

## **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 of a viscous flow at 8-30<sup>0</sup>C  $U$ . 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<sup>0</sup>C to 39-40<sup>0</sup>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 water-free 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<sup>0</sup>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<sup>0</sup>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<sup>0</sup>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<sup>0</sup>C to 65<sup>0</sup>C), followed by cooling to the lowest measurement (flow) temperature (8<sup>0</sup>C) at the rate of 1-1,5<sup>0</sup>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<sup>0</sup>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 narrow-band light filters (cf. [15]). The absorptivities  $\varepsilon$  were calculated by using the Beer-Lambert’s law:  $\log(I_0/I) = \varepsilon bC$  , 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 cuvetts.

## 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 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  $T_m = 8-32^0C$ . As a next approximation, we determined the effects of the measurement temperature on the “current” activation energy  $U(T_m)$ , calculated for consecutive 2<sup>0</sup>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 Pa·s (as recommended by the XI’s World Petroleum Congress, London 1983).

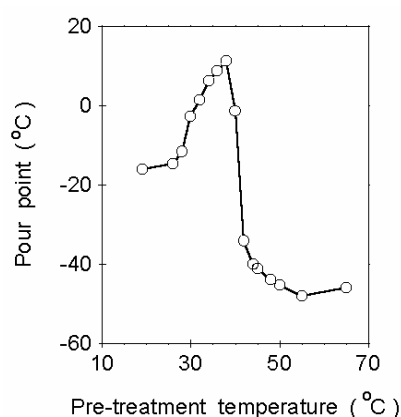
## 3. Results and discussion

### 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 shows, that such technologically important parameter as the pour point, dramatically increased from -16.2 <sup>0</sup>C to +11.2 <sup>0</sup>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  $39-40^{\circ}\text{C}$ , while the anomalous increase of  $T_{pour}$  is registered when the pre-treatment temperatures exceed the characteristic value of  $28-30^{\circ}\text{C}$ . It should be noted, that the thermally pre-treated crude oil is a strongly non-equilibrium 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 ( $18-22^{\circ}\text{C}$ ). 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  $3^{\circ}\text{C}$ ).



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

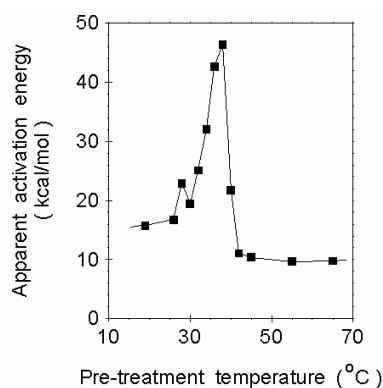
Taking into account our previous results [4-6], the the anomalous pour point increase in Fig. 1 may be due to the formation in the specific temperature range ( $28-30^{\circ}\text{C} < T_{pt} < 39-40^{\circ}\text{C}$ ) of structurally ordered oil domains reinforced by asphaltene nanoparticles. At lower 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  $< 10^{-3}-10^{-2}$  wt. %. At higher concentrations, the structural unit of the asphaltene disperse phase is evidently a quasispherical “molecular

nanocluster” (MNC), which has a diameter of 1.5-2 nm, is composed of four stacked asphaltene monomers (with  $MW=750-1000$ ) held together primarily by the  $\pi-\pi$  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 favourable) “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  $28-30^{\circ}\text{C}$ , 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  $18-20^{\circ}\text{C}$ , 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<sup>0</sup>C) or, better, above the WAT (39-40<sup>0</sup>C in the studied crude oil).

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

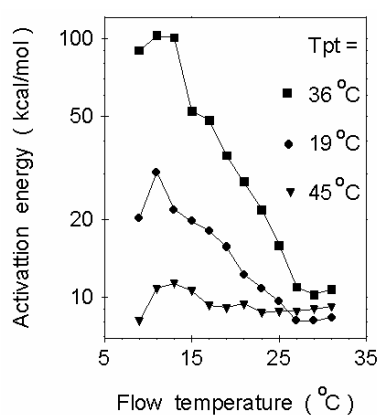
The phase transition, involving asphaltenes, is accompanied by an increase of the apparent Arrhenius activation energy  $U_{app}$ , determined for the entire range of the measurement (flow) temperatures  $T_m=8-30^0C$ .



**Fig. 2.** Effects of the thermal pre-treatment of the crude oil on the apparent activation energy at 8-30<sup>0</sup>C.

Fig. 2 shows that in the oil samples, pre-treated at “moderately warm conditions” ( $T_{pt}=18-26^0C$ )  $U_{app}$  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  $T_{pt}=36-38^0C$ . In the samples, pre-heated to temperatures, exceeding the WAT ( $T_{pt}>39-40^0C$ ),  $U_{app}$  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<sup>0</sup>C) intervals of the measurement (flow) temperature  $T_m$ .



**Fig. 3.** Variations of the activation energy of the viscous flow in the thermally pre-treated oil samples

The dependencies  $U(T_m)$  are shown in Fig. 3 for three oil samples, subjected to different thermal pre-treatment:  $T_{pt}=19, 36$  and  $45^0C$ . 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

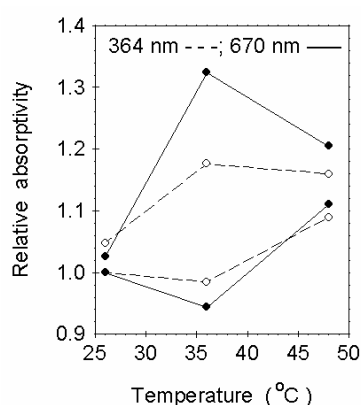
of up to 70 kJ/mol. Our results of Fig. 3 show that, depending on the pre-treatment temperature, different types of bonds may be formed in the crude oil, as indicated by different

values of activation energies in samples, cooled to 10-13<sup>0</sup>C. These bonds are evidently removed by re-heating the oil to the temperatures of the assumed phase transition: at  $T_m \approx 28^0\text{C}$  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 ( $T_{pt}=19^0\text{C}$ ), 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  $T_{pt}=36^0\text{C}$ , 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  $T_{pt}=45^0\text{C}$ , 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<sup>0</sup>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. %.



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

Optical absorptivities  $\epsilon$  of oil solutions were measured at  $\lambda=364$  and 670 nm, at room temperature (19-21<sup>0</sup>C), and were normalised to the value of  $\epsilon$  for the “lower layer” sample of the oil, heated to 26<sup>0</sup>C.

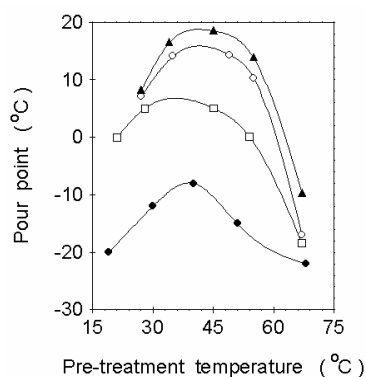
The results are presented in Fig. 4. Two top curves and two bottom curves show the effects of temperature on normalised absorptivities of the upper and lower oil layers, respectively. At temperatures of 26<sup>0</sup>C and 48<sup>0</sup>C the respective values of  $\epsilon$  are close to each other, indicating a minor vertical gradient of oil composition. In the crude oil, heated to 36<sup>0</sup>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. 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 wide-spread 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.



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

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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