38\text{-}40\text{ }^{\circ}\text{C}$ , we registered a large increase of the measured viscosities, as compared to emulsions fabricated at room temperature (cf. the results for  $T_F=36\text{ }^{\circ}\text{C}$  in Fig. 1). The magnitude of this increase depends on the current shear stress, as well on the flow (measurement) temperature. At  $\sigma=0.7$  Pa, in measurements at  $16\text{ }^{\circ}\text{C}$  (Fig. 1) viscosity increases approximately by 50%, from  $101\text{ mPa}\cdot\text{s}$  ( $T_F=24\text{ }^{\circ}\text{C}$ ) to  $155\text{ mPa}\cdot\text{s}$  ( $T_F=36\text{ }^{\circ}\text{C}$ ); at flow temperature of  $10\text{ }^{\circ}\text{C}$  this increase is almost four-fold - from  $372\text{ mPa}\cdot\text{s}$  to  $1440\text{ mPa}\cdot\text{s}$ . The increase of viscosity may be attributed to formation of some comparatively strongly-bound molecular structures, which are destroyed only at high flow temperatures (cf. Fig. 5). The results for  $T_F=36\text{ }^{\circ}\text{C}$  in Fig. 1 show yet another effect of formation at temperatures in the above critical range, namely an

appearance of a pronounced non-Newtonian shear thinning for  $\sigma < 0.5$  Pa. This effect is indicative of a mechanical destruction of certain loosely-bound molecular networks which are effectively destroyed at  $\sigma = 0.7$  Pa and hence are not revealed in the below discussed data of Fig. 5. Finally, in measurements below  $10$  °C, the emulsions fabricated in the above critical range of  $T_F$  clearly exhibited gel-like properties with a considerable yield stress.

The observed strong non-monotonic dependence on the fabrication temperature, the viscosity increase and the apparent gelation of emulsions were totally unexpected and may be regarded as “thermal anomalies”, as it is generally assumed (cf., e.g. [8,12]) that an increase of the fabrication temperature always improves the rheology of petroleum emulsions. A literature analysis has shown that the observed anomalies obviously are novel features not only for petroleum-based, but for a wider range of liquid disperse systems. We have found only one recent publication [13] which reports an increase of room-temperature viscosity after high-temperature fabrication of micellar surfactant/water dispersions. The authors of Ref. 13 also regarded this effect as unexpected and did not propose any plausible molecular mechanism, merely suggesting that some “irreversible residual structure remains from the high temperature fabrication process”.

In our studies, the “expected” improvement of the flow properties of petroleum emulsions with increasing fabrication temperature, namely a decrease of the viscosities as compared to the RT-fabrication data, was observed only for  $T_F > 40$ - $42$  °C. For example, the results of Fig. 1 show that in emulsions fabricated at  $T_F = 45$  °C, viscosity at  $\sigma = 0.7$  Pa decreases to  $75$  mPa·s, well below the value of  $101$  mPa·s for  $T_F = 24$  °C.

In order to determine the role of emulsion constituents in the observed thermal effects, we made similar viscosity measurements with the separated phases, pre-heated to the above fabrication temperatures. The viscosity of the mineralised reservoir water did not show any peculiarities in the studied ranges of the fabrication/flow temperatures. The viscosity of the matrix crude oil exhibited qualitatively the same effects of the fabrication temperature, even more pronounced than those in the studied crude oil emulsions, as shown in Fig. 2. This indicates that the thermal effects in emulsions are determined not only by molecular processes at the water/oil interface, but also (and, supposedly, mostly) by those in the bulk of the oil phase.

In course of all experiments, the individual “signatures” of the fabrication temperatures (gel-like behaviour, modified viscosities) were still detected even after prolonged (up to 6 hours) annealing at increasing flow temperatures, in conditions of a continuing mechanical agitation. This indicates that some long-lived residual structures remained in the crude oil emulsions after the fabrication processes (the effect of long-term “thermal memory”). In the matrix crude oil, this “thermal memory” was found to extend for a period of at least four months, as revealed by viscosity measurements after storage at room temperatures.

An anomalous increase of viscosity in samples, fabricated at the above critical temperatures, was also observed for bitumen emulsions, as shown in Fig. 3. At flow temperature of 16 °C the viscosity at  $\sigma=0.7$  Pa increases from 67 mPa·s (RT fabrication,  $T_F=24$  °C) to 101 mPa·s ( $T_F=36$  °C). The main difference from the data for crude oil emulsions is that fabrication at  $T_F=45$  °C also results in viscosities higher than those after RT fabrication. It should be noted also that for  $T_F=45$  °C the flow curve of bitumen emulsion is distinctly non-Newtonian in the entire range of the

employed shear stresses. This indicates that at our standard stress  $\sigma=0.7$  Pa some weak (flow-affected) structures still remained in emulsions, which could be a reason for the below discussed peculiar behaviour of activation energies (cf. Fig. 4).

### 3.2. Effects of the fabrication temperature on activation energies of the viscous flow

Activation energies  $E_{act}$  were calculated in the assumption that temperature effects on viscosity may be described by exponential Arrhenius laws (cf. Section 4.2). Hence, numerical values of  $E_{act}$  were determined from the dependencies of the logarithm of viscosity at  $\sigma=0.7$  Pa on the reciprocal flow temperature, by fitting straight line approximations (the Arrhenius plots) between the consecutive experimental points. To reduce a random scatter, the obtained sets of activation energies were smoothed with a three-point sliding data window. The results of these calculations are presented in Figs.4-6, where circles, squares and triangles denote the data for samples fabricated at  $T_F=24$  °C,  $T_F=36$  °C and  $T_F=45$  °C, respectively. The calculated activation energies are further compared to the relevant literature values in Section 4.2.

Fig. 4 shows the complex dependencies of  $E_{act}$  on the flow (measurement) temperature for bitumen emulsions. After fabrication at room temperature ( $T_F=24$  °C) the activation energy exhibits a step-like decrease with increasing flow temperature, indicating a break-up of some comparatively strong intermolecular/interaggregate bonds. Namely,  $E_{act}$  decreases by  $\approx 15$  kcal/mol ( $\approx 63$  kJ/mol) – from 26 kcal/mol at 10-15 °C to 10 kcal/mol at 23-30 °C. The main effect of fabrication at  $T_F=36$  °C (i.e., in the above critical range) is an apparent formation of very loosely-bound structures - at 10-13 °C  $E_{act}$  does not exceed 2 kcal/mol. At higher flow temperatures (21-30 °C) the break-up of these weaker bonds restores  $E_{act}$  to a level of 16-17 kcal/mol. Finally,



in emulsions fabricated at “high” temperatures ( $T_F=45$  °C) neither “stronger” or “weaker” bonds are retained. At all flow temperatures the activation energy remains fairly constant, close to 10-12 kcal/mol.

For crude oil emulsions the dependencies of  $E_{act}$  on the flow temperature are somewhat simpler, as shown in Fig. 5. For the cases of room temperature fabrication and for  $T_F=45$  °C the results virtually coincide with those for bitumen emulsions. Namely, for  $T_F=24$  °C the break-up of some “stronger” bonds with increasing flow temperature is indicated by a step like decrease of  $E_{ac}$  by  $\approx 17$  kcal/mol ( $\approx 71$  kJ/mol) - from 27-28 kcal/mol at 10-17 °C to 10-11 kcal/mol at 22-30 °C. For  $T_F=45$  °C at all flow temperatures the activation energies are reduced approximately to the level, observed at 22-30 °C in case of RT fabrication. In contrast, fabrication at critical temperatures ( $T_F=36$  °C) leads to “thermal anomalies” qualitatively different from those in bitumen emulsions. In this case activation energies at flow temperatures 10-12 °C become as high as  $\approx 80$  kcal/mol ( $\approx 330$  kJ/mol), indicating an emergence of some tightly-bonded structures. With flow temperatures increasing to 30 °C, the activation energies gradually decrease to  $\approx 12$  kcal/mol ( $\approx 50$  kJ/mol).

Fig. 6 shows the behaviour of activation energies for the matrix crude oil, pre-heated to the same fabrication temperatures. The results virtually coincide with those for crude oil emulsion in Fig. 5. The only quantitative difference is a somewhat larger increase of activation energies (up to 99 kcal/mol) after pre-heating at 36 °C. A comparison of Figs 5 and 6 confirms the above conclusion that that the thermal anomalies in the oil emulsions are related mainly to the changes in the properties of the matrix crude oil. To reveal these changes in more detail, we have studied flow properties of the matrix crude oil pre-heated to 14 different temperatures in the range from 19 to 67 °C. This time the “average” activation energy was determined by fitting

a single straight line to the dependence of the logarithm of viscosity at  $\sigma=0.7$  Pa on the reciprocal flow temperature in the entire range of 10-30 °C. The results, presented in Fig. 7, show that the thermally-induced anomalous increase of the activation energy is observed in a narrow critical range of pre-heating temperatures, from 28-30 °C to 42-43 °C, and is most pronounced in the crude oil pre-heated to 36-38 °C.

Finally, in course of preparation of the revised version of this paper, we have obtained a new water/crude oil sample from a different production well at the Romashkinskoje reservoir, with somewhat higher contents of asphaltenes ( $\approx 4.5$  wt. % in the oil phase) and water ( $\approx 40$  vol. %) and with unspecified contents of resins and waxes. Rheological tests at some selected temperatures indicated that the above reported viscosity anomalies are qualitatively reproduced in the newly acquired emulsions. In particular, the new critical range of  $T_F$  appear to differ from the above described one by no more than 3-5 °C. The main quantitative difference is a much lower viscosity increase in the pre-heated new emulsions, which may be preliminary ascribed to different content of waxes.

## 4. Discussion

### *4.1 Relative roles of asphaltenes/resins/waxes in the observed thermal anomalies*

The observed large variations of viscosities and activation energies are indicative of notable modifications of the molecular structures in the studied emulsions, induced by fabrication in the critical range of  $T_F$ . These structural modifications we attribute primarily to specific processes, involving asphaltene dispersions in the oil and bitumen phases of emulsions.

It is a well-known fact that the presence of asphaltene fractions serves to stabilise the emulsions formed during crude oil production [5,14-16] and that

asphaltenes also play a dominant role in the stabilisation of diluted bitumen emulsions [17-19]. Evidently, it is mostly the aggregation state of the dispersed asphaltenes and not their amount that controls the stability of an emulsion [20,21].

Asphaltene colloidal dispersions are known to be sterically stabilised by solvated resins [22]. A structural transformation of asphaltene aggregates may occur when resin molecules “desorb” from asphaltenes. In our previous studies of model crude oils [10,11] we have obtained experimental evidence of a structural phase transition in the asphaltene/resin subsystem at temperatures close to 30 °C and suggested two possible effects that trigger the apparent desorption of resins. One is a first-order transition between closely packed and loosely bound structures in the adsorbed layers of resin molecules. Another possible “trigger mechanism” is the change of the surface energy of  $\pi$ -stacked asphaltene aggregates due to phase transformation of their inner molecular structure.

It is also recognised that thermally-induced effects in the asphaltene/resin subsystem determine the structure-rheology relationship in bitumen [23]. Indeed, in recent rheological studies of bitumen a broad peak at  $\approx 30$  °C was observed in mechanical loss tangent plots against temperature [24]. Based on the scheme proposed in [23], this peak was attributed to a thermally activated structural transition in asphaltene aggregates, triggered by the destruction of stabilising resin shells.

In view of the above evidence, we suggest that the structural transition in the asphaltene/resin subsystems of the studied emulsions is the primary cause of the observed thermal anomalies. Structurally modified asphaltene particles are no longer fully solvated by resins. As a result, they show a higher propensity to adsorb at other solid particles, e.g. at wax crystallites. It is a well known fact that wax crystallisation and network formation in colloidal suspensions of wax particles are responsible for

low-temperature gelation of crude oils (cf. e.g. [25] ). On the other hand, it has been repeatedly shown [5,16,25] that the wax fractions (aliphatic hydrocarbons) alone are unable to stabilise petroleum emulsions. In the absence of asphaltenes, wax crystals remain completely oil-wet (hydrophobic) and are dispersed in the oil phase. However, when asphaltene aggregates adsorb on the surfaces of wax particles, their wettability changes from completely oil wetting to a mixed (intermediate) wetting. The asphaltene-solvated wax particles migrate to the oil–water interface, contributing to the formation of rigid layers around water droplet and to the emulsion tightness [5,16].

The rheological properties of colloidal suspensions are known to be controlled by the magnitude of the attractive energy  $U$  between particles [26,27]. In particular, attraction in wax suspensions is modified by an adsorption of asphaltenes [5,16]. This can have a dramatic effect on the rheological behaviour of the suspension, being the main cause of its apparent gelation. In case of a noticeable attractive interactions; gelation occurs via the diffusion-limited cluster aggregation (DLCA) [28]. Colloid particles form fractal clusters which at any (however low) volume fraction, ultimately interconnect into a continuous, though weakly-bound, network. The main reason that DLCA does not lead to an irreversible precipitation is the so-called “crowding” [26], a steric effect which arrests of the kinetics of aggregation [27].

Recent theoretical/experimental studies have shown that gelation at a characteristic temperature  $T_G$  in any system of attractive colloidal particles may be viewed as a “jamming transition” [26]. At sufficiently high  $U$  all jamming transition from fluid to gel were shown to be governed by a scaled parameter  $k_B T_G / U$  and to exhibit a critical behaviour, with a sudden onset of the elasticity. Hence any increase of  $U$  should result in a decrease of  $T_G$ .

We suggest, that in our petroleum systems the magnitude of interaction  $U$  between wax particles is increased by an adsorption of structurally modified asphaltene aggregates. Consequently, a gelation transition (the pour point) in emulsions, formed at critical  $T_F$ , is shifted to higher temperatures, being the reason for the observed increase of activation energy/viscosity at studied flow conditions.

The critical range of  $T_F$  evidently commences at  $\approx 30$  °C (cf. Fig. 7), i.e. at the structural phase transition in the asphaltene/resin subsystem. The upper limit of this range (42-43 °C) we ascribe to the wax melting point (wax appearance temperature).

In course of fabrication of emulsions at sufficiently high temperatures ( $T_F=45$  °C, above both the asphaltene/resin phase transition and the wax melting point) all the existing wax particles melt away. When emulsions are quenched to initial measurement temperatures (8-10 °C), the new microscopic wax crystals start appearing only below the wax melting point. We presume, that in this case larger asphaltene aggregates can not form “adsorbed layers” around smaller wax crystals. With decreasing temperature, the newly-formed wax crystals form networks, directly interacting with each other. Direct interaction of the wax crystals is a weak physical one [25] so that such crystal networks are loosely-bound. The results in Figs.1-6 show that these networks are easily destroyed by increased mechanical agitation even at the lowest flow temperatures and hence are virtually unaffected by a subsequent temperature increase.

In course of fabrication of emulsions at the critical temperatures ( $T_F=36$  °C, below the wax melting point, but above the asphaltene/resin phase transition) the existing wax particles readily adsorb the structurally modified asphaltene aggregates. During a quench to lower measurement temperatures, asphaltene-covered wax particles form strongly bound networks. The increased viscosity is preserved even at

high shear stresses (Figs. 1-3) and a “memory” of the fabrication conditions is destroyed only at high flow temperatures (Figs.4-6). The relatively smaller thermal effects in the bitumen emulsions may be due to the weakening of asphaltene-mediated networks by other strong surfactants introduced into the concentrated product.

#### *4.2 Interpretation of the activation energies*

The means by which asphaltenes, resins and waxes interact to exist in petroleum remains the subject of speculation but association by hydrogen bonding and by formation of charge-transfer  $\pi$ - $\pi$  complexes have been cited as the causative mechanisms [22]. Through these noncovalent interactions, asphaltene molecules may influence the structure of emulsions by forming a mechanical barrier around the water droplets [29].

The strength of intermolecular bonds may be evaluated from the changes in activation energies of the viscous flow [30]. It is usually assumed that when heated above their pour point, most petroleum fluids, despite their enormous compositional complexity, behave like simple liquids with their viscosities following temperature dependencies described by exponential Arrhenius-type equations with certain activation energies  $E_{act}$  [30-32]. Viscosity studies in solutions of coal macromolecules, including asphaltenes, revealed [30] that the removal (by chemical means) of hydrogen bonds and of  $\pi$  interactions decreased activation energies by 33 kJ/mol and by 30 kJ/mol, respectively. These results are close to the bond strengths in coal solutions directly determined by IR-spectroscopy [33]. The IR average strengths of hydrogen bonds were 30-50 kJ/mol, while some individual bonds had the strengths of up to 70 kJ/mol.

Our measurements after room temperature fabrication ( $T_F=24\text{ }^{\circ}\text{C}$  in Figs.4-6) show a step-like decrease of activation energies by 50-60 kJ/mol for flow temperatures exceeding  $20^{\circ}\text{C}$ . In view of the above arguments, this decrease may be attributed to a (reversible) thermally-induced break-up of intermolecular hydrogen and/or  $\pi$ -bonds in the asphaltene subsystems of the studied emulsions. Accordingly, an overall (in the entire range of flow temperatures) decrease of activation energies after a fabrication at high temperatures ( $T_F=45\text{ }^{\circ}\text{C}$  in Figs.4-6) should be due to an irreversible removal of noncovalent bonds present in the RT-formed samples.

Finally, fabrication of emulsions in the “critical” temperature range ( $T_F=36\text{ }^{\circ}\text{C}$  in Figs.4-6) induces the structural changes, characterised by a large increase of activation energies of up to 300-380 kJ/mol, indicative of a possible covalent bonding. Namely, this increase is close to the energies ( $\approx 380\text{-}420\text{ kJ/mol}$ ) of unactivated CH and CC bonds, the least reactive parts of organic compounds.

## 5. Conclusions

We found that fabrication temperature has a very strong impact on a dynamic viscosity of crude oil and bitumen emulsions. At room temperature the materials retain a long-term memory of fabrication conditions. This memory is especially strong after fabrication at “critical” temperatures of about  $36\text{-}38\text{ }^{\circ}\text{C}$ . The “critical” sharp increase of viscosity is attributed to structural phase transitions in asphaltene molecular aggregates. In crude oil emulsions and in the matrix crude oil these aggregates presumably stabilise the extended networks of wax particles by emerging covalent bonding. The weakening of the inner structures in bitumen emulsions may be due to the presence of producer-added surfactants, other than asphaltenes. In all studied emulsions, effects of fabrication at temperatures higher than  $42\text{-}43\text{ }^{\circ}\text{C}$  may be

explained by destruction of noncovalent hydrogen bonds and  $\pi$ -interactions. This study demonstrates the effectiveness of rheological measurements as a means to indirectly elucidate the inner structures of petroleum and bitumen emulsions over a wide range of temperatures. With this paper we hope to stimulate further research work on thermodynamics and dynamics of asphaltene-containing emulsions.

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**Figure captions**

Fig. 1. Flow curves at 16 °C for bitumen emulsions fabricated at temperatures  $T_F$  (°C), indicated in the figure.

Fig. 2. Flow curves at 16 °C for crude oil emulsions fabricated at temperatures  $T_F$  (°C), indicated in the figure.

Fig. 3. Flow curves at 16 °C for the matrix-crude oil pre-heated to temperatures  $T_F$  (°C), indicated in the figure.

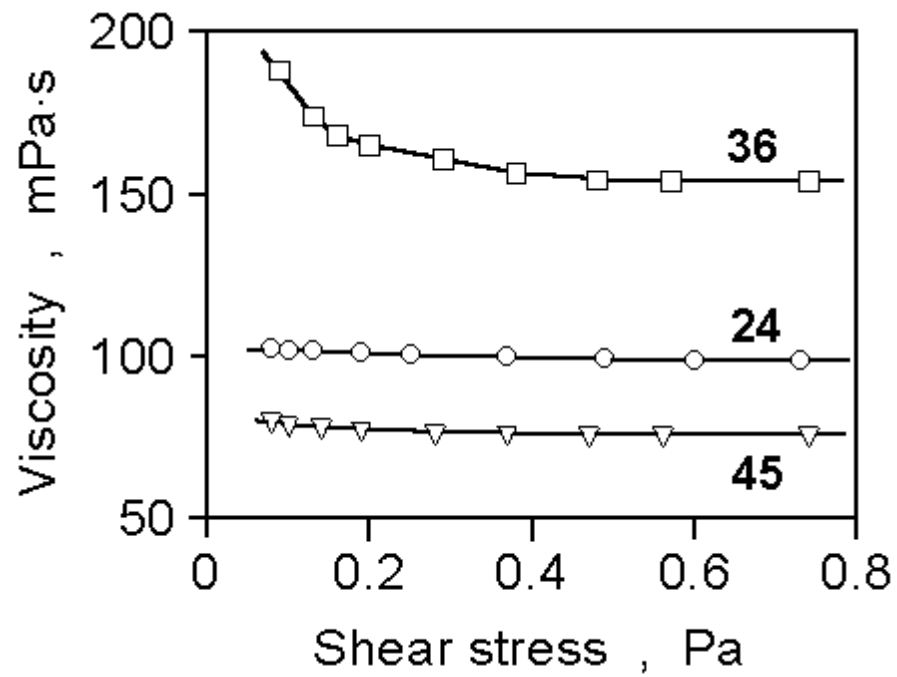
Fig. 4. Activation energies of a viscous flow for bitumen emulsions fabricated at temperatures  $T_F$  (°C), indicated in the figure.

Fig. 5. Activation energies of a viscous flow for crude oil emulsions fabricated at temperatures  $T_F$  (°C), indicated in the figure.

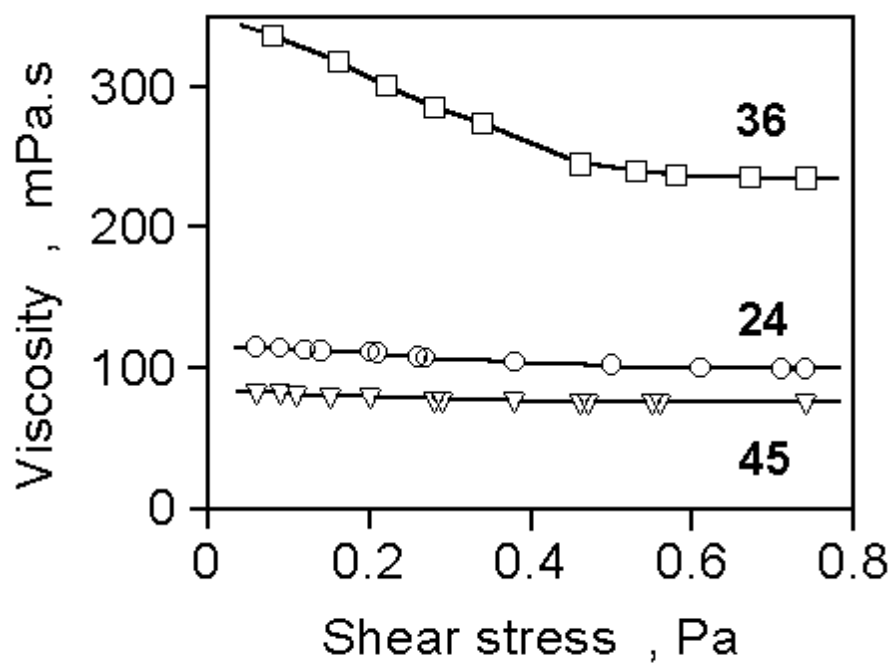
Fig. 6. Activation energies of a viscous flow for the matrix-crude oil pre-heated to temperatures  $T_F$  (°C), indicated in the figure.

Fig. 7. Effects of pre-heating temperature on average activation energies of a viscous flow for the matrix-crude oil.

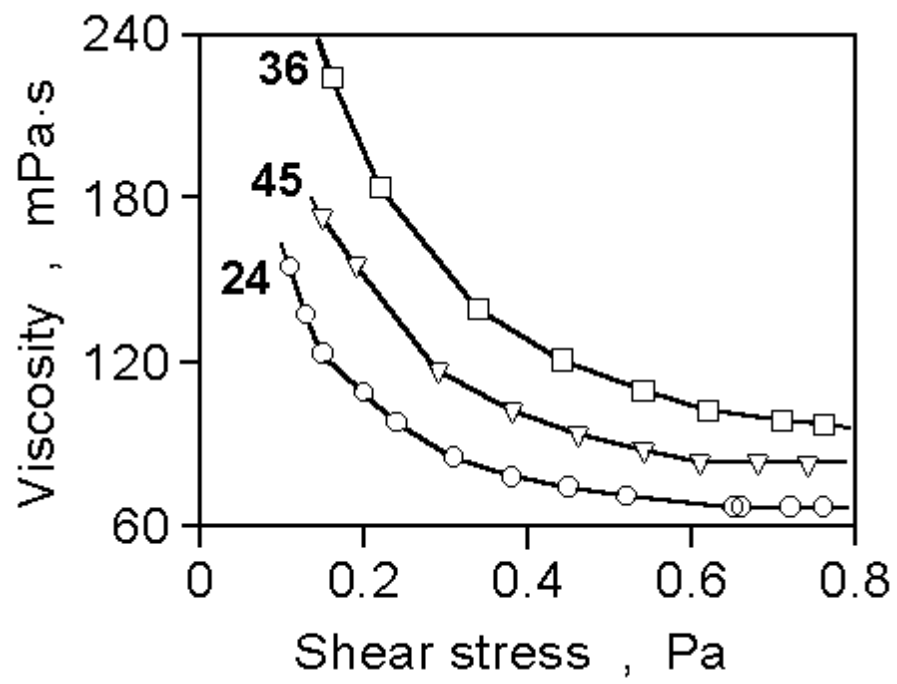
**FUEL** I.N. Evdokimov et.al. “ Effect of asphaltenes .....” Figure 1.

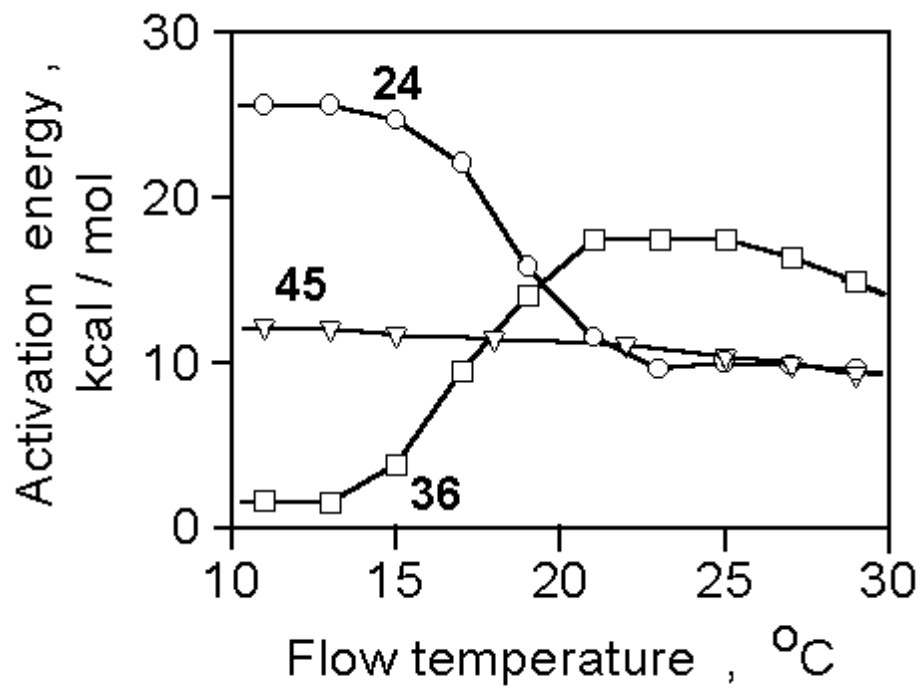


**FUEL** I.N. Evdokimov et.al. “ Effect of asphaltenes .....” Figure 2.

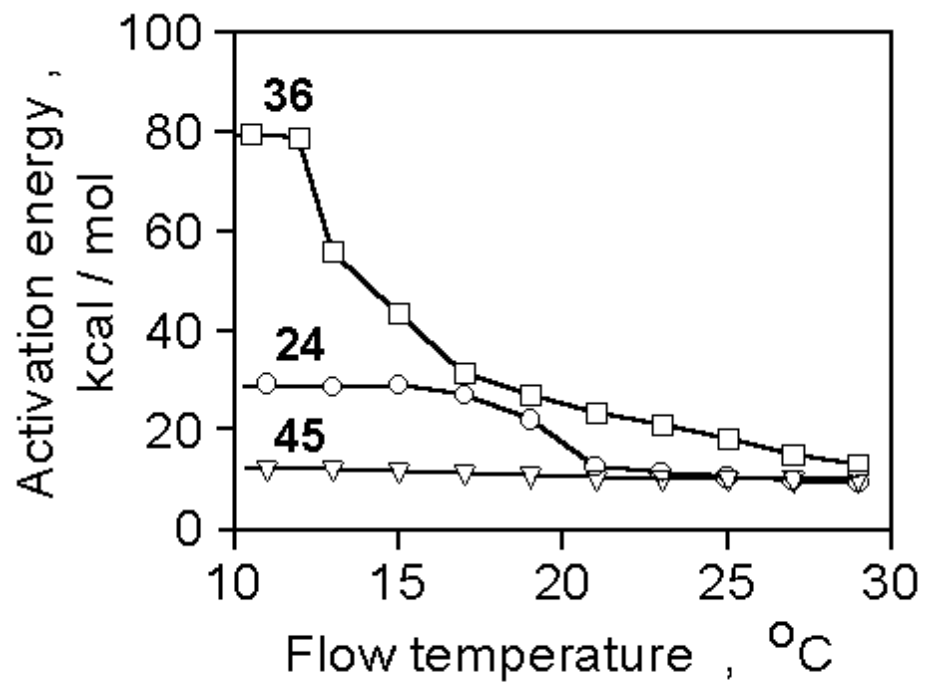


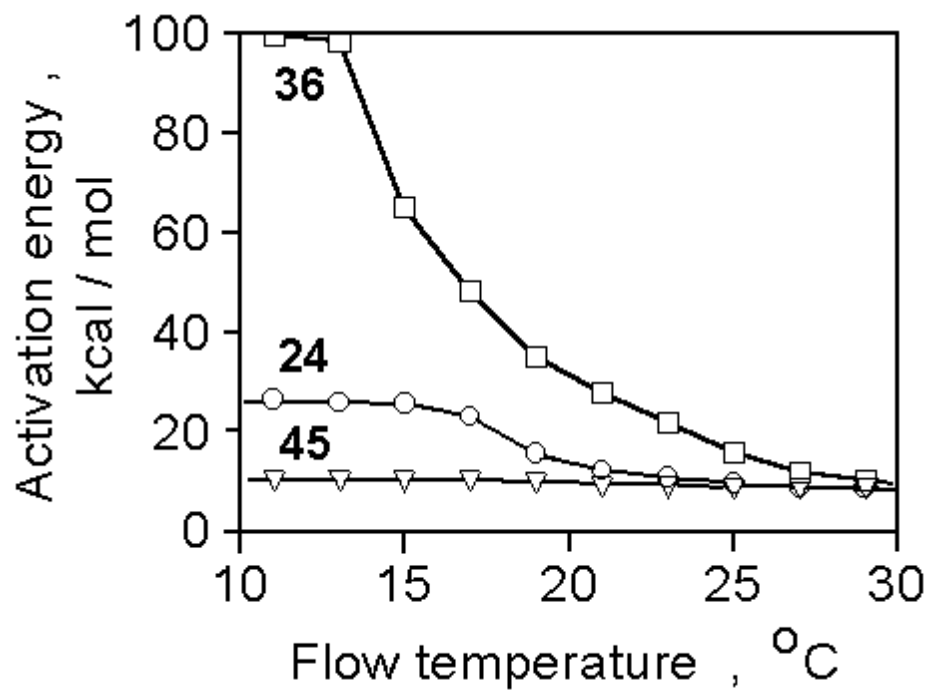
**FUEL** I.N. Evdokimov et.al. “ Effect of asphaltenes .....” Figure 3.



**FUEL** I.N. Evdokimov et.al. “ Effect of asphaltenes .....” Figure 4.

**FUEL** I.N. Evdokimov et.al. “ Effect of asphaltenes .....” Figure 5.



**FUEL** I.N. Evdokimov et.al. “ Effect of asphaltenes .....” **Figure 6.**



**FUEL** I.N. Evdokimov et.al. “ Effect of asphaltenes .....” Figure 7.

