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по программе магистерской подготовки  
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## WELL-DEFINED METASTABLE (TRANSIENT) STATES OF ASPHALTENE COLLOIDS

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### **Abstract**

Experiments with crude oils, toluene solutions of oils and of vacuum residua have shown that the colloidal subsystems of these fluids may be transformed to long-lived (up to 6 months at RT) metastable (possibly transient) states merely by a mild thermal pre-treatment (e.g. 0.5 hr at 28–36°C). These states are fairly well-defined as revealed by distinctly different data sets for various parameters in non-treated (equilibrium) and pre-treated (metastable) fluids. In particular, at 20°C a metastable (transient) state is distinguished by  $\approx 25\%$  increase of the mass of deposits at metal surfaces, by  $\approx 5\%$  decrease of dynamic viscosity, etc. A plausible mechanism of transition to a metastable (transient) state is partial “desorption” of resin “shells” from asphaltene molecular nano-clusters (MNCs) as a result of a structural transformation of MNCs at  $\approx 28^\circ\text{C}$ . Consequently, steric stabilization of asphaltene colloids by resins is disrupted and directly interacting MNCs may form more complex aggregates, fairly long-lived at lower temperatures.

## Introduction

A typical petroleum fluid contains millions of different molecules and is a hybrid of a solution and a colloidal dispersion (of crystallizing waxes, self-associating asphaltenes, etc.). Hence, understanding its phase behaviour should be expected to be a challenge. The surprise is that relatively simple (although, possibly, “unconventional”) experiments can shed light on details of phase transformations in such complex fluids.

E.g., for long time a commonly accepted view in petroleum science has been that asphaltene molecules start to form colloidal particles (“micelles”, “aggregates”, “agglomerates”) only at concentrations above a “CMC” of about several grams per litre (Andersen and Christensen, 2000; Sheu, 1996). However, our recent measurements of optical absorptivities in “unconventional” highly diluted toluene solutions of oils and of solid asphaltenes (Evdokimov et al., 2003a,b) have revealed that association of asphaltene monomers apparently begins at concentrations not exceeding 1–2 mg/l, while massive aggregation of asphaltenes occurs at 60–100 mg/l (cf. Fig.1).

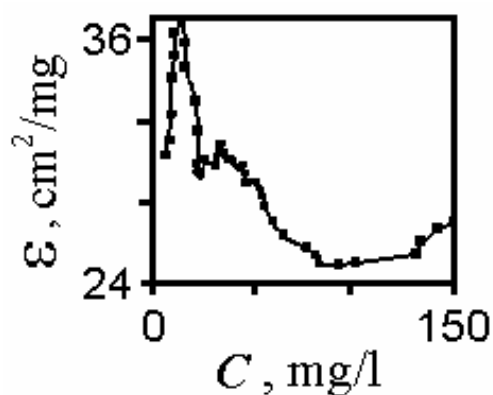


Fig. 1. Optical absorptivity  $\epsilon$  of asphaltenes at 540 nm as a function of asphaltene concentration  $C$  in crude oil/toluene solutions (adapted from Evdokimov et al., 2003c).

These results have been further supported by our measurements of refraction indexes and of dielectric constants in crudes of different origin (submitted for publication). An independent confirmation of asphaltene aggregation at 50–75 mg/l has been recently obtained in absorbance/fluorescence experiments (Goncalves

et al., 2004). Moreover, our studies of viscosity and NMR relaxation in dilute solutions (Evdokimov et al., 2003c) indicated that the phenomenon of asphaltene aggregation at  $\approx 100$  mg/l may be described as a liquid-liquid phase separation (demixing transition), a conclusion recently supported by other authors (Sirota, 2004).

Other common concepts are that at concentrations, typical for natural petroleum systems: 1) the structure of asphaltene dispersion is fairly insensitive to small variations of ambient conditions, and 2) the state of asphaltenes is thermodynamically controlled. Hence, usually it is implicitly assumed that far from obvious critical/transition points the properties of asphaltene colloids are slowly varying smooth functions of external conditions, e.g. of temperature. Consequently, in a lot of conventional experiments temperature dependencies are investigated with fairly large intervals between consecutive data points, e.g. 15–40°C (Wong and Yen, 2000); 10–20°C (Priyanto et al., 2001) etc. Over the past several years we have conducted a series of rheological experiments with “unconventionally” small temperature increments of 1–2°C (Evdokimov et al., 2001;2003d;2004). Unexpectedly, we have observed reproducible non-monotonous temperature dependencies of some rheological parameters at temperatures of 10–50°C. These results were interpreted as an evidence of noticeable structural transformations in asphaltene colloids, induced by comparatively small temperature variations. These new states of asphaltenes may become long-lived metastable ones at lower temperatures (or long-lived transient ones due to a strong kinetic control of thermally-induced transformations of asphaltenes). Whatever the explanation, these experiments have shown that the current properties of an asphaltene-containing fluid may strongly depend on its thermal history. E.g., Fig. 2 shows that a low-temperature association energy of asphaltene particles in a model crude remains at a level of 8-11 kcal/mol (presumably characteristic of an “equilibrium” state of asphaltene colloids), in case the fluid previously has never been pre-heated at temperatures above 27–28°C. Thermal pre-treatment at temperatures 28–45°C evidently strongly trans-



forms the structures and interaction energies of asphaltene particles – at low temperatures a new metastable (transient) state of asphaltene colloids is characterised by association energy of 32–34 kcal/mol. A plausible mechanism of transition to a metastable state is formation of more complex asphaltene associates, as confirmed by direct measurements by other authors (cf. Fig. 3).

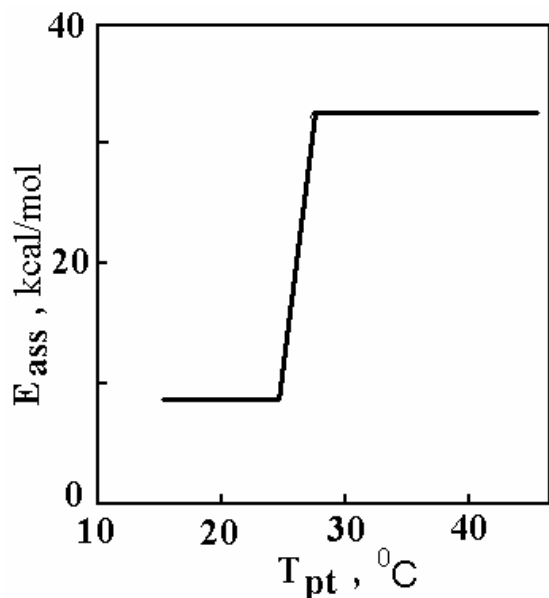
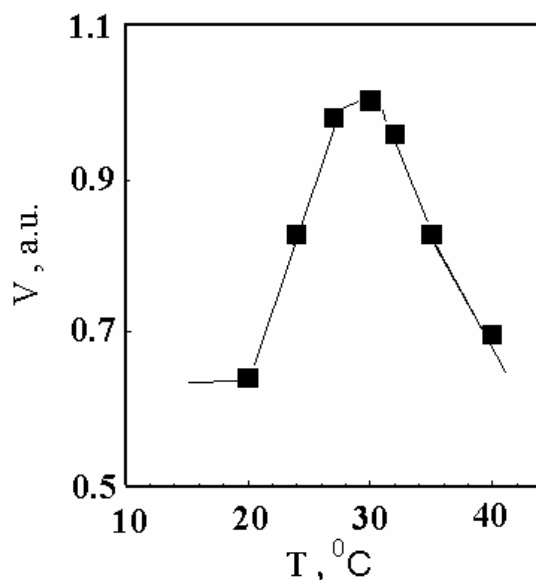


Fig. 2. Schematic behaviour of asphaltene association energies at 8–18°C  $E_{ass}$ , after 1 hr thermal pre-treatment at  $T_{pt}$  of a model crude oil with asphaltene concentration of 40 g/l (adapted from Evdokimov et al., 2001).

Fig. 3. Effects of temperature on the volume of asphaltene colloid particles in a model crude with asphaltene concentration of 36 g/l. (Fluorescence measurements of Dr. R.Z. Syunyaev, adapted from Evdokimov et al., 2001).



In the present communication we report the results of new experiments in support of thermally induced metastable (transient) states in asphaltene-rich fluids.

## **Experimental**

### **Samples**

Experiments have been carried out with asphaltene-rich model oil (asphaltene concentration 12.3 g/l). The light hydrocarbon fractions were represented by toluene, the heavy oil fractions – by 11.6 wt. % of a vacuum residue from Western Siberian crudes (density at 20°C – 979 kg/m<sup>3</sup> ; pour point - 18°C; boiling point – 342°C; asphaltenes – 10.9 wt. % ). The components were mixed at room temperature 1 month before the experiments and were stored at RT (18–20°C) in a dark glass vessel, in air.

Measurements of heavy organic deposition were performed at metal substrates – two 1 mm thick steel plates with the total surface area of 256.1 cm<sup>2</sup>.

### **Apparatus and Procedure**

Deposition studies were conducted in a temperature controlled ( $\pm 0.1^\circ\text{C}$ ) glass cell with steel substrates vertically immersed into the model oil, to minimise sedimentation effects. The mass of deposits was determined with an analytical balance (100 g capacity, 0.1 mg precision). Oil viscosities were measured in a temperature controlled Hoppler-type viscometer.

Between deposition/viscosity experiments, the model oil was stored at RT (18–20°C). Each individual experiment commenced with pre-heating the entire quantity of the model oil to the required measurement temperature for 15–20 minutes. Afterwards several ml of the liquid were transferred either to the deposition cell or to the viscometer. A standard deposition time was 20 minutes. Steel samples covered with deposits were dried in warm air and weighted. Before a new experiment the samples were washed in toluene, wiped with a cotton cloth and dried in warm air. This procedure restored the mass of steel plates to within 1 mg of its initial value.

It should be noted, that we had no strict scenario for choosing the individual measurement temperatures (i.e. no prescribed “descending order” or “ascending order”). To improve statistics, each

next temperature was set virtually at random in the range of 11–40°C. Hence, in continuing experiments, the state of our model oil acquired more and more complicated thermal history.

## Results and Discussion

### Deposition Data

The results of a series of deposition experiments are shown in Fig. 4. Open squares denote the data set for an “equilibrium” state of the model oil, which in its thermal history has never been heated above 28°C (cf. Introduction). The apparent property of an “equilibrium” state (1) is an increase in the mass of deposits with increasing temperature up to  $\approx 20^\circ\text{C}$ , followed by a decrease of  $M$  at higher  $T$ .

Filled circles in Fig. 3 denote the data for the model oil with thermal histories including a structural transition at  $\approx 28^\circ\text{C}$ . A new state of the oil, induced by this transition, is distinguished by a notable increase in the mass of deposits at any measurement’s temperature (e.g.  $\approx 25\%$  at  $20^\circ\text{C}$ ). A prevailing tendency in this state (2) is a continuing increase of deposits with increasing temperature. The thermally transformed oil is apparently in an “equilibrium” state (energetically preferable one) at 28–40°C, while below 28°C this state should be regarded as a metastable (transient) one.

The month-long experiments have shown that the discussed metastable state is fairly long-lived. E.g., in measurements at 17–27°C we never observed a relaxation of the oil to the low-temperature “equilibrium” state (denoted as “1” in Fig.4). In measurements at 11–16°C such relaxation occurred only in 40% of samples (cf. the respective bifurcation of data points in Fig.4). Moreover, at 20°C we have tested the thermally transformed model oil after six months storage at RT (18–20°C) and still observed a mass of deposits characteristic for a metastable (transient) state.

### Viscosity Data

Some of the deposition experiments have been supplemented by measurements of viscosity in the model oil with the same ther-

mal history. The results are presented in Fig. 5. Open squares and filled circles denote the same data as in Fig. 4. In this case a metastable (transient) state in oil, subjected to pre-heating above 28°C is distinguished by a persistent decrease of dynamic viscosity. In viscosity measurements we have never observed relaxation of the oil from a metastable state (2) to a low temperature “equilibrium” state (2), probably due to a comparatively smaller number of experiments.

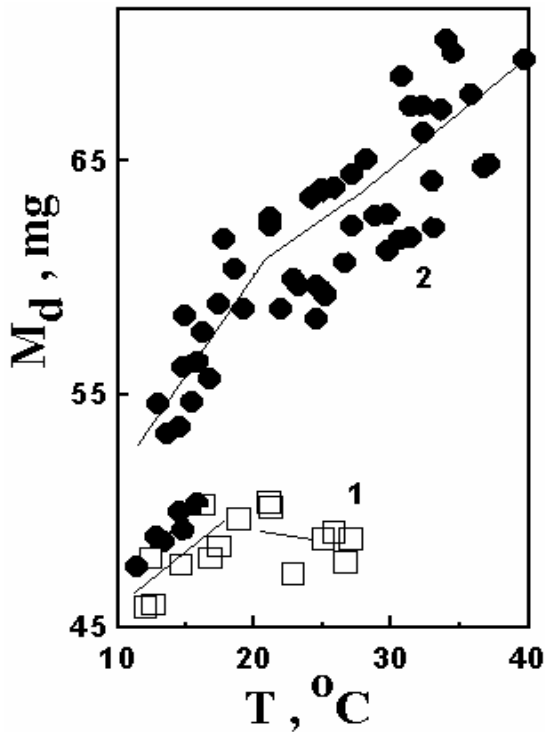
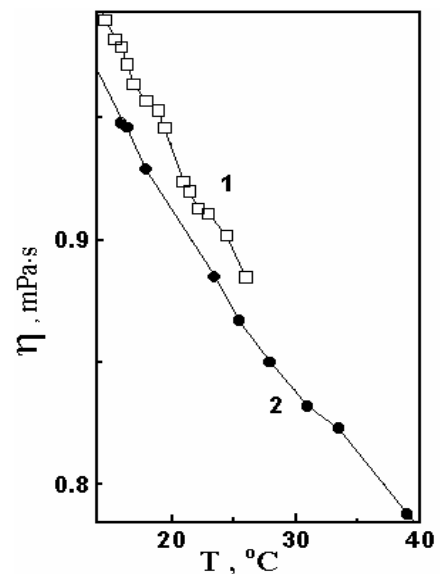


Fig. 4. Effects of deposition temperature and of the thermal history of asphaltene-rich model oil on the mass of deposits at steel samples. Open squares – data for the oil never heated above 28°C. Filled circles – data for the oil at least once pre-heated to 28°C, or to higher temperatures (note bifurcation of low-temperature deposits in this data set).

Fig. 5. Effects of deposition temperature and of the thermal history of asphaltene-rich model oil on its dynamic viscosity. Open squares – data for the oil never heated above 28°C. Filled circles – data for the oil at least once pre-heated to 28°C, or to higher temperatures.



## Discussion

In accordance with our previous results (cf. Introduction), a plausible conclusion is that the observed transformations of the state of the studied multicomponent model oil are governed by equilibrium-metastable transitions in asphaltene colloids.

A schematic description may be that at  $\approx 28^\circ\text{C}$  a structural transformation occurs in basic “molecular nanoclusters” (MNCs) of asphaltenes. As a result, MNC–MNC interactions become somewhat stronger, while interactions of MNCs with solvent molecules become somewhat weaker. Consequently, steric stabilization of asphaltene colloids by resins is disrupted and directly interacting MNCs may form more complex aggregates, fairly long-lived at lower temperatures.

For a given concentration (volume fraction) of asphaltenes, formation of complex deformable aggregates may indeed result in a lower viscosity, as follows from rheological theories for suspensions of deformable particles (e.g. Brenner, 1975; Manga et al., 1998, and references therein). This viscosity decrease by itself may facilitate a transport of depositing material to a metal surface and may be responsible (at least partially) for the observed increase in the mass of deposits from the oil in a metastable (transient) state. Another reason for increased deposition may be the presumed higher activity of structurally transformed asphaltene MNCs.

Literature analysis has revealed some experimental results by other authors in favour of our basic assumption that the observed specific temperature of  $\approx 28^\circ\text{C}$  is singled out by the processes involving solely asphaltenes and not other constituents of our multicomponent model oil. It should be emphasised that in respective publications the existence of this specific temperature remained unnoticed by the authors.

E.g. Ramos et al., 2001 measured viscosities and surface tensions as functions of concentration of pure C5I and C7I asphaltenes in various solvents. The inflections on concentration dependencies they ascribed to a “critical micelle concentration” (CMC) and to a “second aggregation concentration” (SAC). In Tables 1,2 of their

paper the authors report the values of CMC and CAS at various temperatures, but do not plot the respective temperature dependencies. In Fig. 6 we show such a plot for toluene solutions of asphaltenes where the temperatures in the vicinity of 28°C are clearly singled out indisputably due to some physicochemical processes involving asphaltenes.

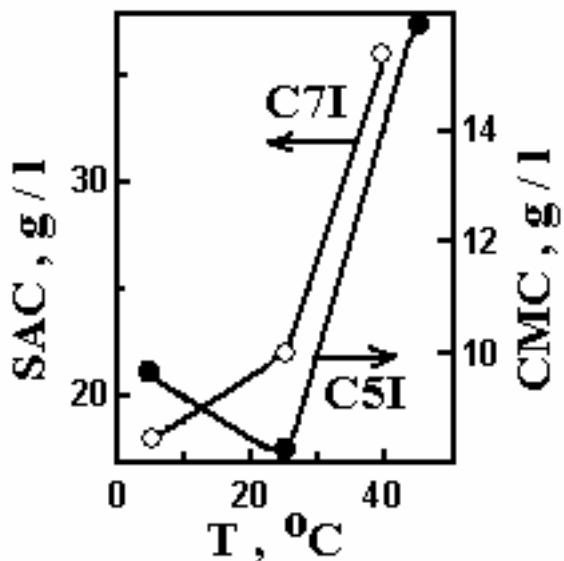


Fig. 6. Non-monotonous temperature dependencies of critical aggregation concentrations of asphaltenes in toluene (adapted from Ramos et al., 2001).

## Conclusions

Measurements of various properties of asphaltene-containing fluids indicate the existence of a specific temperature close to 28°C, apparently singled out by some noticeable transformation of asphaltene colloids. The transformed structures are evidently equilibrium above 28°C and are quenched to a long-lived (up to six months) metastable (transient) state at lower temperatures. This state may be easily resolved from the corresponding equilibrium one by a well-defined difference in the values of the liquid's bulk properties.

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# OIL RECOVERY-2003

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## THERMALLY-INDUCED VISCOSITY ANOMALIES IN EMULSIONS UTILISED IN OIL RECOVERY OPERATIONS

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### 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 development of oil reservoirs. Crude oils are mostly 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 to increase recovery efficiency. 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. Still, only a limited number of results are available on emulsion viscosities as detailed functions of such important external parameter as temperature. Moreover, the determination of the inner structure of emulsions via the majority of structure-sensitive measurements is only possible when the fluid is at rest. In contrast, rheometrical measurements offer means to evaluate the inner structure of emulsions in course of their flow.



Recently [1–3], we have shown that the rheological parameters of some petroleum fluids are sensitive to such subtle structural transformations, which often can not to be detected by other experimental techniques. Hence, in this study we regarded a viscometer as a probe not only of the macroscopic flow parameters but also of the microscopic features of the molecular-structure in petroleum emulsions

### **Samples and Experimental Methods**

The crude oil/water samples (25 vol.% of the emulsified reservoir water) were obtained directly from the oil-production well (Romashkinskoje reservoir, Tatarstan). The water-free oil phase contained 3.5 wt.% asphaltenes, 1.6 wt.% waxes, 22 wt.% resins. During prolonged laboratory storage at room temperature, oil and water phases separated from the samples by gravity, so that the studied W/O emulsions were formed again by intensive mixing of the separated phases.

The bitumen emulsions were formed from the “HIMEKO” concentrate (HIMEKO Co., Moscow) which contains 50 vol.% of bitumen, 40 vol.% of water and 10 vol. % of stabiliser ( $\text{CaCl}_2$ ), acid (HCl), various surfactants, dispersants and modifiers. According to the technological recommendations of by the producer, the final bitumen emulsions were formed by 1/1 dilution of the concentrate with the separately provided “KORE” solvent (hydrocarbon rectification residues).

The effect of formation temperature on rheology of all samples have been investigated at flow temperatures of 8–30°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 new, freshly-prepared sample.

In studies of water/oil emulsions (25 vol.% of reservoir water), two gravitationally separated phases were mixed again directly in

the rheometer's measurement cell. The bitumen concentrates also were diluted in the rheometer's cell by adding an equal volume of industrial dilutant so that a studied emulsions contained 25 vol.% of bitumen and 20 vol.% of water. Each emulsion was formed by mixing for 1 hour at conditions close to a maximum rheometer's torque (shear stresses  $\approx 0.7\text{--}0.8\text{ N/m}^2$ ), at a fixed formation temperature TF in the range from 20 to 60°C. After formation was completed, each sample under constant mixing was cooled at the rate of 1–1,5°C per minute to the lowest measurement (flow) temperature of 8–10°C.

At each operating temperature, the system was initially maintained at a constant shear rate for 20 min. The measurements continued with a step-like decrease of the shear rate 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 (flow) temperature (in 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.

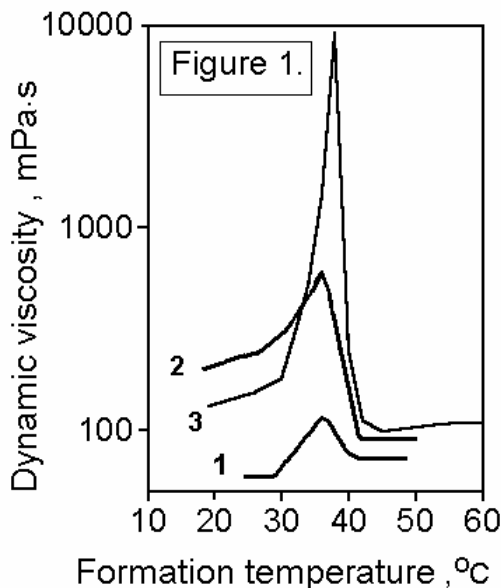
In all studied samples non-Newtonian flow behaviour was observed at shear stresses below 0.2–0.5 Pa. Hence, to characterise the temperature-induced effects, we have used the viscosity values at shear stress of 0.7 Pa, i.e. at flow conditions close to Newtonian.

## **Experimental results**

### **1. The effect of the formation temperature on the viscosity of emulsions**

It was observed, that viscosities of emulsions, measured at industrially-important flow temperatures 10–28°C is strongly affected by their formation temperature TF. Figure 1 shows the effect of TF on the dynamic viscosity for (1) the bitumen emulsions, at 16°C; (2) the water/crude oil emulsions, at 12°C; (3) the water-free oil phase of the W/O emulsions, at 12°C. Note, that the viscosity values are plotted on a log-scale. As can be seen in Figure 1, in all samples even relatively small variations of the formation tem-

perature may lead to very large changes of dynamic viscosity, measured at lower temperatures. All results show a technologically unfavourable sharp increase of viscosity for the “critical” formation temperatures of 36–38°C. For example, the viscosity of the water-free oil, pre-heated to these temperatures, increases by a factor of 70, to 9070 mPa·s, as compared to 129 mPa·s, measured for unheated oil, stored at 19°C. In the water/oil emulsions the corresponding viscosity increase is somewhat lower – from 200 mPa·s to 600 mPa·s. Obviously, the thermal effects in water/oil emulsions should be attributed to its oil component. A smaller effect of heating for water/oil emulsions, as compared to the original crude may be explained by the fact that the viscosity of the mineralised reservoir water, contained in such emulsion, did not show any viscosity anomalies in the studied temperature range. The results of Figure 1 show that unfavourable increase of viscosity after formation at “critical” temperatures is also observed in bitumen emulsions. The reason why this increase is only two-fold (from 60 to 120 mPa·s) may be due to a presence of specially introduced surfactants/stabilisers, as discussed above.



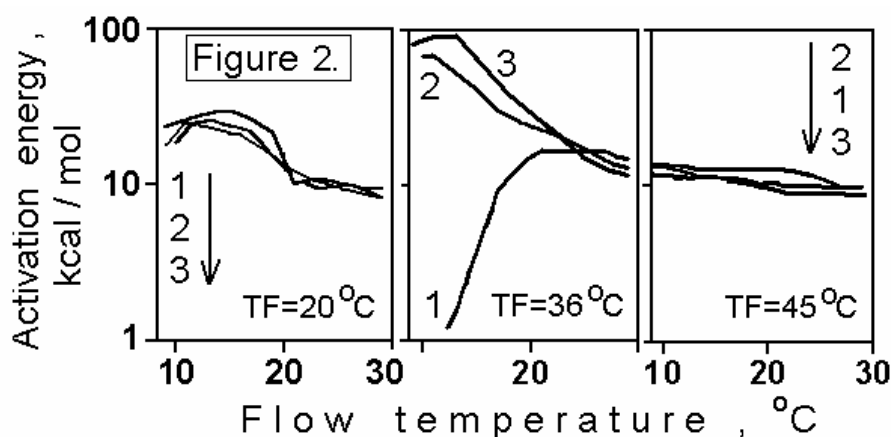
The data of Figure 1 reveal the small width of the “critical range” of formation temperatures, leading to the observed unfavorable thermal effects. At the FWHM of the crude oil viscosity peak, this TF range may be determined as 2,2°C. The most conservative estimates at the base of the viscosity peak give for the critical TF range the value not exceeding 10°C.

In course of all experiments, the results of the thermal treatment (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 extended molecular structures appeared in the emulsions after the fabrication processes at “critical” temperatures (the effect of long-term “thermal memory”). In the matrix crude oil phase, this “thermal memory” was found to extend for a period of at least four months.

## 2. Activation energies of the viscous flow

Activation energies were determined from the dependencies of the logarithm of viscosity 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 Figure 2 for (1) the bitumen emulsions; (2) the water/crude oil emulsions; (3) the water-free crude oil.



The left part of Figure 2 shows the dependencies of activation energies on the flow (measurement) temperature for samples, subjected to room temperature formation (TF=20°C).

The notable feature is a virtual coincidence of activation energies for all studied samples. For flow temperatures decreasing from 30°C down to 20°C all activation energies remain fairly constant, slowly increasing within the limits of 8.5–10.5 kcal/mol ( $\approx 36$ –44 kJ/mol).

At temperatures close to 20°C there is a step-like increase of the activation energies to a new level of 22–29 kcal/mol ( $\approx 92$ –121 kJ/mol). Below 10–12°C the activation energies show the tendency of decreasing, so the shape of the curves in the range of 8–20°C may be described as a “flat maximum”.

The right part of Figure 2 shows the results for  $TF=45^{\circ}C$ , above the critical formation temperatures. The effects of such a strong pre-heating are rather small. For all flow temperatures the activation energies are reduced approximately to the level, observed at  $20-30^{\circ}C$  in case formation at  $TF=20^{\circ}C$ .

The most pronounced changes of activation energies were registered (central part of Figure 2) after formation of emulsions at  $TF=36^{\circ}C$ , close to the critical temperature in the matrix crude oil. In this case activation energies for the W/O emulsion and the crude sharply increase from  $10-12$  kcal/mol ( $42-50$  kJ/mol) to  $70-100$  kcal/mol ( $290-420$  kJ/mol) with flow temperatures decreasing from  $30^{\circ}C$  to  $10-12^{\circ}C$ . In contrast, activation energies for bitumen emulsion sharply decrease at low flow temperatures, down to  $1.5$  kcal/mol ( $6.3$  kJ/mol) at  $13^{\circ}C$ . The observed large variations of activation energies are indicative of notable modifications of the emulsion' molecular structures induced by formation in the critical TF range. These structural modifications we attribute primarily to the specific molecular processes involving asphaltenes.

## Discussion

It is known that asphaltenes may stabilise water (oil) droplets in emulsions formed by recovery of crudes [4–7] and in bitumen emulsions [8, 9]. It is mostly the aggregation state of the asphaltenes and not their amount that controls the stability of an emulsion. When asphaltenes start to form large aggregates, their impact on emulsion stability is the greatest [10, 11]. Accordingly, when the asphaltene particles/aggregates are dissolved to substantially smaller units, they no longer produce stabilising effects.

Based on these results, it can be concluded that the asphaltene fractions, are primarily responsible for the stability of the emulsion's inner structure. The degree of asphaltene aggregation determines the strength of this structure. Hence the observed sharp variations of viscosity may be attributed to some specific aggregation processes involving asphaltene molecules.

Asphaltene colloids are known to be sterically stabilised by solvated resins [13]. Formation of larger asphaltene aggregates may occur when resin molecules “desorb” from the surfaces of asphaltenes. The sharp dependence of the measured viscosities on the value of TF (Figure 1) suggests that the changes in solvation is triggered by a structural phase transition in the asphaltene/resin molecular subsystem. In [2,3] we discussed two possible types of these transitions at temperatures just above 30°C. One is a first-order transition between closely packed and loosely bound structures in the adsorbed layers of resin molecules. Another possible mechanism is the change of the surface energy of the asphaltene aggregates due to phase transformation of their inner molecular structure.

An important role in the observed thermal effects is evidently played by paraffins. It has been repeatedly shown [6, 7, 12] that the paraffins alone are unable to stabilise petroleum emulsions. In the absence of asphaltenes, paraffin crystals remain completely oil-wet (hydrophobic) and are dispersed in the oil phase. However, when asphaltene aggregates adsorb on the surfaces of paraffin particles, their wettability changes. The asphaltene-solvated paraffin particles migrate to the oil–water interface, contributing to the formation of rigid layers around water droplet and to the emulsion stability [6, 7].

Types of paraffin fractions may determine the role of paraffins in the observed thermal effects in petroleum emulsions. The studied crude oils contained predominantly normal paraffins with the melting points of 40–50°C. Bitumen are known to contain also the microcrystalline paraffins (isoparaffin and cycloparaffin) with higher melting points of 60–90°C.

During a sufficiently strong pre-heating (TF above both the asphaltene/resin phase transition and the melting point of paraffins) all the existing paraffin particles melt away. The new microscopic crystals start appearing in the emulsion only when it is cooled below the melting point. We presume, that large asphaltene aggregates can not form an “adsorbed layer” around a small paraf-

fin crystal. Hence, with decreasing temperature, the newly-formed paraffin crystals form networks, directly interacting with each other. Direct interaction of paraffins is a weak physical one [12], so that the resulting increase of viscosity is comparatively small and such loosely-bound crystal networks quickly disappear when the temperature is increased again.

During a moderate pre-heating (TF below the melting point of paraffins, but above the asphaltene/resin phase transition) the existing paraffin particles in emulsions readily adsorb the newly-formed asphaltene aggregates, so that their interaction properties of these particles are notably altered. After cooling, asphaltene-covered paraffin particles form strongly bound networks, so that the viscosity is greatly increased and “memory” of the pre-heating parameters is preserved at varying measurement conditions.

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.

The means by which asphaltenes, resins and paraffins interact in petroleum fluids 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 [13]. Through these noncovalent interactions, asphaltene molecules may influence the structure of emulsions by forming a mechanical barrier around the water droplets [14].

The strength of intermolecular bonds of asphaltenes may be evaluated from the changes in activation energies of the viscous flow, as shown by viscosity studies in solutions, containing coal asphaltenes [15]. The removal of hydrogen bonds and of  $\pi$  interactions decreased activation energies by 33 kJ/mol and by 30 kJ/mol, respectively. These results were verified by IR-spectroscopy [16], which showed that energies of hydrogen bonds were on average 30–50 kJ/mol (for some individual bonds up to 70 kJ/mol).

Our measurements after formation at 20°C (Figure 2) show a step-like decrease of activation energies by 50–60 kJ/mol for flow

temperatures exceeding 20°C. This decrease may be attributed to a (reversible) thermally-induced break-up of intermolecular hydrogen and/or  $\pi$ -bonds in the asphaltene subsystems. Accordingly, an overall decrease of activation energies after the strong pre-heating (TF=45°C, Figure 2) should be due to an irreversible removal of these noncovalent bonds.

Finally, formation of emulsions in the “critical” temperature range (TF=36°C, Figure 2) 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 ( $\approx$ 380–420 kJ/mol) of unactivated CH and CC bonds in organic compounds.

## Conclusions

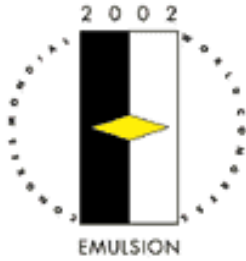
We found that formation temperature of emulsions has a very strong impact on viscosity of crude oil and bitumen emulsions. At normal technological conditions these emulsions possess a long-term “memory” of a thermal preheating. This memory is especially strong after formation of emulsions at “critical” temperatures of about 36–38°C. The “critical” sharp increase of the technological viscosity is attributed to structural phase transitions in asphaltene molecular aggregates. In W/O emulsions and in the crude oil these aggregates presumably stabilise the extended networks of paraffin particles by emerging covalent bonding. The relative weakening of the inner structures in bitumen emulsions may be due to the presence of producer-added surfactants. In all studied emulsions, the “memory” of a strong pre-heating (formation temperatures above the melting point of paraffins) may be explained by destruction of noncovalent hydrogen bonds and  $\pi$ -interactions.

This study demonstrates the effectiveness of rheological measurements as a means to 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 mechanics of asphaltene-containing emulsions utilised in recovery of oil reservoirs.



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## PECULIARITIES OF RHEOLOGY OF CRUDE OIL AND BITUMEN EMULSIONS AT INDUSTRIALLY IMPORTANT TEMPERATURES

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### 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. Crude oils are mostly 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 to increase recovery efficiency. 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. Still, only a limited number of results are available as detailed functions of such external parameter as temperature. The determination of the inner structure of emulsions via the majority of structure-sensitive measurements is only possible when the fluid is at rest. In contrast, rheometrical measurements offer an indirect means to

determine the inner structure of emulsions, and can often also provide evidence of structural changes.

Recently, we have shown that the rheology of petroleum fluids may be sensitive to structural transformations, which often are far too subtle to be detectable by other experimental techniques (1, 2). Hence, in this study we regard a viscometer as a probe not only of the macroscopic flow parameters but also of the subtle molecular-structure features of petroleum emulsions

## **2. Materials and Methods**

### **2.1. Samples**

The crude oil/water samples (25 vol.% of the emulsified reservoir water) were obtained directly from the oil-production well (Tatarstan, Russia). The water-free oil phase contained 3.5 wt.% asphaltenes, 1.6 wt.% waxes, 22 wt% resins. During prolonged laboratory storage at room temperature, oil and water phases separated from the samples by gravity, so that the studied W/O emulsions were prepared by re-mixing the separated phases at the initial v/v ratio.

The bitumen emulsions 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, industrial bitumen emulsions are produced by 1/1 dilution of the concentrate with the separately provided “KORE” solvent (hydrocarbon rectification residues). Both products were used as received.

### **2.2 Apparatus and procedure**

The effect of formation temperature on rheology of all samples have been investigated at flow temperatures of 8–30°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 rheologi-

cal experiment has been performed with a freshly prepared sample.

In studies of water/oil emulsions, two gravitationally separated phases were introduced into the rheometer'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 rheometer's cell by adding an equal volume of industrial dilutant so that a 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 rheometer's torque (shear stresses  $\approx 0.7\text{--}0.8\text{ N/m}^2$ ), at a fixed formation temperature TF in the range from 20 to 60°C. Under constant mixing, each sample was cooled to the lowest operating (flow) temperature (8–10°C) at the rate of 1–1,5°C per minute.

At each operating 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 an 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 operating temperature (in 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 all studied samples the measured flow curves (viscosity vs. shear stress) exhibited a more or less pronounced shear-thinning (i.e. non-Newtonian) behaviour. In case of W/O emulsions and the parent matrix crude oil, the flow curves were approximately Newtonian at shear stresses  $\geq 0.15\text{--}0.4\text{ Pa}$ , depending on the formation and the flow temperatures. For bitumen emulsions, the Newtonian approximation could be applied only at much higher shear stresses, above 0.6 Pa.

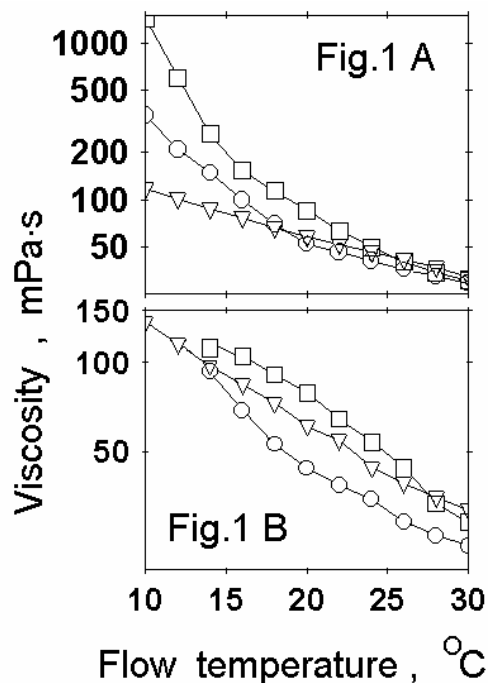
As a measure of temperature-induced effects in all samples,

we have used the viscosity value at a common shear stress of 0.7 Pa, i.e. at flow conditions closest to Newtonian.

### 3.2. Constant-shear viscosities before after thermal preload

The viscosity of the emulsions was strongly affected by their fabrication temperature TF.

Fig.1(A,B) shows the effect of TF on the dependencies of viscosity at a constant shear stress (0.7 N/m<sup>2</sup>) on the flow (measurement) temperature, for the water/crude oil emulsions (A) and for the bitumen emulsions (B). Note, that the viscosity values are plotted on a log-scale. The data denoted by circles were obtained after fabrication at room temperature (TF=24°C), without thermal preload. Squares and triangles denote the results for TF=36°C and TF=45°C, respectively. In all cases the viscosity decreases with increasing flow temperature due to the enhanced thermal mobility of the molecular, aggregate and colloidal species. However, the rate of this decrease (as well as the viscosity value at any flow temperature) shows a strong non-monotonic dependence on the fabrication temperature.



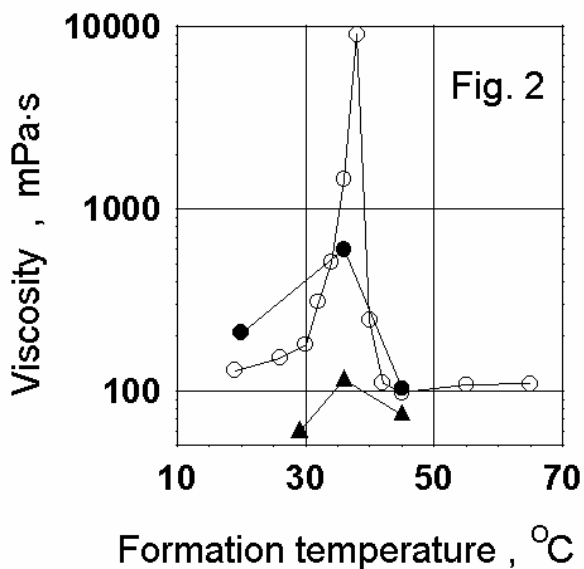
For the water-crude oil emulsions (Fig.1 A), a moderate thermal preload (TF=36°C) leads to a large increase of viscosities as compared to emulsions, fabricated at room temperature. At flow temperature of 10°C this increase is almost four-fold – from 372 mPa·s to 1440 mPa·s. A somewhat stronger thermal preload (TF=45°C) causes a qualitatively opposite effect of decreasing the viscosities as compared to the RT data. At flow temperature of 10°C the decrease is from 372 mPa·s to 116 mPa·s. For W/O emul-

sions the effects of the thermal preload are largest at low flow temperatures and are gradually levelled off as the flow temperature is increased up to 30°C. Qualitatively similar (but much stronger) effects were observed also for the matrix crude oil (cf. Figs.2,3).

For the bitumen emulsions (Fig.1 B) a moderate thermal preload (TF=36°C) also leads to the viscosity increase, but only at flow temperatures above 13–14°C. At flow temperature of 16°C the viscosity increases from 61 mPa·s (RT fabrication) to 115 mPa·s. However, below 13°C there is an apparent reversal of the TF effect: viscosity values for TF=36°C show a tendency to be lower than those for TF=24°C. A higher thermal preload (TF=45°C), leads to a general decrease of measured viscosities but, as distinct from crude oil emulsions, these viscosities (at least for flow temperatures above 13°C) remain larger than those measured after RT formation.

### 3.3. The critical formation temperatures and the effect of thermal memory

As follows from the previous section, relatively small variations of the thermal preload (formation temperature) may lead to quantitatively large and even qualitatively different changes in the rheological parameters, measured at lower temperatures in various types of petroleum emulsions. In order to determine the role of oil emulsion constituents in this effect, we made similar rheological measurements with the separated phases. The viscosity of the mineralised reservoir water did not show any peculiarities in the studied ranges of the formation/flow temperatures. The viscosity of the matrix crude oil showed qualitatively



the same effects of formation temperature, but much more pronounced than those in the studied emulsions, as illustrated in Fig.2.

Filled triangles in Fig.2 denote the viscosity values (measured at 16°C) for the bitumen emulsions prepared at different formation temperatures. Filled circles denote the analogous data for the crude oil emulsions (measured at 12°C). The results for the matrix crude oil (also measured at 12°C) are denoted by open circles and show a very sharp peak of viscosity for the “critical” formation temperature of 38°C.

The peak viscosity value is 9070 mPa·s, as compared to 129 mPa·s, measured after room temperature (19°C) formation of the crude oil sample. The data of Fig.2 reveal the small width of the “critical range” of formation temperatures, leading to the observed thermal effects. As the FWHM of the crude oil viscosity peak, this TF range may be determined as 2,2°C. The most conservative estimates at the base of the viscosity peak give for the critical TF range the value not exceeding 10°C.

The results of Fig.2 definitely prove that the observed effects of a thermal preload in the W/O emulsions are related mainly to the changes in the properties of the matrix crude oil. The considerably smaller effect in the bitumen emulsions may be due to a presence of specially introduced surfactants/stabilisers, as discussed in section 4.3.

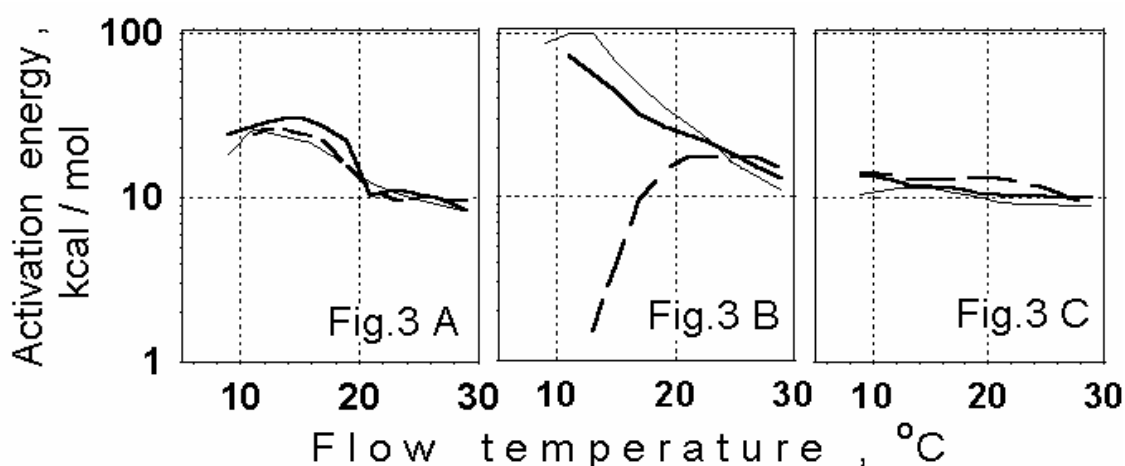
In course of all experiments, the results of the thermal preloads (modified viscosities) were still detected even after prolonged (up to 6 hours) annealing at increasing flow temperatures in conditions of a continuing mechanical agitation. This indicates that some long-lived residual structures remained in the emulsions after the fabrication processes at “critical” temperatures (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.

### 3.4. Activation energies of the viscous flow

Activation energies were determined from the dependencies of the logarithm of viscosity 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 Fig.3 A, B, C, where the thick solid lines are the data for W/O emulsions, thin solid lines – the data for the matrix crude oil and the dashed lines – the data for bitumen emulsions (note the log scale for activation energies).

Fig.3A shows the dependencies of activation energies on the flow (measurement) temperature for samples, subjected to room temperature formation (20°C for W/O emulsion and the matrix crude oil, 26°C for bitumen emulsions). The notable feature of Fig.3A is a virtual coincidence of activation energies for all studied samples.

For flow temperatures decreasing from 30°C down to about 20°C all activation energies remain fairly constant, slowly increasing within the limits of 8.5-10.5 kcal/mol ( $\approx$ 36-44 kJ/mol).



At temperatures close to 20°C there is a step-like increase of the activation energies to a new level of 220–29 kcal/mol ( $\approx$ 92–121 kJ/mol). Below 10–12°C the activation energies show the tendency of decreasing, so the shape of the curves in the range of 8–20°C may be described as a “flat maximum”.



Fig.3C show the results for  $TF=45^{\circ}C$ , i.e. above the critical formation temperatures. The effects of such a strong thermal pre-load are rather small. For all flow temperatures the activation energies are reduced approximately to the level, observed at  $20-30^{\circ}C$  in case of RT formation (Fig.3A).

The most pronounced changes of activation energies were registered (Fig.3B) after formation of emulsions at  $TF=36^{\circ}C$ , close to the critical temperature in the matrix crude oil. In this case activation energies for the W/O emulsion and the crude sharply increase from  $10-12$  kcal/mol ( $42-50$  kJ/mol) to  $70-100$  kcal/mol ( $290-420$  kJ/mol) with flow temperatures decreasing from  $30^{\circ}C$  to  $10-12^{\circ}C$ . In contrast, activation energies for bitumen emulsion sharply decrease at low flow temperatures, down to  $1.5$  kcal/mol ( $6.3$  kJ/mol) at  $13^{\circ}C$ . The observed large variations of activation energies are indicative of notable modifications of the emulsion' molecular structures induced by formation in the critical TF range. These structural modifications we attribute primarily to the specific molecular processes involving asphaltenes.

## **4. Discussion**

### **4.1. The role of asphaltenes**

It is a well-known fact that the presence of asphaltene fractions serves to stabilise the emulsions formed during crude oil production (3–6) and that asphaltenes also play a dominant role in the stabilisation of water droplets in diluted bitumen emulsions (7, 8).

It is mostly the aggregation state of the asphaltenes and not their amount that controls the stability of an emulsion. When asphaltenes start to form large aggregates, their impact on emulsion stability is the greatest (9, 10). For example, it was observed (8) that in diluted bitumen emulsions, the emulsified water droplets are stabilised by steric repulsion between adsorbed “monolayers” (8–10 nm thick) of asphaltene aggregates on the droplet surfaces. Similarly, it was concluded from rheological measurements of asphaltene-containing crude oil - water emulsions (9), that the water droplets are stabilised by adsorbed 10 nm asphaltene layers, con-

sistent with the size of asphaltene aggregates. Accordingly, when the asphaltene particles/aggregates are dissolved to substantially smaller units, they no longer produce stabilising effects.

Based on the above arguments, it can be concluded that the asphaltene fractions, when present, are primarily responsible for the stability of the emulsion's inner structure. The degree of asphaltene aggregation determines the strength of this structure (emulsion "tightness"). Hence the observed sharp variations of viscosity may be attributed to some specific aggregation processes involving asphaltene molecules.

#### **4.2. The "trigger" mechanism of asphaltene aggregation after thermal preload**

Asphaltene colloids are known to be sterically stabilised by solvated resins (12). Formation of larger asphaltene aggregates may occur when resin molecules "desorb" from asphaltenes. The sharp dependence of the measured viscosities on the value of TF (Fig.2) suggests that the changes in solvation is triggered by a structural phase transition in the asphaltene/resin subsystem. In (1, 2) we discussed two possible types of these transitions at temperatures just above 30°C. 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 the  $\pi$ -stacked asphaltene aggregates due to phase transformation of their inner molecular structure.

#### **4.3. The role of waxes**

It has been repeatedly shown (5, 6, 11) 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 alteration of wettabil-

ity allows the wax crystals to have affinity to the aqueous phase. 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, 6).

Types of wax crystals and their thermal properties may determine, how wax could interfere with the thermally-induced effects in petroleum emulsions. The studied crude oils contained predominantly normal paraffin waxes with the melting points in the range of 40–50°C. Bitumen are known to contain also the microcrystalline (isoparaffin and cycloparaffin) waxes with higher melting points, in the range of 60–90°C.

During a sufficiently strong thermal preload (TF above both the asphaltene/resin phase transition and the wax melting point) all the existing wax particles melt away. The new microscopic wax crystals start appearing in the emulsions only when it is cooled below the melting point. We presume, that large asphaltene aggregates can not form an “adsorbed layer” around small wax crystals. Besides, above the phase transition point asphaltenes may even become wax inhibitors, because larger aggregates no longer serve as crystallisation centres. 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 (11), so that the resulting increase of viscosity is comparatively small and such loosely-bound crystal networks quickly disappear when the temperature is increased again.

During a moderate thermal preload (TF below the wax melting point, but above the asphaltene/resin phase transition) the existing wax particles in emulsions readily adsorb the newly-formed asphaltene aggregates, so that their interaction properties of these particles are notably altered. After cooling, asphaltene-covered wax particles form strongly bound networks, so that the viscosity is greatly increased and “memory” of the thermal preload is preserved at varying measurement conditions.

The relatively smaller thermal effects in the bitumen emulsions may be due to the weakening of asphaltene-mediated net-

works by other strong surfactants introduced into the concentrated product.

#### 4.4. 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 (12). Through these noncovalent interactions, asphaltene molecules may influence the structure of emulsions by forming a mechanical barrier around the water droplets (13).

The strength of intermolecular bonds may be evaluated from the changes in activation energies of the viscous flow, as shown by viscosity studies in solutions of coal macromolecules, including asphaltenes (14). The removal (by chemical additives) 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 (15). 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 RT formation (Fig.3A) show a step-like decrease of activation energies by 50–60 kJ/mol for flow temperatures exceeding 20°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 decrease of activation energies after the strong thermal preload (TF=45°C, Fig.3C) should be due to an irreversible removal of noncovalent bonds present in the RT-formed samples.

Finally, formation of emulsions in the “critical” temperature range (TF=36°C, Fig.3B) 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 ( $\approx$ 380–420 kJ/mol) of unacti-

vated CH and CC bonds, the least reactive parts of organic compounds.

## 5. Conclusions

We found that formation temperature has a very strong impact on viscosity of crude oil and bitumen emulsions. At normal conditions the materials possess a long-term memory of a thermal preload. This memory is especially strong after formation at “critical” temperatures of about 36–38°C. The “critical” sharp increase of viscosity is attributed to structural phase transitions in asphaltene molecular aggregates. In W/O 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, the “memory” of a strong thermal preload (formation temperatures above the wax melting point) may be explained by destruction of noncovalent hydrogen bonds and  $\pi$ -interactions.

We expect the observed thermally-induced aggregation to be a common phenomenon in fluids, containing asphaltenes of any geographical or geological origin. This phenomenon could be the explanation for some puzzling experiments where an enhanced aggregation was registered in a regime where the destructive effect of increased thermal motion was expected to dominate.

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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## Thermophysical properties and phase-behaviour of asphaltene-containing petroleum fluids

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### Abstract

We have measured the effects of a thermal pre-treatment of a crude oil on its pour point  $T_{pour}$  and on the activation energy  $U$  of a viscous flow at 8–30°C. A dramatic increase of both  $T_{pour}$  and  $U$  was observed in oil samples pre-heated to temperatures in the specific range from 28–30°C to 39–40°C. This effect may be triggered by a structural phase transitions in the oil asphaltene/resin subsystem, resulting in formation of asphaltene molecular aggregates. Below the wax appearance temperature these aggregates evidently act as cementing species in extended networks of wax crystals. The optical absorption measurements revealed an increase of a vertical concentration gradient in the samples, heated to the above specific temperatures, which may be indicative of some phase separation in the studied crude oil.

**Keywords:** *Crude oil; Thermal treatment; Pour point; Activation energy; Asphaltenes; Aggregation; Phase transition*

## 1. Introduction

In petroleum fluids, phase transformations, involving asphaltenes, may trigger the processes (e.g. flocculation and precipitation) [1–3], which cause troubles in the petroleum production, transportation and processing.

Recently [4–6] we have observed thermal anomalies of some “model oils” which we attributed to a previously unreported structural phase transition in the asphaltene subsystem. We concluded that this transition is defined by specific molecular interactions of asphaltenes, viewed not just as a solubility class, but as true chemical species [7–9]. Hence, the characteristics of the observed transition point should be fairly insensitive both to the geographical/geological origin of asphaltene species and to the nature of the bulk petroleum fluid.

In the present study, we have measured thermal effects on the dynamic viscosity of an unprocessed crude oil. The results definitely prove that in this complex fluid strong structural transformations occur in the same temperature range as in our “model oils”. The viscosity results are supported by the measurements of optical absorptivities, indicating that the structural transformations may be accompanied by a macroscopic phase separation in a heated crude oil.

## 2. Experimental

### 2.1. Oil samples

The virgin crude was collected directly from a well-head at the Romashkinskoye reservoir (Tatarstan) and separated from reservoir water by mechanical methods. The waterfree crude had a density of 895 g/l, contained ~3.5 wt. % asphaltenes, ~20 wt. % resins, ~0.3 wt. % waxes. The obtained crude oil was stored at room temperature (19–22°C), in the dark, in air, and no special precautions were taken to prevent its possible oxidation. Oil solutions for light scattering studies were prepared with a “chemically pure” grade toluene.



## 2.2. Apparatus and experimental procedure

The dynamic viscosity was measured at 8–32°C, for shear rates up to 150 s<sup>-1</sup>, in a Brookfield Programmable DV-II+ Viscometer. In each experiment a fresh crude oil sample was introduced into the viscometer's cell at room temperature (19–20°C) and was given an individual thermal pre-treatment. The sample preconditioning was conducted at rest for 1 hour at a constant pre-treatment temperature  $T_{pt}$  (15°C to 65°C), followed by cooling to the lowest measurement (flow) temperature (8°C) at the rate of 1–1,5°C per minute. At each measurement temperature  $T_m$ , the system was initially held at rest for 20 min. The tests began at the lowest shear rate and continued 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. This procedure was repeated at new values of  $T_m$ , increased by 2°C increments.

For the optical studies we used oil solutions in toluene with a standard concentration ( $C \approx 0.1$  vol.% of oil). The optical absorption spectra have been measured within 10–15 minutes after preparation of each solution, using a KFK–2 photocolormeter equipped with a set of narrowband light filters (cf. [15]). The absorptivities  $\epsilon$  were calculated by using the Beer–Lambert's law:  $\log(I_0/I) = \epsilon b C$ , where  $I_0$  is the intensity of the light emerging from a reference (toluene) cuvette,  $I$  is the intensity of light emerging from a crude oil solution,  $b$  is the optical path length of cuvettes.

## 2.3. Determination of the activation energies of a viscous flow and of the pour points

In all oil samples a measurable “shear thinning” was registered, characteristic for heavy crudes [6]. The observed dependencies of the shear stress  $\sigma$  on the shear rate  $\dot{\gamma}$  we approximated by the two-parameter Bingham's model [11]:  $\sigma = \sigma_e + \eta_p \dot{\gamma}$ , where  $\sigma_e$  is the apparent yield stress and the constant  $\eta_p$  usually is referred to as the plastic viscosity. In all studied samples, for shear rates exceeding 30–50 s<sup>-1</sup>,  $\eta_p$  practically coincided with the Newtonian dy-

dynamic viscosity  $\eta = \sigma / \dot{\gamma}$ .

It is frequently assumed that above the pour point, the parameters of a crude oil (e.g., its viscosity) follow temperature dependencies, described by Arrhenius-type equations with a constant activation energy  $U$  [12,13]. Accordingly, we calculated the “apparent” Arrhenius activation energies of a viscous flow  $U_{app}$  for the entire temperature range  $T_m = 8\text{--}32^\circ\text{C}$ . As a next approximation, we determined the effects of the measurement temperature on the “current” activation energy  $U(T_m)$ , calculated for consecutive  $2^\circ\text{C}$  intervals of  $T_m$ .

The pour points  $T_{pour}$  of oil samples we determined as temperatures, at which the measured or extrapolated plastic viscosities reached the value of  $10 \text{ Pa}\cdot\text{s}$  (as recommended by the XI’s World Petroleum Congress, London 1983).

### 3. Results and discussion

#### 3.1. Effects of thermal pre-treatment on pour points of crude oil samples

One of the main results of the present studies is that even comparatively small variations of the pre-treatment temperature  $T_{pt}$  may lead to the drastic changes of thermophysical parameters of crude oils, measured at lower temperatures.

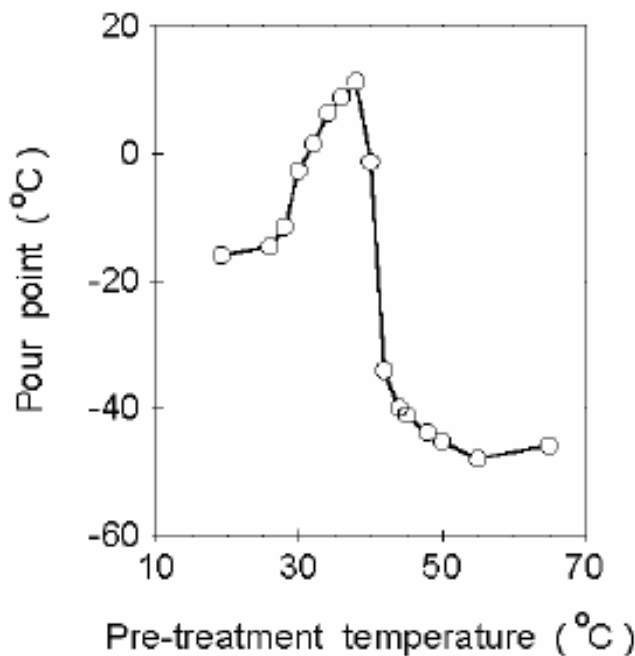


Fig. 1. Effects of the thermal pre-treatment of the crude oil on its pour point.

Fig. 1 shows, that such technologically important parameter as the pour point, dramatically increased from  $-16.2$  to  $+11.2^\circ\text{C}$  after thermal pre-treatment of the studied oil at  $T_{pt}=37.5^\circ\text{C}$ . Such increase of the pour point was quite unexpected, as in conventional technological recommendations heating of crude oils is proposed as a method of decreasing the pour points. Our data, presented in Fig. 1, show that the expected decrease was observed only after thermal pre-treatment at temperatures, higher than  $39\text{--}40^\circ\text{C}$ , while the anomalous increase of  $T_{pour}$  is registered when the pre-treatment temperatures exceed the characteristic value of  $28\text{--}30^\circ\text{C}$ . It should be noted, that the thermally pre-treated crude oil is a strongly nonequilibrium system, so its altered pour point eventually relaxes to its initial value. Slow relaxation of the decreased pour points is a fairly well-known phenomenon in the practice of petroleum industry [14]. In our studies, we have registered sufficiently low relaxation rates for the increased pour points in oil samples, stored at room temperature ( $18\text{--}22^\circ\text{C}$ ). For example, in a sample, pre-treated at  $T_m=37.5^\circ\text{C}$ , after four months of R.T. storage, the altered pour point changed to  $T_{pour}\approx 8^\circ\text{C}$  (i.e. only by about  $3^\circ\text{C}$ ).

Taking into account our previous results [4–6], the anomalous pour point increase in Fig. 1 may be due to the formation in the specific temperature range ( $28\text{--}30^\circ\text{C} < T_{pt} < 39\text{--}40^\circ\text{C}$ ) of structurally ordered oil domains reinforced by asphaltene nanoparticles. At lower temperatures these domains interconnect, forming networks extending over the entire oil volume. The probable mechanism that trigger the observed anomalous effects is a structural phase transition in the asphaltene/resin subsystem of the crude oil [6]. Our optical absorption studies [15] have shown that asphaltenes may form molecular solutions in crude oils only at concentrations  $< 10^{-3}\text{--}10^{-2}$  wt. %. At higher concentrations, the structural unit of the asphaltene disperse phase is evidently a quasispherical “molecular nanocluster” (MNC), which has a diameter of  $1.5\text{--}2$  nm, is composed of four stacked asphaltene monomers (with  $\text{MW}=750\text{--}1000$ ) held together primarily by the  $\pi\text{--}\pi$  and the dipole-

dipole interactions [15]. For the first time, the existence of such structural units has been pointed out by T.F. Yen (cf. [3]). In crude oils, the disperse phase of asphaltenes is stabilised by resins. In the thermally untreated, “annealed” crudes, close to the thermodynamical equilibrium, resins evidently form closely-packed (energetically most favorable) “inert hard shells” around asphaltene MNC’s. Association of MNC’s (e.g. via dipole-dipole interactions) is limited by the steric action of these “shells”.

The effects, initiated at temperatures 28–30°C, may be promoted by a first-order structural phase transition either in the “shells” of resins or in the MNC’s themselves [6,15]. In both cases, the “shells” become less compact, some resin molecules “desorb” into the oil phase, which increases attractive interactions between MNC’s.

As a result, colloid particles start to form more complex aggregates. In asphaltene binary solutions in organic solvents, the aggregates are evidently formed solely by asphaltene MNC’s [15], via the diffusion-limited or the reaction-limited aggregation (cf. [16]). In a multicomponent crude oil, the asphaltene aggregates (in contrast to monomers or non-associated MNC’s) may act as cementing species in the colloid structures formed of microparticles of crystallising saturates (e.g. waxes, provided the oil temperature is below the wax appearance temperature, WAT) [17,18].

By cooling a crude oil below 18–20°C, some newly-acquired properties of the asphaltene/resin subphase may be temporarily conserved in this temperature range. In conditions of a decreased thermal movement, asphaltene/wax aggregates evidently form extended networks, which lead to the dramatic increase of dynamic viscosity, as seen in Fig. 1. At low ambient temperatures such “supercooled” state of the crude oil is certainly unstable but rather long-lived, the ordered structures are only partially broken in a shear flow. However, this non-equilibrium oil phase is easily destroyed by re-heating the sample to temperatures above the asphaltene/resin phase transition (>28–30°C) or, better, above the WAT (39–40°C in the studied crude oil).

### 3.2. Effects of the thermal pre-treatment on the activation energies of a viscous flow

The phase transition, involving asphaltenes, is accompanied by an increase of the apparent Arrhenius activation energy  $U_{app}$ , determined for the entire range of the measurement (flow) temperatures  $T_m=8-30^\circ\text{C}$ .

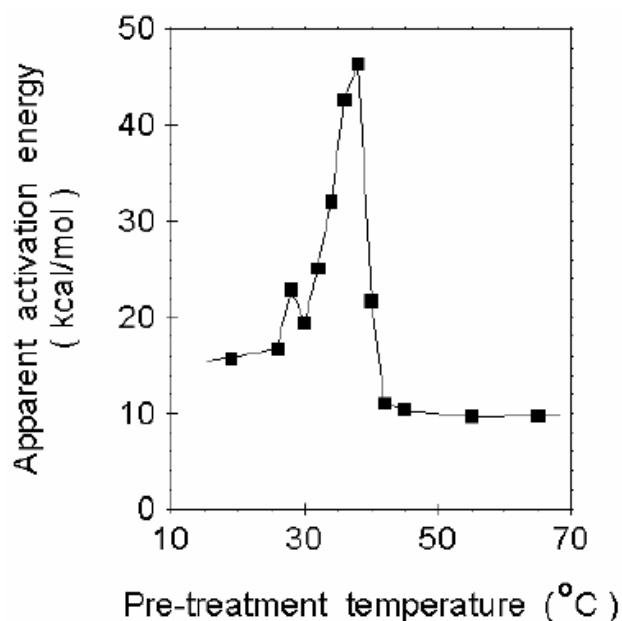


Fig. 2. Effects of the thermal pre-treatment of the crude oil on the apparent activation energy at 8–30°C.

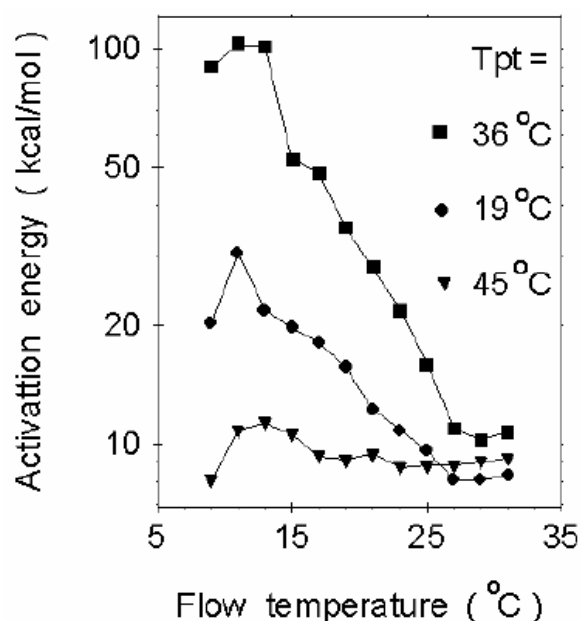


Fig. 3. Variations of the activation energy of the viscous flow in the thermally pretreated oil samples.

Fig. 2 shows that in the oil samples, pre-treated at “moderately warm conditions” ( $T_{pt}=18-26^\circ\text{C}$ )  $U_{app}$  remains fairly constant and close to 16–17 kcal/mol (67–72 kJ/mol), which is within the range of 14–20 kcal/mol, reported by other authors for asphaltene activation/association energies (cf. [3]). After the assumed phase transition in the pre-treated crude oil,  $U_{app}$  increases up to a maximum of to 43–46 kcal/mol (181–193 kJ/mol) at  $T_{pt}=36-38^\circ\text{C}$ . In the samples, preheated to temperatures, exceeding the WAT ( $T_{pt}>39-40^\circ\text{C}$ ),  $U_{app}$  is again decreased to 10–11 kcal/mol (42–46 kJ/mol). The observed variations of  $U_{app}$  are indicative of the formation/destruction of interparticle bonds in the disperse

phase of the crude oil. More detailed information on the magnitude of these bonds may be obtained by the analysis of the “current” activation energies of the viscous flow  $U$ , determined in the narrow ( $2^\circ\text{C}$ ) intervals of the measurement (flow) temperature  $T_m$ .

The dependencies  $U(T_m)$  are shown in Fig. 3 for three oil samples, subjected to different thermal pretreatment:  $T_{pt}=19, 36$  and  $45^\circ\text{C}$ . In the studies of petroleum systems, an Arrhenius activation energy is frequently assumed to be equal to an energy of association of asphaltenes [3]. A more correct procedure appears to be an evaluation of the intermolecular bonds from the changes in  $U$ , as shown by viscosity studies in solutions of coal macromolecules, including asphaltenes [19]. In [19], the removal (by chemical means) of hydrogen bonds and of  $\pi$  interactions decreased activation energies by the values, close to the bond strengths directly determined by IR-spectroscopy [20]. 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 results of Fig. 3 show that, depending on the pre-treatment temperature, different types of bonds may be formed in the crude oil, as indicated by different values of activation energies in samples, cooled to  $10\text{--}13^\circ\text{C}$ . These bonds are evidently removed by re-heating the oil to the temperatures of the assumed phase transition: at  $T_m\approx 28^\circ\text{C}$  the values of  $U$  in all samples decrease to a new level of  $\approx 8.5\text{--}10.5$  kcal/mol ( $\approx 36\text{--}44$  kJ/mol), almost independent on the pre-treatment history of the crude oil. The corresponding changes of  $U$  may be interpreted as the average strengths of the respective bonds. In particular, in samples stored for a long time at room temperature ( $T_{pt}=19^\circ\text{C}$ ), the strength of the bonds is 15–20 kcal/mol (63–84 kJ/mol), typical for noncovalent hydrogen bonding in asphaltene-containing systems [20]. The results of Fig. 3 show, that the above discussed phase transition in the sample, pre-treated at  $T_{pt}=36^\circ\text{C}$ , triggers the formation of bonds with the strengths up to 85–95 kcal/mol (360–400 kJ/mol), indicative of a possible covalent bonding. Namely, this is close to the energies  $\approx 380\text{--}420$  kJ/mol, frequently cited for unactivated CH and CC bonds in organic compounds. Finally, in oil samples, pre-

treated at  $T_{pt}=45^{\circ}\text{C}$ , all types of the above bonds are effectively destroyed, as indicated by a virtually constant activation energy in the studied range of the flow (measurement) temperature.

The observed effect of structural ordering in a heated crude oil strongly resembles the phenomenon of cold crystallisation, extensively studied in solid polymers [21]. Moreover, the specific temperatures, registered in our studies, are close to the temperatures of cold crystallisation in solidified fractions of petroleum bitumen, measured in [22]. Whether such resemblance is due to a common molecular mechanisms, is an open question. The existence of cold crystallisation in crude oils would imply a possibility of uncontrollable spatial phase separation due to small changes of ambient temperatures in a variety of technological processes. In the next section we present preliminary evidence of such phase separation.

### **3.3. Composition stratification in the heated crude oil, studied by optical absorption**

The measurements were conducted in cylindrical glass vessels, 15 mm in diameter, filled to a height of  $\approx 105$  mm with the crude oil. Each oil vessel was introduced in a vertical position into a thermostat at 26, 36 and  $48^{\circ}\text{C}$  for 1.5 hour.

At the end of that period, two 0.5 ml oil samples were collected  $\approx 5$  mm below the oil/air interface and  $\approx 5$  mm above the bottom of the vessel. Each sample was diluted with toluene to the oil concentration of  $\approx 0.1$  vol. %. Optical absorptivities  $\varepsilon$  of oil solutions were measured at  $\lambda=364$  and 670 nm, at room temperature ( $19\text{--}21^{\circ}\text{C}$ ), and were normalised to the value of  $\varepsilon$  for the “lower layer” sample of the oil, heated to  $26^{\circ}\text{C}$ .

The results are presented in Fig. 4. Two top curves and two bottom curves show the effects of temperature on normalised absorptivities of the upper and lower oil layers, respectively. At temperatures of  $26^{\circ}\text{C}$  and  $48^{\circ}\text{C}$  the respective values of  $\varepsilon$  are close to each other, indicating a minor vertical gradient of oil composition. In the crude oil, heated to  $36^{\circ}\text{C}$  (i.e. to the temperature, providing the anomalous pour point increase in Fig. 1), absorptivities of the

upper and lower layers strongly diverge, apparently due to an appearance of a significant concentration gradient (or, possibly, due to some sort of a phase separation in the multicomponent crude). Our studies [15] have shown that an absorptivity of an oil/toluene solution is determined mainly by the concentration of asphaltenes in the original crude oil sample.

Accordingly, the results of Fig. 4 for 36°C indicate that an asphaltene content increased in the lower-density upper oil layers and decreased in the higher-density bottom layers. An unexpected enrichment of upper oil layers with asphaltenes, possessing high molecular weights, may be hypothetically viewed as a result of some sort of flotation.

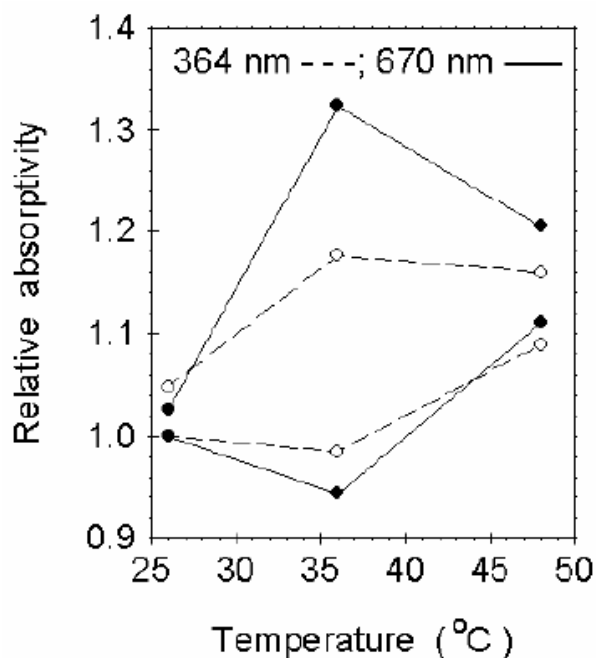


Fig. 4. An apparent phase separation in the heated crude oil, revealed by optical absorption measurements.

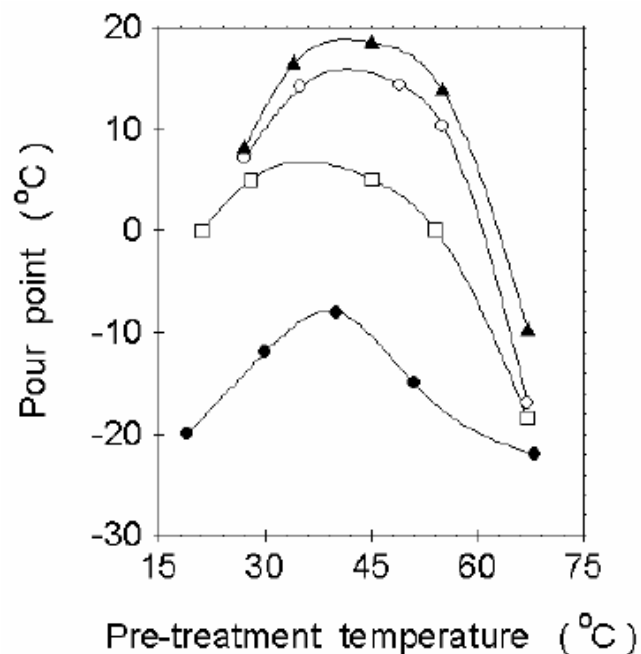


Fig. 5. A common effect of the thermal pre-treatment on pour points of petroleum fluids of various origin (cf. text).

The asphaltene aggregates may be carried to the oil surface by low-density wax crystals. If the above results would be confirmed by further studies, the obvious practical application may be an economical process of de-asphalting of crudes.



### 3.4. Evidence for the observed thermal effects in other studies of petroleum fluids

In line with the definition of asphaltenes as true chemical species (cf. Introduction) and attribution of the observed thermal effects to phase transitions, involving asphaltenes, we concluded that the specific pour point behaviour of Fig. 1 may be a widespread phenomenon, inherent to various asphaltene-containing petroleum fluids, irrespective of their individual composition, geological or geographical origin.

Confirmations of this conclusion have been found by an extensive literature analysis (presently limited to Russian-language publications), including field laboratory reports, reference books, technological recommendations, etc.

Some of the relevant data are presented in Fig. 5. The three curves at the top are reproduced from [23] and show the dependencies of  $T_{pour}$  on the pre-treatment temperatures of three crude oils from: 1) the Zhetibaj reservoir in Kazakhstan (filled triangles); 2) the Koturtepe reservoir in Turkmenistan (open circles); 3) the Kara-Chukhur reservoir in Azerbaijan (open squares).

Filled circles in Fig. 5 show the dependence on  $T_{pt}$  of the pour point of a residual fuel oil (reproduced from [24]). In spite of a low resolution of the data sets in Fig. 5 (10–15°C increments of  $T_{pt}$ ), there is an apparent similarity of these results with our data of Fig. 1. This similarity is not only qualitative (an increase of the pour point in pre-heated fluids), but also quantitative with respect to the specific temperatures  $T_{pt}$ , providing the largest pour points (35–41°C in Fig. 3, as compared to 36–38°C in our studies).

It should be noted, that in the original publications [23, 24] the existence of the discussed thermal effects have not been recognised. The experimental results, reproduced in Fig. 5, obviously have been presented by the authors just as some “excess information” and the anomalous pour point behaviour have not been discussed, or even referred to, in the respective texts.

## 4. Conclusions

Our measurements have shown that even a short-term heating to specific temperatures of 28–39°C may lead to drastic changes of thermophysical properties of crude oils, observed at lower ambient temperatures.

The experimental results indicate also, that the processes at the above specific temperatures may cause a phase separation in the crude oil. A comparison with our previous studies allows to suggest that the specific temperature range is possibly delimited by: 1) the temperature of a structural phase transition in the asphaltene/resin subsystem; 2) the wax appearance temperature. The observed effects require further investigation from the point of view of industrially important applications.

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## Glossary of Some Technical Terms

### A

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abrupt	<i>прил.</i> внезапный, резкий
absorption	<i>сущ.</i> поглощение
absorptivity	<i>сущ.</i> коэффициент поглощения, коэффициент экстинкции; molar~ молярный коэффициент экстинкции
acquire	<i>гл.</i> приобретать
aggregated state	агрегированное состояние; “steady”~ стабильное, равновесное состояние агрегирующей системы
alteration	<i>сущ.</i> изменение, перемена
apparently	<i>нареч.</i> очевидно, явно
association colloids	ассоциативные коллоиды
association state	ассоциированное состояние
assumption	<i>сущ.</i> предположение

### B

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blending	<i>сущ.</i> смешивание
boundary	<i>сущ.</i> граница, контур
brine	<i>сущ.</i> рассол, пластовая минерализованная вода
bulk	<i>прил.</i> объемный

### C

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CMC	<i>аббр.</i> critical micellization concentration – критическая концентрация мицеллообразования, ККМ
coincidence	<i>сущ.</i> совпадение
compatibility	<i>сущ.</i> совместимость
consecutive	<i>прил.</i> последующий
consistent	<i>прил.</i> сообразный, соответствующий, подходящий

## D

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dead crude	«мертвая», «сырая» дегазированная нефть
decisive	<i>прил.</i> имеющий решающее значение
demixing systems	несмешивающиеся, расслаивающиеся системы
derivative	<i>сущ.</i> производная (функции); ~spectrum спектр производной
determination	<i>сущ.</i> установление (границ и т.п.), определенность; coefficient of~ коэффициент множественной регрессии
dilute	<i>гл.</i> растворять, разбавлять; <i>прил.</i> разбавленный
distinct	<i>прил.</i> отличающийся, отчетливый, различный

## E

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emphasize	<i>гл.</i> выделять, особо обращать внимание, подчеркивать
entrapment	<i>сущ.</i> ловушка, захватывание, улавливание; ~of light fractions захватывание и удержание легких фракций нефти
EOR	<i>аббр.</i> enhanced oil recovery – методы увеличения нефтеотдачи, МУН
evidence	<i>[ˈevɪd(ə)ns]</i> <i>сущ.</i> основание, факт, свидетельство, очевидность
evolve	<i>гл.</i> развиваться, эволюционировать, развирываться (о теории)
excess volume	избыточный объем

## F

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facilitate	<i>гл.</i> облегчать, способствовать, оказывать содействие
foreseeable	<i>прил.</i> предвидимый заранее, предсказуемый, обозримый (в будущем)
forthcoming	<i>прил.</i> предстоящий, грядущий, ожидаемый

**H**

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heat capacity                      теплоемкость

**I**

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immiscibility                      *сущ.* расслоение (фаз), несмешиваемость

increment                      *сущ.* приращение, прирост, прибавляемая величина

indigenous                      *прил.* местный, туземный, собственный

inflection                      *сущ.* перегиб (кривой), изгиб, излом

inherent                      *прил.* внутренний (о свойстве), присущий, свойственный

inner                      *прил.* внутренний

instigate                      *гл.* побуждать, провоцировать, инициировать

intentional                      *прил.* преднамеренный, умышленный

interchangeably                      *нареч.* взаимозаменяемо

interpenetrate                      *гл.* взаимно проникать, наполнять собою

intrinsic                      *прил.* подлинный, присущий

IOR                      *аббр.* improved oil recovery – увеличение нефтеотдачи

IR                      *аббр.* infrared – инфракрасный

**L**

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log–log plot                      график в двойных логарифмических координатах

**M**

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merely                      *нареч.* только, попросту, всего лишь, всего-навсего

micellization                      *сущ.* мицеллообразование

**N**

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narrow-band                      *прил.* узкополосный; ~light filters узкополосные светофильтры

neglect                      *гл.* пренебрегать, игнорировать, не учитывать

## O

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opaque	<i>прил.</i> непрозрачный, мутный
overlook	<i>гл.</i> игнорировать, пренебрегать, пропускать, просматривать

## P

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peculiar	<i>прил.</i> особенный, особый, специфический
phase behavior	фазовое поведение; rich~ богатое фазовое многообразие
polarizability	<i>сущ.</i> поляризуемость
polymorphism	<i>сущ.</i> полиморфизм
pour point	температура застывания
precipitation	<i>сущ.</i> выделение, образование твердой фазы в среде жидкой фазы; <i>ср.</i> deposition – выпадение, отложение
precise	<i>прил.</i> определенный, прецизионный, точный
precursor	<i>сущ.</i> предшественник, исходное вещество (материал, реагент)
predominantly	<i>нареч.</i> главным образом, преимущественно
preliminary	<i>прил.</i> предварительный
preserve	<i>гл.</i> сохранять, предохранять
presumable	<i>прил.</i> возможный, предполагаемый

## R

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refraction	<i>сущ.</i> рефракция
refractive index	показатель преломления
resemble	<i>гл.</i> походить, иметь сходство, напоминать
reveal	<i>гл.</i> выявлять, обнаруживать
RT	<i>аббр.</i> room temperature – комнатная температура

## S

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SANS	<i>аббр.</i> small-angle neutron scattering – малоугловое рассеяние нейтронов
saturation	<i>сущ.</i> насыщение
scatter	<i>гл.</i> разбрасывать, рассеивать, рассеиваться

shrinking	<i>сущ.</i> усадка, сжатие, сокращение объема
solidify	<i>гл.</i> застывать, затвердевать, кристаллизоваться
solubility limit	предел растворимости
stirred	<i>прил.</i> взбалмученный, перемешанный
subtle	<i>прил.</i> тонкий, нежный, трудноуловимый
substantial	<i>прил.</i> значительный, крепкий, прочный, существенный
succession	<i>сущ.</i> последовательность, преемственность, ряд
surfactant	<i>сущ.</i> поверхностно-активное вещество, ПАВ

## T

terminate	<i>гл.</i> завершать(ся), истекать
tiny	<i>прил.</i> очень маленький, крошечный, миниатюрный
transfer rate	<i>хим.</i> скорость массообмена, коэффициент массообмена; ~in catalysts porous networks скорость массообмена в пористых катализаторах
transient	<i>прил.</i> переменный, переходный, нестационарный

## U

unattainable	<i>прил.</i> недостижимый, неосуществимый
unfavorable	<i>прил.</i> неблагоприятный, отрицательный
UV	<i>аббр.</i> ultra violet – ультрафиолетовый, УФ; short~ ближний УФ, коротковолновый УФ

## V

vice versa	<i>нареч.</i> наоборот, обратно
vicinity	<i>сущ.</i> близость, соседство, окружающее пространство



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