Rheological properties of crude oils in Yaregskoye and Yaraktinskoye oil fields

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Abstract. Rotary viscometer tests of crude oil with a high content of resins and asphaltenes (Yaregskoye oil field) and crude oil with high paraffin content (Yaraktinskoye oil field) have been conducted. The typical flow curves for these oil types have been plotted. It has been detected that these oils are non-Newtonian fluids, viscosity of which is dependent on shear rate. Based on Arrhenius-Eyring equation, calculations of viscous flow activation energy and complex structural unit (CSU) sizes have been performed. It has been stated that there is a tenfold reduction in CSU size in asphaltic crude oil with the increase in shear rate in a rotary viscometer, while particle size in paraffinic crude oil does not essentially change under the same hydrodynamic conditions.

1. Introduction

For the extraction and the pipeline transport of crude oils with anomalous properties, detailed information about the features of its rheological behavior at different shear stresses in a predetermined temperature range is required. Non-Newtonian properties are typically discovered in high-viscosity oils with a high content of asphaltenes, resins and paraffins. As the study objects, crude oils with a high content of resins and asphaltenes (Yaregskoye oil field) and crude oils with high paraffin content (Yaraktinskoye oil field) were used. The typical flow curves for the shear stress (τ) versus shear rate (γ) dependence obtained by rotary viscometry method are presented in figures 1, 3.

2. Materials and Methods

Crude oil with high resin and asphaltene content (figure 1) has a pseudoplastic properties (flow index is in the range 0 <n <1) and analytically can be described by Oswald de Ville equations $\tau = K \cdot \gamma^n$ and $\eta_{eff} = K \cdot \gamma^{n-1}$. The effective viscosity of that oil ($\eta_{eff.}$) decreases with increasing shear rate, which is particularly noticeable at low values of γ <50 s^{-1}. There is the largest destruction of supramolecular structures in this range. A further increase in shear stress has little effect on the rheological properties of oil, which becomes essentially a Newtonian fluid with a viscosity depending only on the temperature.

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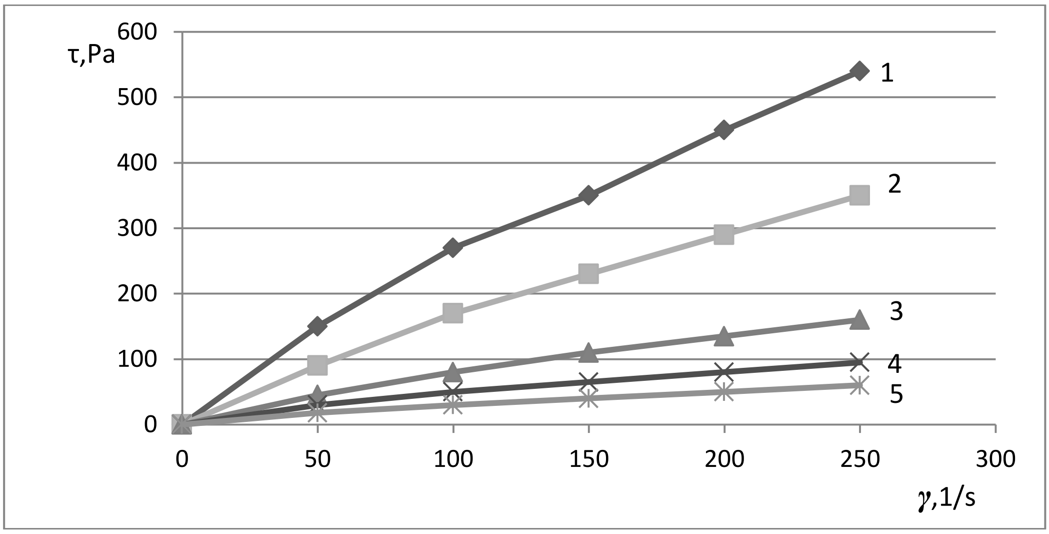

Figure 1. Shear stress (τ) versus shear rate (γ) dependence at different temperatures: 1 – 298K, 2 – 303K, 3 – 313K, 4 – 323K, 5 – 333K, crude oil in Yaregskoye oil field

Asphaltic crude oil in Yaregskoye oil field has thixotropic properties. The hysteresis loop for this oil (figure 2) is obtained by the sequential increase, followed by the reduction of the shear rate during its testing in a rotary viscometer. Thixotropy, depending on the rate of deformation of the material and duration of an external force effect, is the result of mechanical destruction of supramolecular structures (agglomerates and associates) which are present in high-viscosity oils. Restructuration occurs along with the structure destruction. At a certain point the speed of deformation can be equal to the speed of structure formation. Thereby, the equilibrium state is achieved, which is characterized by a definite value of the effective viscosity. As follows from figure 2, the disappearance of the hysteresis loop occurs at a shear rate higher than $\gamma \sim 30\ s^{-1}$, which, in its turn, indicates that oil losses anomalous properties immediately at low shear stress range due to the almost complete destruction of supramolecular structures.

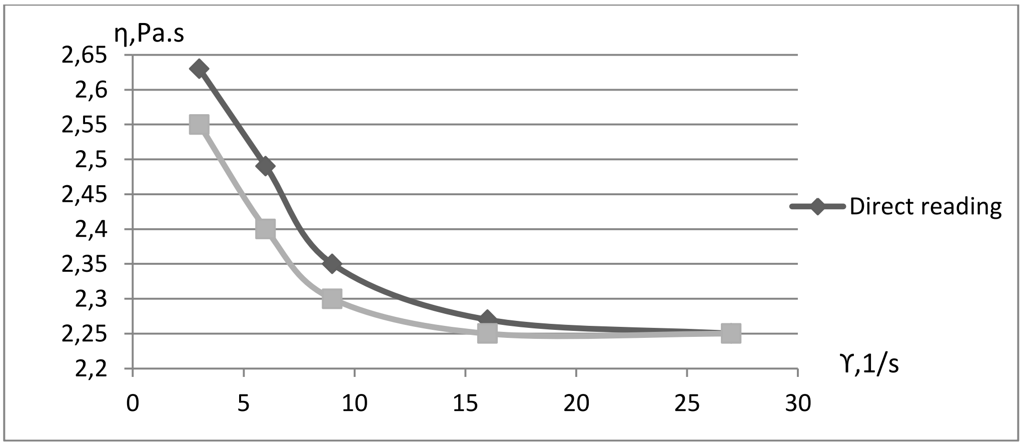

Figure 2. Dynamic viscosity (η) versus shear rate (γ) dependence at the temperature of 298K, crude oil in Yaregskoye oil field

Paraffinic crude oil in Yaraktinskoye oil field is a viscous-plastic fluid (figure 3), which has a yield point (τ_0) at temperature below 263 K. The rheological properties of this oil are described by the equations, which are deduced based on the rheological Bingham - Shvedova model $\tau = \tau_0 + K \cdot \gamma^n$

and $\eta_{eff} = \frac{\tau - \tau_0}{\gamma} = K \cdot \gamma^{n-1}$. The yield point distinguished in oils at low temperatures is due to the formation of volumetric massive frame structure from paraffin microcrystals, which is destroyed when the temperature rises because of thermal motion [1], and subsequently, oil becomes a pseudo-plastic fluid. When the temperature is within the yield point, crude oils of Yaraktinskoye oil field also reveal thixotropic properties.

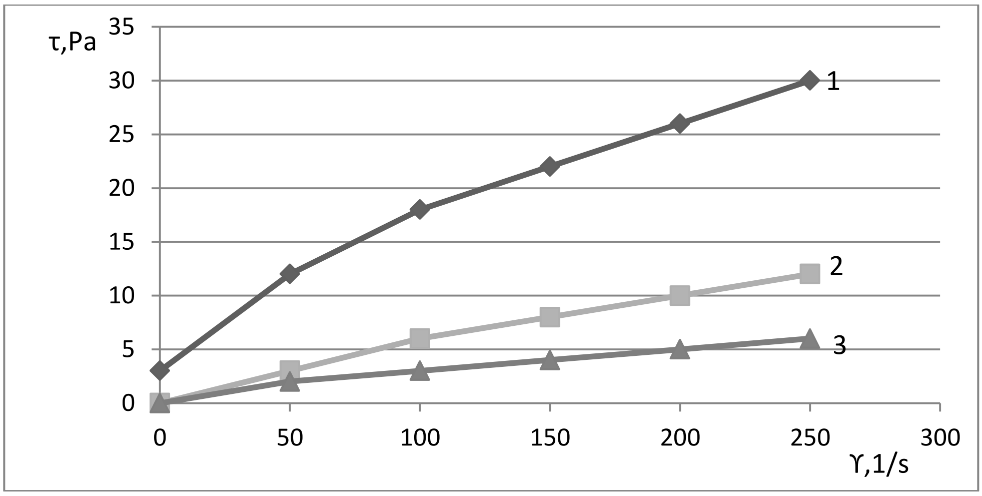

Figure 3. Shear stress (τ) versus shear rate (γ) dependence at different temperatures: 1 – 248K, 2 – 263K, 3 – 283K, crude oil in Yaraktinskoye oil field

3. Results and Discussion

The formal rheological Oswald de Ville and Bingham-Shvedova equations describe the dependence of viscosity on the shear rate only, but does not explicitly consider the temperature effect, which, in turn, makes it difficult to understand the physical nature of the processes occurring in the system at the molecular level. Therefore, under these conditions the search for other ways of analytical interpretation of the rheological properties of oil is reasonable. Using Arrhenius-Eyring equation $\eta = A \cdot e^{\frac{E_a}{RT}}$ for analytical description of the properties of liquids in a wide temperature range can determine the energy and geometric parameters of oil particles for different shear stresses. By analyzing the results of viscometric experiments with the coordinates lnη - 1/T (figures 4, 5), the values of viscous flow activation energy (Ea), pre-exponential factor (A) and average particle size (r), in different hydrodynamic conditions can be identified (table 1, 2).

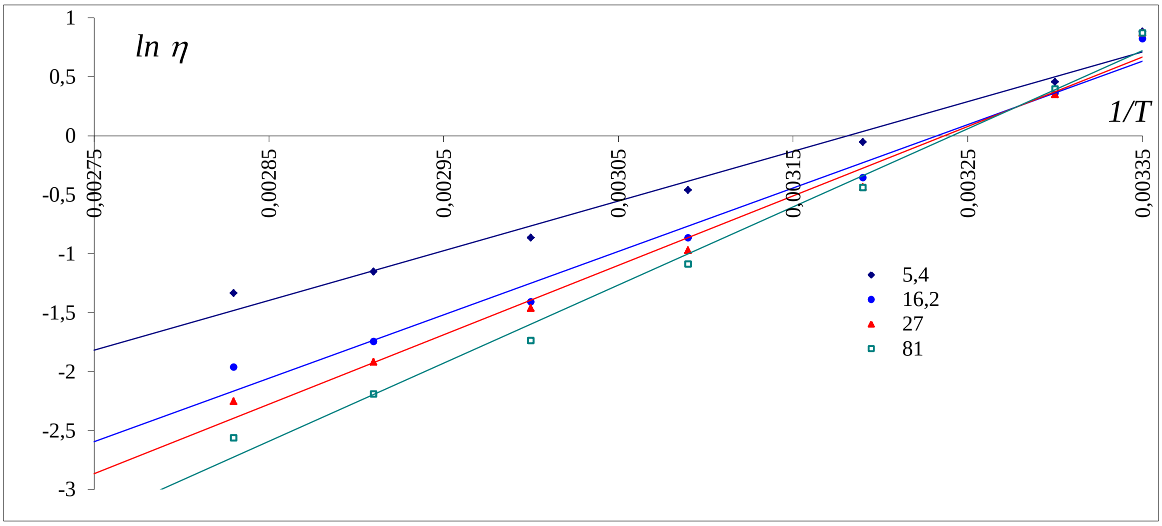

Figure 4. lnη viscosity versus inverse temperature (1/T) dependence, asphaltic crude oil

As follows from figures 4 and 5, the tangents of curve inclination angles are proportional to the activation energy of viscous flow (Ea), and they increase with increasing shear rate in case of Yarega (asphaltic) crude oil, whereas they remain practically constant considering crude oil (paraffinic) of Yaraktinskoye oil field. Average radii of colloidal dispersed associates shown in tables 1 and 2 were calculated according to the formula $r = \left[\frac{A}{\tau \cdot (16\pi\rho / 3kT)^{1/2}}\right]^{2/5}$ after experimental determination of the numerical values of the pre-exponential factor (A), which according to Frenkel-Eyring equation is dependent on the geometric dimensions of complex structural units (CSU) varying in structure due to oil composition.

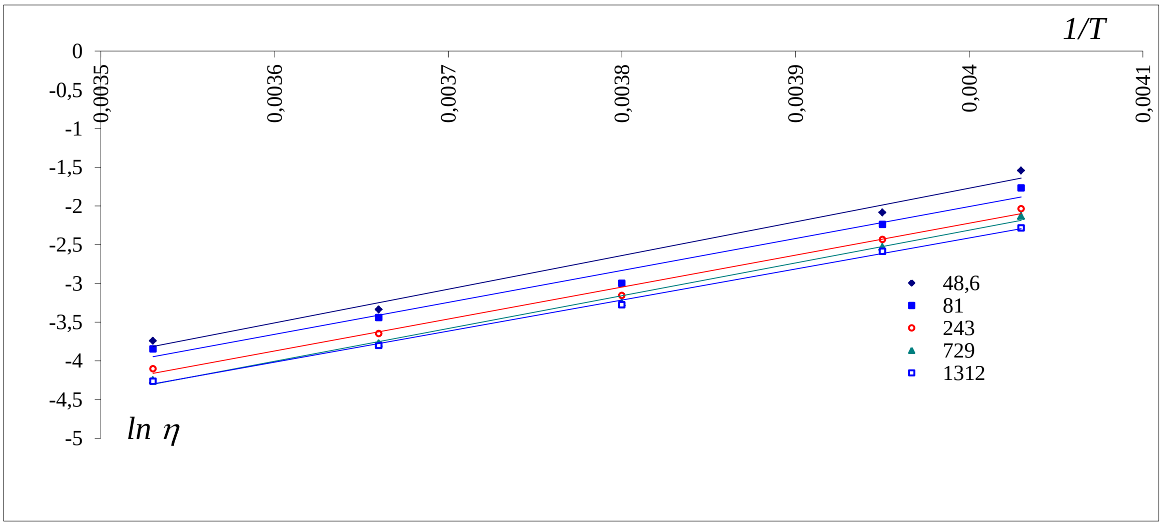

Figure 5. lnη viscosity versus inverse temperature (1/T) dependence, paraffinic crude oil

According to modern concepts, crude oil is not a simple mixture of a large number of organic compounds dispersed to the molecular state, but it is a colloidal dispersion system [2]. The intermolecular forces in this system can form supramolecular associates, composed of many individual molecules which are arranged in ordered structures. The composition and size of CSU depend on relative content of paraffin molecules in the oil or the total amount of resin and asphaltene molecules. The dominance of a certain class of chemical compounds results in particular rheological behavior of crude oil.

The central nucleus of a complex structural unit (CSU) formed in asphaltic crude oil is composed of a large number of high and polycyclic asphaltenes which are bound together in an aggregate due to weak intermolecular interaction. Resin molecules are less connected to each other at the periphery of the nucleus in the solvate-adsorption layer. CSU nucleus formed in paraffinic crude oil contains a great number of high molecular chain alkanes (paraffins), which are tightly packed together. Resin molecules in the solvate-adsorption membrane (periphery of the nucleus) being weakly bound to the nucleus, diffusive scattering of the membrane occurs with a shift of particles due to movement which results in the decrease in CSU size to a constant value characteristic of a competent paraffin nucleus.

Table 1. Activation energy (E_a), pre-exponential value (A) and average particle radius (r) of asphaltic crude oil at various shear rates (γ).

Parameters	Shear rates γ, s^{-1}			
	5.4	16.2	48.6	145.8
E_a, kJ/mol·K	30.6	37.2	45.1	51.3
$A \cdot 10^8$, Pa.s	715	41.4	1.8	0.2
r, nm	47.8	10.9	1.9	1.1

The results in table 1 indicate that asphaltic crude oil associates in Yaregskoye field are highly susceptible to the destructive influence of the shear flow. Their mean radii in low shear rate range decrease from the colloidal particle size (~ 50 nm) to values close to the molecular size (~ 1 nm). Stronger particles (paraffin microcrystals) of oil in Yaraktinskoye field (table 2) almost do not reduce their dimensions in the wide range of shear rates.

Table 2. Activation energy (E_a), pre-exponential value (A) and average particle radius (r) of paraffinic crude oil at various shear rates (γ).

Parameters	Shear rates γ, s^{-1}			
	48.6	81.0	146	243
E_a, kJ/mol·K	36.2	34.3	33.6	34.3
$A \cdot 10^8$, Pa·s	0.47	0.9	1.1	0.73
r, nm	4.5	4.9	4.4	3.1

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