

PREPRINT of the paper, published in :

Fluid Phase Equilibria. 2003. V. 212, Iss.1-2. P. 269-278.

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

Igor N. Evdokimov *, Nikolaj Yu. Eliseev, Dmitrij Yu. Eliseev

Department of Physics, Gubkin Russian State University of Oil and Gas, Leninsky

Prospekt, 65, Moscow B-296, GSP-1, 119991, Russia

* Corresponding author. *E-mail address*: physexp@gubkin.ru

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 U at 8-30⁰C. A dramatic increase of both T_{pour} and U was observed in oil samples pre-heated to temperatures in the specific range from 28-30⁰C to 39-40⁰C. 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; Asphaltenes; Aggregation

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. In our recent studies [4-6] we have investigated the rheological and precipitation properties of some “model oils” and have observed thermal anomalies 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 some chemical species. Such definition of asphaltenes is being supported by a constantly increasing number of independent studies [7-9]. Consequently, it may be expected that 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 the heated crude oil.

2. Experimental

2.1. Oil samples

The crude oil was provided by the “TATNEFT” oil production company and used as received. 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 (19-22⁰C), 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 of the crude oil has been investigated at 8-32⁰C , for shear rates up to 150 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 on a new oil sample. A sample was introduced into the viscometer’s cell at room temperature (19-20⁰C) and was given an individual thermal pre-treatment before standard rheological tests. The sample preconditioning was conducted at rest for 1 hour at a constant pre-treatment temperature T_{pt} (15⁰C to 65⁰C), followed by cooling to the lowest measurement (flow) temperature (8⁰C) at the rate of 1-1,5⁰C 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 the measurements continued with a unidirectional cylinder rotation in an ascending-rate order up to the maximum torque limit. At each shear rate the torque and shear stress data were collected for 90-120 s and averaged. The above procedure was repeated at new values of T_m , increased by 2⁰C increments.

Owing to the high absorptivity of the original crude oil, 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 in the wavelengths range $\lambda = 315-750$ nm have been measured using a KFK-2 photocolormeter equipped with a set of narrow-band light filters (cf. [15]). The sample and the reference (toluene) optical cuvettes had the path lengths $b = 5.07$ mm. The measurements of optical absorption were performed within 10-15 minutes after preparation of each oil solution. The absorptivities ε at each wavelength λ were calculated from the measured light intensities by using the Beer-Lambert's law:

$$\log(I_0/I) = \varepsilon b C \quad (1)$$

where I_0 is the intensity of the light emerging from a reference cuvette, I is the intensity of light emerging from a crude oil solution.

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

In all oil samples a measurable "shear thinning" (decrease of viscosity η with increasing shear rate $\dot{\gamma}$) was registered, characteristic for heavy crudes [6].

We have tested several rheological models to describe the observed shear thinning behaviour. For further analysis of temperature effects, the most adequate was found to be a two-parameter model for a Bingham plastic fluid [11]:

$$\sigma = \sigma_e + \eta_p \dot{\gamma} \quad (2)$$

where σ is the shear stress, σ_e is the apparent yield stress and the constant η_p usually is referred to as the plastic viscosity. Fig. 1 illustrates the goodness of fit of eq.(2) in the range of small $\dot{\gamma}$ for flow curves $\sigma(\dot{\gamma})$ measured at 20°C in a sample, stored at 19°C (triangles) and in a sample, pre-treated at 36°C (circles). The presence of the

Bingham's apparent yield stress is clearly seen in both cases. In all studied samples, for shear rates exceeding $30\text{-}50\text{ s}^{-1}$, η_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} in the temperature range $T_m = 8\text{-}32^\circ\text{C}$ by fitting single straight lines to the plots of $\ln(\eta_P)$ vs. the reciprocal measurement temperature $1/T_m$. It was found though, that for oil samples pre-treated at $T_{pt} = 30\text{-}40^\circ\text{C}$ the measured dependencies of $\ln(\eta_P)$ on $1/T_m$ notably deviated from the linear ones. Hence, as a next approximation, we determined the effects of the measurement temperature on the "current" activation energy $U(T_m)$, calculated for consecutive 2°C intervals of T_m .

The pour points T_{pour} of oil samples were 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). Extrapolations were performed by fitting appropriate polynomials (first or second order) to the plots of $\ln(\eta_P)$ vs. $1/T_m$. For some pre-treated samples, the pour points were also determined by a standard technique of an "inclined vessel", which provided the values, differing from the "extrapolated" T_{pour} no more than by $1\text{-}1.5^\circ\text{C}$.

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. For example, as shown in Fig. 2, such technologically important parameter as the pour point, dramatically increases from -16.2°C 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. 2, 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 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 ($18\text{-}22^{\circ}\text{C}$). 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°C).

Taking into account the results of our previous publications [4-6], the nature of the anomalous pour point increase in Fig. 2 may be 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. In the samples, cooled to lower temperatures, these domains interconnect, forming networks extending over the entire oil volume. The probable molecular 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 exist as monomers in crude oils only at concentrations below $\approx 10^{-3}$ wt. %. At somewhat higher

concentrations we observed several distinct extrema of absorptivity, which we attributed to formation of asphaltene dimers, trimers and, finally, tetramers. The latter aggregate, which appears to be stable at still higher concentrations may be described [15] as a quasispherical “molecular nanocluster” (MNC), which has a diameter of 1.5-2 nm, is composed of four stacked asphaltene monomers held together primarily by the π - π and the dipole-dipole interactions. We presume, that these “molecular nanoclusters” are the structural units of more complex aggregates in the asphaltene disperse phase of petroleum fluids. 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 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”. In the framework of the discussed model, the effects, initiated at temperatures 28-30⁰C, 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]. Wax crystallisation and formation of the networks of wax crystallites

is known to be the main cause of the viscosity increase and eventual gelation in crude oils at low temperatures [19]. The propensity of asphaltene aggregates to adsorb on the surfaces of wax particles was demonstrated in recent studies of petroleum emulsions [17,18]. Hence, the dramatic increase of the dynamic viscosity and, consequently, of the pour point, seen in Fig. 2 may be explained by “quenching” of the new wax/asphaltene structures formed in the pre-heated samples. By cooling a crude oil below 18-20⁰C, some newly-acquired properties of the asphaltene/resin subphase may be temporarily conserved in this temperature range. In conditions of a decreased thermal movement wax aggregates, mediated by asphaltenes, may form extended networks, which increases the pour point. 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 (>28-30⁰C) or, better, above the WAT (39-40⁰C in the studied crude oil).

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

The phase transition, involving asphaltenes, is accompanied by a noticeable increase of the apparent Arrhenius activation energy U_{app} , determined for the entire range of the measurement (flow) temperatures $T_m=8-30^0\text{C}$. The data, presented in Fig. 3, show that in the oil samples, pre-treated at “moderately warm conditions” ($T_{pt}=18-26^0\text{C}$) 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, pre-heated 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 studied crude oil. More detailed information on the magnitude of these bonds may be obtained by analysis of the “current” activation energies of the viscous flow U , determined in the narrow (2°C) intervals of the measurement (flow) temperature T_m .

The dependencies $U(T_m)$ are shown in Fig. 4 for three oil samples, subjected to different thermal pre-treatment: $T_{pt}=19, 36$ and 45°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 strength of intermolecular bonds from the *changes* in U , as has been shown by viscosity studies in solutions of coal macromolecules, including asphaltenes [20]. In [20], the removal (by chemical means) of hydrogen bonds and of π interactions decreased activation energies by the values, close to the bond strengths directly determined by IR-spectroscopy [21]. 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. 4 show that, depending on the temperature of the thermal pre-treatment, different types of bonds may be formed in the crude oil, as indicated by different values of activation energies measured in samples, cooled to $10-13^{\circ}\text{C}$. 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 activation energies in all samples decrease to a new level of $\approx 8.5-10.5$ kcal/mol ($\approx 36-44$ kJ/mol), almost independent on the pre-treatment history of the crude oil samples. 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 bonding in asphaltene-containing systems [21]. The results of Fig. 4 show, that the above discussed phase transition in the sample, pre-treated at $T_{pt}=36^{\circ}\text{C}$, triggers the formation of the 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 [22]. Moreover, the specific temperatures, registered in our studies, are close to the temperatures of cold crystallisation in solidified fractions of petroleum bitumen, measured in [23]. 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 ≈ 105 mm with the studied crude oil. Each oil vessel was introduced in a vertical position into a thermostat at 26, 36 and 48°C for 1.5 hour. At the end of that period, two 0.5 ml samples oil were collected from the upper and the

lower oil layers (≈ 5 mm below the oil/air interface and ≈ 5 mm above the bottom of the vessel). Each sample was diluted with toluene to the same oil concentration of ≈ 0.1 vol. %. Optical absorptivities ε of all oil solutions were measured at $\lambda=364$ and 670 nm, at room temperature ($19-21^{\circ}\text{C}$), and were normalised to the value of ε for the “lower layer” sample of the oil, heated to 26°C . The results of the optical absorption studies are shown in Fig. 5. 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°C and 48°C the respective values of ε are close to each other, indicating a minor vertical gradient of oil composition. In the crude oil, heated to 36°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 previous 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. Accordingly, the results of Fig. 5 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 enrichment of upper oil layers with asphaltenes was certainly unexpected, knowing that the density of solid asphaltenes is ≈ 1.1 g/cm³ [24], considerably higher than the bulk density of the studied crude oil (0.895 g/cm³). Such enrichment may be hypothetically viewed as a result of some sort of flotation. The asphaltene aggregates may be carried to the oil surface by the wax crystals of comparatively low density (not higher than 0.8 g/cm³ close to the melting point [25]). 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 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. 2 may be a wide-spread phenomenon, inherent to various asphaltene-containing petroleum fluids, irrespective of their individual composition, geological or geographical origin. Independent 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. 6. The three curves at the top are reproduced from [25] and show the dependencies of pour points 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. 6 show the dependence on T_{pt} of the pour point of a residual fuel oil (reproduced from [26]).

In spite of a low resolution of the data sets in Fig. 6 (10-15⁰C increments of T_{pt}), there is an apparent similarity of these results with our data of Fig. 2. 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 (35-41⁰C in Fig. 6, as compared to 36-38⁰C in our studies). It should be noted, that in the original publications [25, 26] the existence of the discussed thermal effects have not been recognised. The experimental results, reproduced in Fig. 6, 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 28-39⁰C 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.

List of symbols and abbreviations

b	optical path length in Eq. (1)
I	intensity of light emerging from a crude oil solution in Eq. (1)
I_0	intensity of light emerging from a reference cuvette in Eq. (1)
MNC	molecular nanocluster
MW	molecular weight (g/mol)
R.T.	room temperature
T_{pt}	oil pre-treatment temperature
T_m	measurement temperature
T_{pour}	pour point
U_{app}	apparent activation energy for the temperature range of 8-32 ⁰ C
U	current activation energy for 2 ⁰ C temperature intervals
WAT	wax appearance temperature
ε	optical absorptivity
$\dot{\gamma}$	shear rate
η	dynamic viscosity
η_p	“plastic viscosity” in the Bingham’s model, Eq. (2)
λ	light wavelength
σ	shear stress
σ_e	apparent yield stress in the Bingham’s model, Eq. (2)

Acknowledgements

This study has been financially supported in part by the Foundation for Fundamental Research of the “GASPROM” company (Grant no. 540-01.3.5). The authors are grateful to B.R. Akhmetov for conducting the scattering experiments.

References

- [1] Y.-F. Hu, T.-M. Guo, *Fluid Phase Equilib.* 192 (2001) 13–25.
- [2] Y.F. Hu, G.J. Chen, J.T. Yang, T.M. Guo, *Fluid Phase Equilib.* 171 (2000) 181–194.
- [3] G.K. Wong, T.F. Yen, *J. Petrol. Sci. Eng.* 28 (2000) 55–64.
- [4] I.N. Evdokimov, N.Yu. Eliseev, *Chemistry and Technology of Fuels and Oils.* 35(6) (1999) 377-381.
- [5] I.N. Evdokimov, N.Yu. Eliseev, *Nauka i Tehnologiya Uglevodorodov* 1 (2000) 52-56. [In Russian]
- [6] I.N. Evdokimov, N.Yu. Eliseev, D.Yu. Eliseev, *J. Petrol. Sci. Eng.* 30(3/4) (2001) 199-211.
- [7] E.Y. Sheu, *Energy & Fuels* 16 (2002) 74-82.
- [8] A. Sharma, H. Groenzin, A. Tomita, O.C. Mullins, *Energy & Fuels* 16 (2002) 490-496.
- [9] H. Groenzin, O.C. Mullins, *Petrol. Sci. and Technology* 19(1/2) (2001) 219-230.
- [10] I.K. Yudin, M.A. Anisimov, V.A. Agayan, V.I. Kosov, G.L. Nikolaenko, J. Sengers, *Int. J. Thermophys.* 18 (1997) 1237-1248.
- [11] H.A. Barnes, J.F. Hutton, K. Walters, *An Introduction to Rheology*, Elsevier, Amsterdam, 1997, 200 p.
- [12] A. Werner, J.C. de Hemptinne, F. Behar, E. Behar, C. Boned, *Fluid Phase Equilib.* 147, (1998) 319–341
- [13] A. Werner, F. Behar, J.C. de Hemptinne, E. Behar, *Fluid Phase Equilib.* 147 (1998) 343–356.

- [14] V.V. Devlikamov, Z.A. Khabibullin, M.M. Kabirov, *Anomalous Crude Oils*, Nedra, Moscow, 1975, 168 p. [In Russian]
- [15] I.N. Evdokimov, N.Yu. Eliseev, B.R. Akhmetov, *J. Petrol. Sci. Eng.* 37 (2003) 135-143; I.N. Evdokimov, N.Yu. Eliseev, B.R. Akhmetov, *J. Petrol. Sci. Eng.* 37 (2003) 145-152.
- [16] I.K. Yudin, G.L. Nikolaenko, E.E. Gorodetskii, E.L. Markhashov, V.A. Agayan, M.A. Anisimov, J.V. Sengers, *Physica A* 251 (1998) 235-244.
- [17] M.F. Ali, M.H. Alqam, *Fuel* 79 (2000) 1309–1316.
- [18] M.A. Khadim, M.A. Sarbar, *J. Petrol. Sci. Eng.* 23 (1999) 213–221.
- [19] K.S. Pedersen,†H.P. Rønningsen, *Energy & Fuels* 14 (2000) 43-51.
- [20] K. Norinaga, M. Kuniya, M. Iino, *Energy & Fuels* 16 (2002) 62-68.
- [21] K. Miura, K. Mae, I. Hasegawa et. al., *Energy & Fuels* 16 (2002) 23-31.
- [22] H.H. Chuah, *Macromolecules* 34 (2001) 6985-6993.
- [23] J.-F. Masson, G.M. Polomark, P. Collins, *Energy & Fuels* 16 (2002) 470-476.
- [24] Y. Bouhadda, D. Bendedouch, E. Sheu, A. Krallafa, *Energy & Fuels* 14 (2000) 845-853.
- [25] R.Z. Safieva *Physicochemistry of Petroleum*, Chimija, Moscow, 1998, 448 p. [In Russian]
- [26] I.G. Anisimov et. al., *Fuels, Lubricants, Technical Liquids. Nomenclature and Applications (Reference Book)*, 2nd edition, Techninform, Moscow, 1999, 596 p. [In Russian]

Figures.

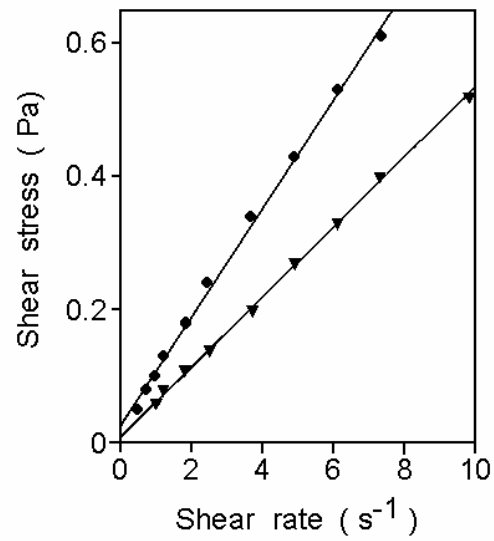


Fig. 1. Flow curves measured at 20°C in a sample of the crude oil, stored at 19°C (triangles) and in a sample, pre-treated at 36°C (circles). Straight lines are Bingham's approximations (eq. 2).

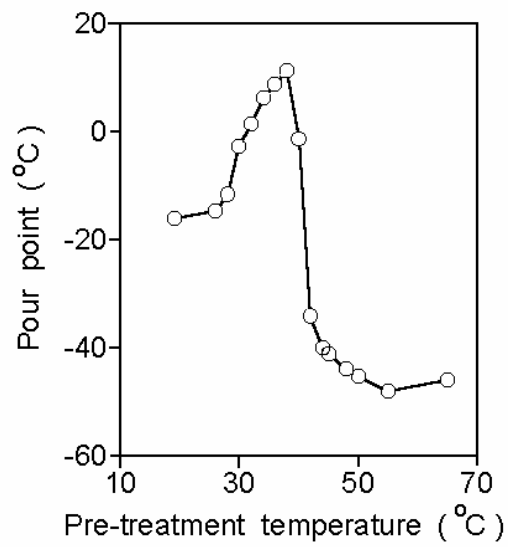


Fig. 2. Effects of the thermal pre-treatment of the crude oil on its pour point.

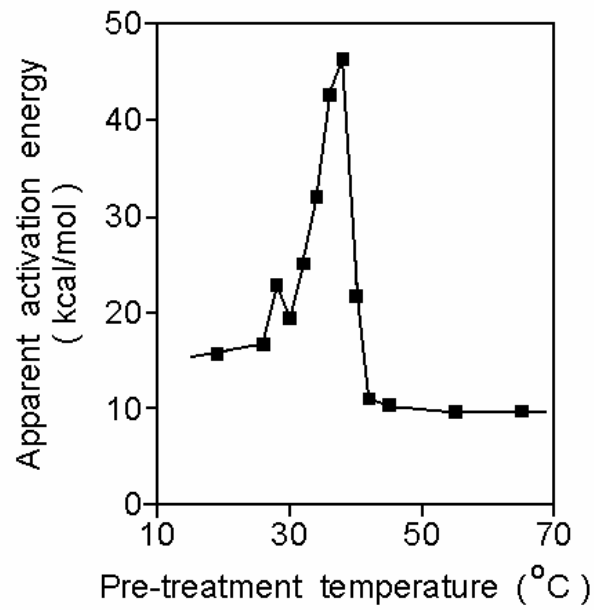


Fig. 3. Effects of the thermal pre-treatment of the crude oil on the apparent activation energy at 8-30°C.

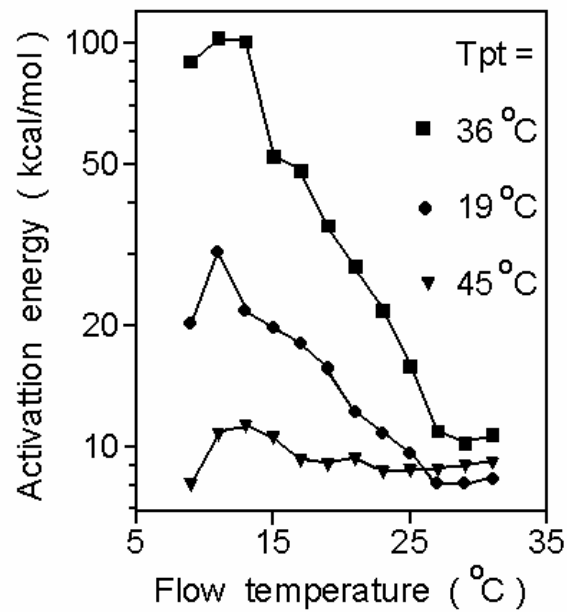


Fig. 4. Variations of the activation energy of the viscous flow in the thermally pre-treated oil samples

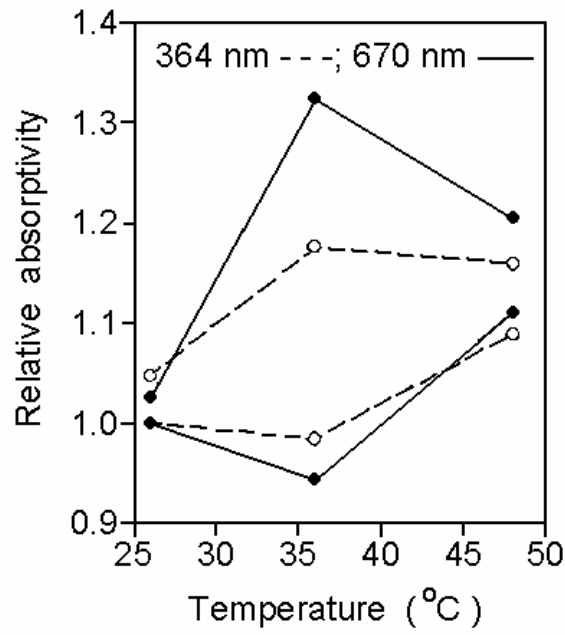


Fig. 5. An apparent phase separation in the heated crude oil, revealed by optical absorption measurements

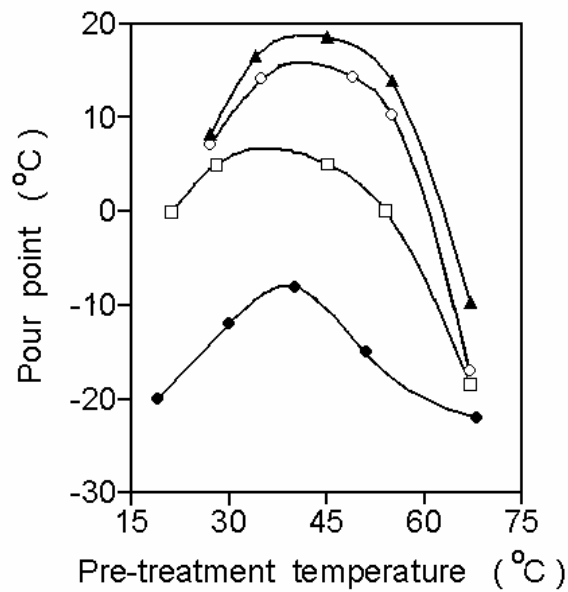


Fig. 6. A common effect of the thermal pre-treatment on pour points of petroleum fluids of various origin (cf. text).