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## Structural and Mechanical Properties of Oils from the Muradkhanly and Sangachal-deniz Fields of Azerbaijan

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### Highlights

- The rheological properties of oil from the Muradkhanly and Sangachal-deniz fields were studied.
- Thermodynamic and rheological characteristics of viscous flow in oil, were studied.
- The results are applicable in the transport of non-Newtonian oils with viscoplastic properties.

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properties

### Abstract

In the range of 278-293 K, the structural-mechanical properties of high-viscosity asphaltene-resinous and highly solidifying paraffinic oils of the Muradkhanly and Sangachal-deniz fields of Azerbaijan, which exhibit abnormal viscosity at various shear rates and are characterized by non-Newtonian, viscoplastic and thixotropic properties, have been studied. According to the Eyring-Frenkel equation, the activation energies of the viscous flow  $E_a$  and the change in the entropy  $\Delta S$  of these oils are calculated for the indicated temperature range. Various algorithms for estimating the thermodynamic parameters of the flow  $\Delta H$  and  $\Delta S$  published in the literature are analyzed, and the scatter of the values of the estimates of parallel calculations is shown. It is shown that with a decrease in temperature, phase transitions in oils are activated, in particular, for the highly solidifying paraffin oil Sangachal-deniz, it originates from 297 K. For the oils under consideration for the selected shear rate of  $64 \text{ s}^{-1}$ , the values of the temperature of the beginning of structure formation, static and limiting dynamic shear stresses were determined: for Muradkhanly oil  $T = 282.83 \text{ K}$ , Sangachal-deniz -  $T = 297.23 \text{ K}$ . The results obtained can be used to predict the behavior of oils.

## 1. INTRODUCTION

Over the past two decades, due to the depletion of light oil reserves in the world, there has been an increase in interest in hard-to-recover, high-viscosity and paraffinic oils. The collection and transport of such oils poses a number of technical problems for oilmen, the solution of which requires the regulation of their rheological properties. When developing methods for extracting and transporting oil, it is necessary to take into account its chemical composition and physical properties. Colloidal nature, structure. Determining the patterns of changes in physical and chemical properties, rheological features of heavy, viscous oils, taking into account the component composition of oil, on which its physical, chemical and rheological properties depend, can be used to increase the efficiency of their production, select the most rational technologies for enhanced oil recovery, transportation, processing and storage. The study of the component composition and physical, chemical properties of oil serves as the basis for optimizing the conditions for oil production, transportation and storage. Therefore, the problems of preventing the formation of asphalt-resin-paraffin deposits (ARPD) and regulating the rheological properties of viscous oils for its transport are still relevant. The formation of supramolecular structures in petroleum dispersed systems, for example, with a significant content of resinous-asphaltene substances (RAS), occurs on the basis of an asphaltene core, which is a layered pack-like associate of polyaromatic structures and a solvate shell consisting of molecules of tar-paraffin components [1,2]. The degree of structuring and mechanical strength of colloidal particles of such

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oils, as well as the nature of the change in properties depending on temperature, are determined to a large extent by the chemical composition and structure of these high-molecular components. At low temperatures and high concentrations of RAS in high-viscosity oils, or a high content of paraffinic hydrocarbons in oils, sharp changes in their rheological properties with temperature can be observed, as a result of which the transportation of such oils is complicated. Obviously, studies of the viscosity-temperature properties of oils of different types, exhibiting non-Newtonian properties, are aimed at finding ways for efficient transport of oils [3].

This paper presents the results of experimental studies of the rheological properties of a number of oils from the Muradkhanly and Sangachal-deniz fields of Azerbaijan and processing of the obtained data based on the activation theory of the Frenkel-Eyring flow, taking into account intermolecular interactions in oils.

## 2. MATERIALS AND METHODS

The composition and some physico-chemical parameters of the studied samples of oils from the Muradkhanly and Sangachal-deniz fields of Azerbaijan are shown in Table 1.

**Table 1.** Physical and chemical parameters of oil samples from the Muradkhanly and Sangachal-deniz fields of Azerbaijan [4]

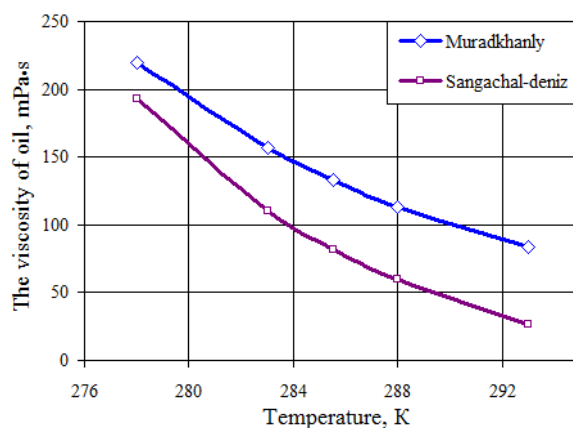
№	Type of oil	Density, g/cm <sup>3</sup> at 293 K	Kinematic viscosity mm <sup>2</sup> /s	Pour point, T, K	Content, % mass		
					Paraffins	Asphaltenes	Resins
1	Muradkhanly	0.923	83.5	275	2.06	4.1 - 8.0	12.4
2	Sangachal-Deniz	0.879	27.3	292	9.3	0.35	8.96

The viscosity of oil samples, its dependence on shear rate and temperature were measured using a Reotest-2, Russia viscometer, Particle size and particle size distribution were determined on an LB-550 analyzer from Horiba, Japan. The analyzer used makes it possible to register particle sizes from 0.001 to 6  $\mu\text{m}$ , to study the dependence of the size and diffusion coefficient of particles on the measurement temperature of samples in the range of 278-343 K.

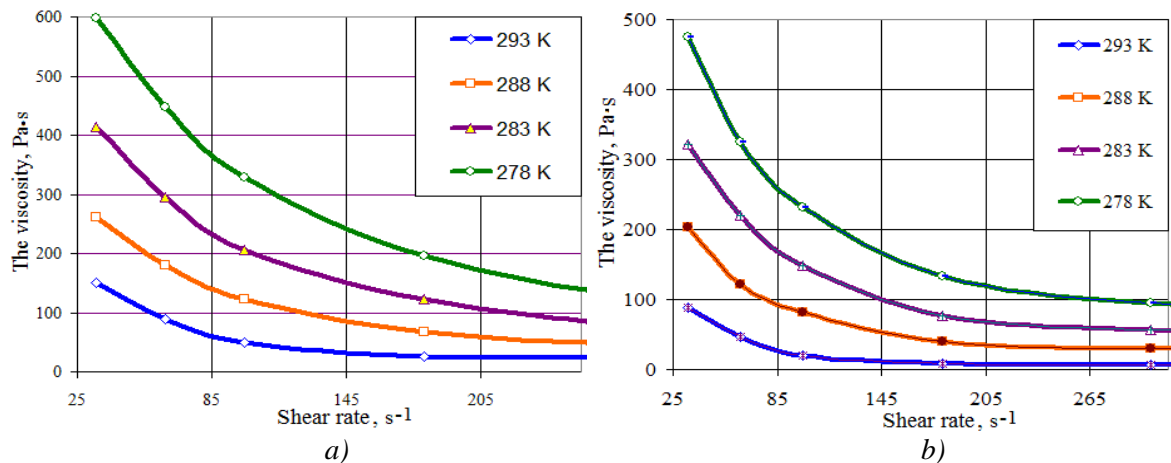
Before measurements, oil samples were dehydrated at room temperature mechanically, mixed until homogeneous; mixtures were also prepared from them.

## 3. THE RESEARCH FINDINGS AND DISCUSSION

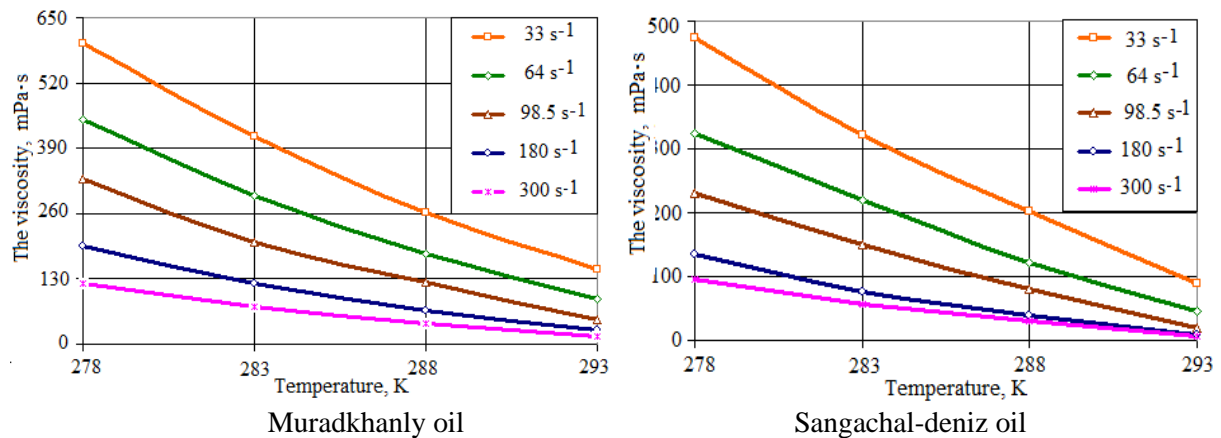
Figures 1, 2 and 3 show the dependences of the viscosity of the studied oils on temperature and shear rate in the studied temperature range.



**Figure 1.** Dependences of the viscosity of oil samples from the Muradkhanly and Sangachal-deniz fields on temperature in the interval 278-293K



**Figure 2.** Dependences of the viscosity of oil samples from the Muradkhanly (a) and Sangachal-deniz (b) fields on the shear rate in the interval 278-293K



**Figure 3.** Dependences of the viscosity of Muradkhanly and Sangachal-deniz oil samples on temperature at different shear rates

To describe the viscous flow rheology of the oils under consideration at a temperature of 298 K Newton, Shvedov-Bingham and Herschel-Bulkley models were used [5,6]. Comparative results of the description by these models, given in Table 2, show that the Herschel-Bulkley model gives the highest accuracy of description.

**Table 2.** Comparative data of rheological models of oil flow from the Muradkhanly and Sangachal-deniz fields at a temperature of 298 K

Type of oil	Rheological equations* of oil flow models at T = 298		
	Newton model	Shvedov-Bingham model	Herschel-Bulkley model
Muradkhanly oil	$\tau = 52.13 \cdot \dot{\gamma}$	$\tau = 7501.1 + 27.66 \cdot \dot{\gamma}$	$\tau = 6481.1 + 4971.2 \cdot \dot{\gamma}^{0.48801}$
Determination coefficient $R^2$	$R^2 = 0.684$	$R^2 = 0.971$	$R^2 = 0.998$
Oil Sangachal-deniz	$\tau = 41.27 \cdot \dot{\gamma}$	$\tau = 6076.2 + 17.01 \cdot \dot{\gamma}$	$\tau = 5124.3 + 1001.91 \cdot \dot{\gamma}^{0.0341}$
Determination coefficient $R^2$	$R^2 = 0.713$	$R^2 = 0.969$	$R^2 = 0.996$

\*  $\tau$  – shear stress, in Pa;  $\dot{\gamma}$  – is the shear rate, in  $s^{-1}$ .

To date, a number of approaches are used for choosing a rheological model of the studied fluid, and all of them are mainly based on the selection of the coefficients of the equations of the studied models of rheological flow curves by the least squares method [7]. A.X. Mirzajanzade [8] proposed a method for choosing models of rheological flow curves. Note that the described models do not take into account the

parameters characterizing intermolecular interactions in dispersed systems. These power models are only a convenient form of regression processing of experimental data and do not sufficiently reflect the rheological patterns of the flow [9].

To date, to study the viscosity of oil dispersed systems, taking into account intermolecular interactions, they mainly use the Eyring-Frenkel equation [10-12]:

$$\eta = B \cdot \exp(\Delta G/RT), \text{ where } \Delta G = \Delta H - T\Delta S \quad (1)$$

$$\text{and } \ln \eta = \ln B + \Delta G/RT = \Delta H/RT + (\ln B - \Delta S/R) = E_a/RT + A \quad (2)$$

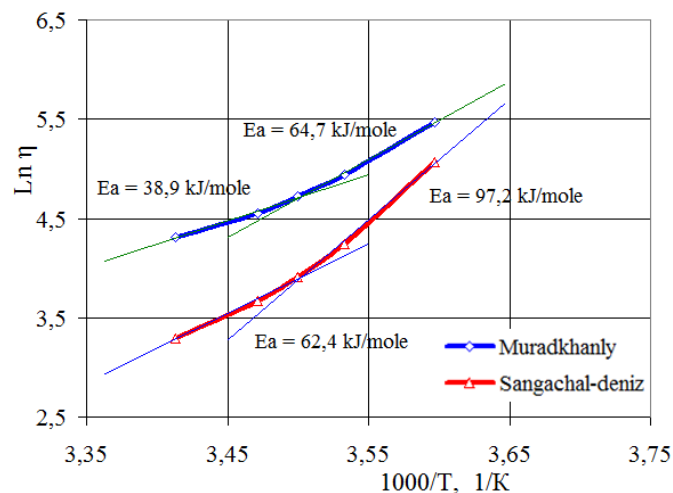
$$\text{where } A = \ln B - \Delta S/R. \quad (3)$$

To determine the value of  $E_a = \Delta H$ , the Frenkel approximation [11]  $\eta = A \exp(E_a/(RT))$  is represented as

$$\ln \eta = E_a/RT + A \quad (4)$$

from which the values of  $E_a$  and  $A$  are calculated from the dependence of  $\ln \eta$  on  $(1/T)$ . Here  $R$  and  $T$ , are the universal gas constant and temperature, respectively.

Using this approach, the dependences of the logarithm of viscosity on the reciprocal temperature  $\ln \eta$  on  $(1/T)$  were determined for oil samples from the Muradkhanly and Sangachal-deniz fields. These dependences presented in Figure 4 have a pronounced non-linear character.



**Figure 4.** Dependences of the logarithm of the viscosity  $\ln \eta$  of oil samples on the reverse temperature  $1/T$

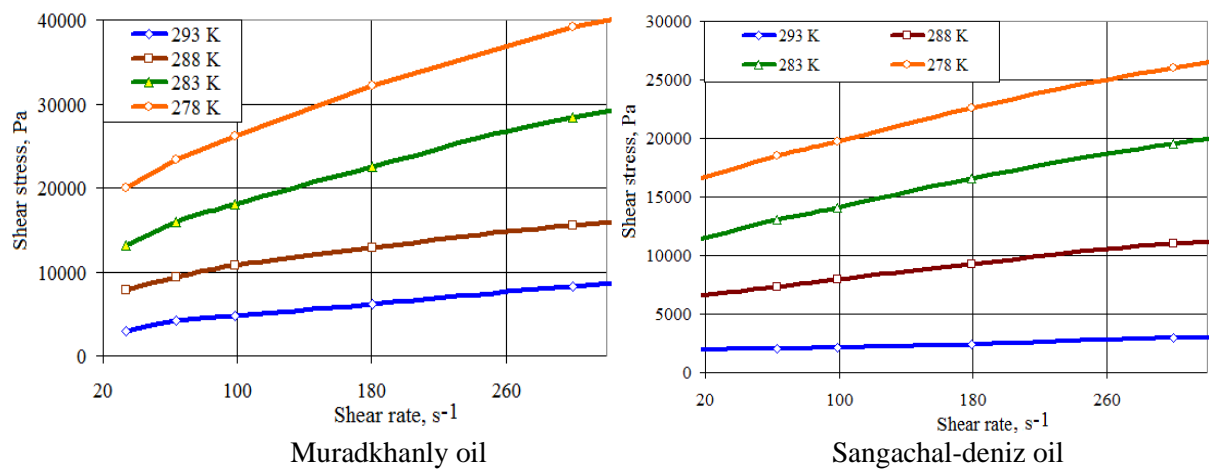
In order to assess the effect of shear loads on the geometric dimensions of structured oil fragments, changes in the average particle size during the movement of oil samples in a pipeline system were studied using the dynamic light scattering (DLS) method. The use of this method to study the granulometric composition and colloid-chemical characteristics of the studied oils made it possible to determine the geometric dimensions of structured oil fragments under various shear loads in the studied temperature range.

The experimental setup was a closed ring-shaped pipeline 9,6 meters long, with an inner diameter of 8 mm, through which it was possible to continuously pump an oil sample with a centrifugal pump, as well as to take its samples. The shear flow rates were chosen from the condition of ensuring aggregation, and then, increasing the head and shear rate, after 15-20 minutes of pumping, a sample was taken to change the particle size distribution. Table 3 shows the DLS data for oils from the Muradkhanly and Sangachal-deniz fields at various shear loads. The dimensional trend indicates the effects of shear rate on particle fragmentation caused by deformation.

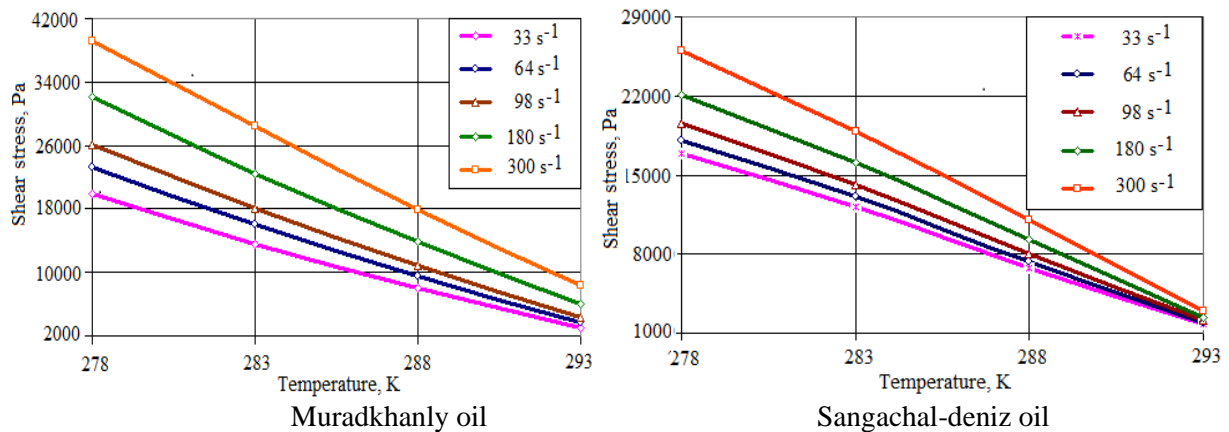
**Table 3.** Values of the average particle diameter at different flow shear rates for oils from the Muradkhanly and Sangachal-deniz fields according to the DLS data

No	Type of oil	Average diameter particles, oil samples, nm	Average diameter particles, oil samples, nm Average particle diameter at different shear rates at 288 K, nm		
			37 s <sup>-1</sup>	142 s <sup>-1</sup>	311 s <sup>-1</sup>
1	Muradkhanly	882.3	772.4	701.3	635.9
2	Sangachal-deniz	621.7	532.6	472.4	436.8

Analyzing the dependencies shown in Figure 2, 3, 5, 6, shows that the order in the supramolecular structure (SMS) is associated with changes in temperature and shear rate, which in turn depends on the shear stress, an increase in which will reduce this order.



**Figure 5.** Dependences of shear stress on shear rates at different temperatures for Muradkhanly and Sangachal-deniz oil samples



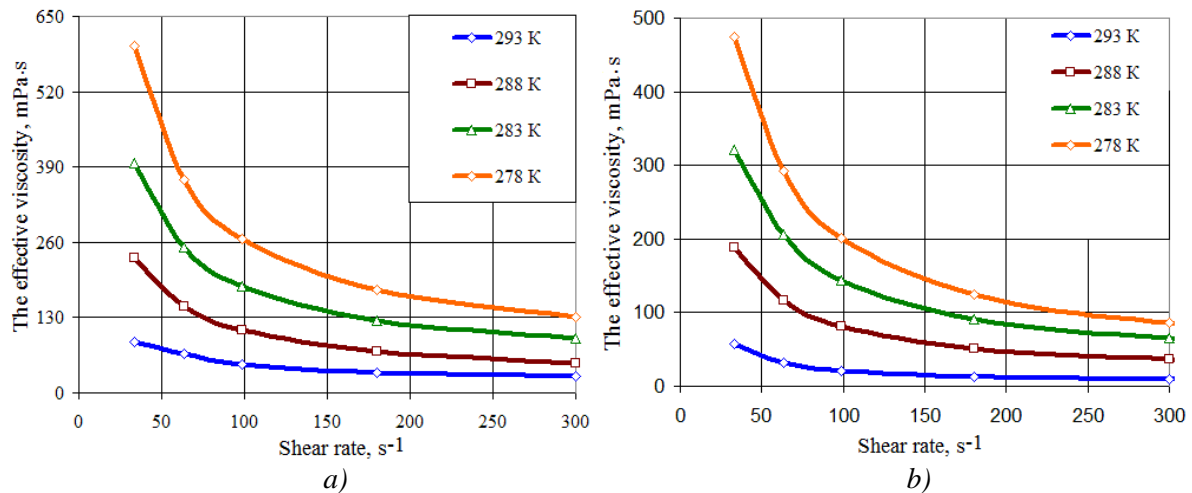
**Figure 6.** Dependences of shear stress on temperature at different shear rates for Muradkhanly and Sangachal-deniz oil samples

In asphalt-resinous oils, which have relatively higher viscosities and low saturation temperatures, at low temperatures, due to increased structuring processes and an increase in viscosity, the effect of the diffusion mechanism will be insignificant and significantly limited. To achieve the required shear rates, a significant increase in the shear stress will be required (Figures 5 and 6). In the range of 278÷293 K, Muradkhanly asphalt-resinous oil will require more shear stress than Sangachal-deniz paraffinic oils (Figure 6).

Despite the relatively mild climatic conditions of the oil region, underloading of the oil pipeline leads to frequent stops in the movement of oil. For such conditions, it becomes necessary to determine the values of the temperature of the beginning of structure formation  $T_s$  for the corresponding shear rate in oils [13].

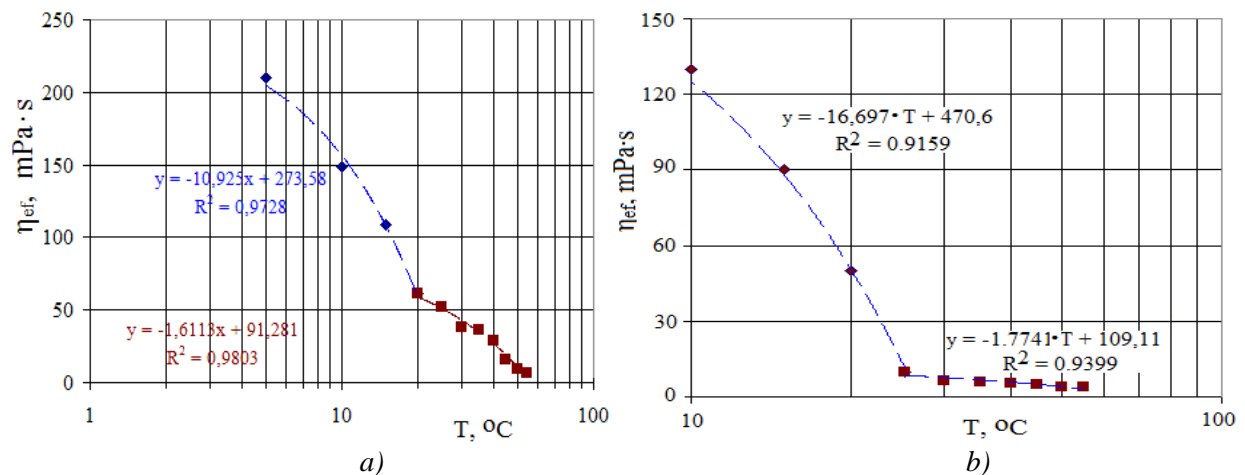
The sequence of calculation of temperature values  $T_s$  for Muradkhanly and Sangachal-deniz oils from the corresponding dependences of the effective viscosity of oil at the corresponding shear rate of  $64 \text{ s}^{-1}$  on temperature in semilogarithmic coordinates is given in Figures 7 - 9. These Figures show that the point of intersection of two tangents to the constructed viscosity-temperature characteristics for each of the considered oils corresponds to the temperature of the beginning of structure formation at the selected shear rate.

Note that the temperature of the beginning of structure formation was found from the dependence of the effective viscosity of oil on temperature (Figure 7) according to the method of processing the viscosity-temperature characteristics of oil at a certain shear rate used in [14].

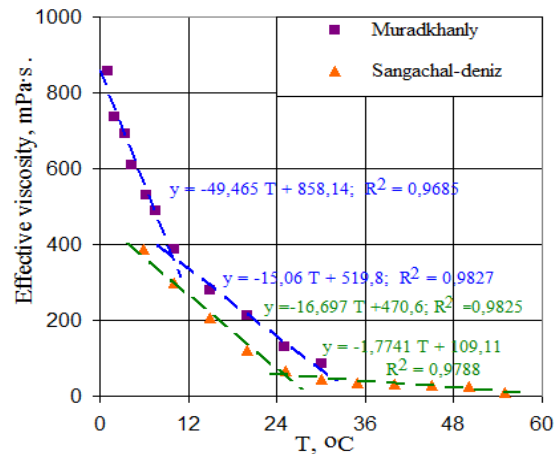


**Figure 7.** Dependence of the effective viscosity of oils Muradkhanly (a) and Sangachal-deniz (b) on shear rate  $s^{-1}$

The dependence of the effective viscosity of oil on temperature at a shear rate of  $64 \text{ s}^{-1}$  is shown in Figures 3 and 5. For this shear rate, the joint solution of the systems of equations of trend lines (Figure 8) determines the values of the temperatures of the onset of structure formation.



**Figure 8.** Dependences of the effective viscosity of oil Muradkhanly (a) and Sangachal-deniz (b) on temperature in semi-logarithmic coordinates at a shear rate of  $64 \text{ s}^{-1}$



**Figure 9.** Dependence of the temperature of the beginning of structure formation on the shear rate  $s^{-1}$

By solving systems of equations of intersecting linear segments:

for Muradkhanly oil:

$$\eta = -49.465 T + 858.14; \quad \eta = -15.06 T + 519.8$$

and for Sangachal -deniz oil:

$$\eta = -16.697 T + 470.6; \quad \eta = -1.7741 T + 109.11$$

the temperature of the beginning of structure formation from a shear rate of  $64 s^{-1}$  was determined: for Muradkhanly oil -  $T = 282.83 K (9.83 ^\circ C)$ , for Sangachal-deniz oil -  $T = 297.23 K (24.23 ^\circ C)$ .

For these oils, the dependence of the temperature of the beginning of structure formation on the shear rate, respectively, is described by the following equations:

$$\begin{aligned} T_{str.M} &= 2.136 \cdot 10^{-9} \cdot \dot{\gamma}^4 - 1.173 \cdot 10^{-6} \cdot \dot{\gamma}^3 + 4.701 \cdot 10^{-4} \cdot \dot{\gamma}^2 - 0.071 \cdot \dot{\gamma} + 34.071; \\ T_{str.S} &= 2.934 \cdot 10^{-9} \cdot \dot{\gamma}^4 - 2.181 \cdot 10^{-6} \cdot \dot{\gamma}^3 + 5.761 \cdot 10^{-4} \cdot \dot{\gamma}^2 - 0.063 \cdot \dot{\gamma} + 44.057; \end{aligned} \quad (5)$$

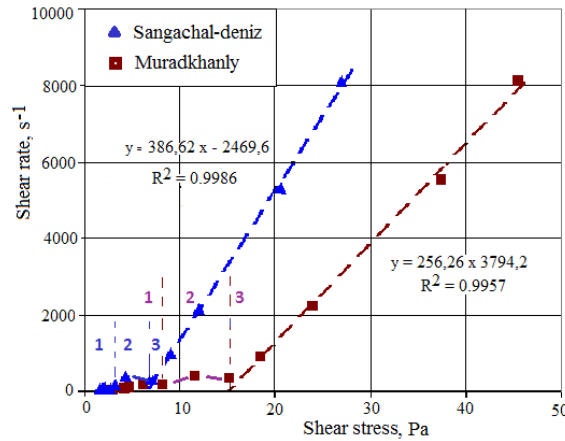
where  $\dot{\gamma}$  - is the shear rate,  $s^{-1}$ .

Note that in the studied oils at a temperature close to the temperature of the beginning of structure formation, a significant increase in static shear stress is observed, which indirectly indicates the beginning of the formation of a strong spatial structure in high-paraffin oils and an increase in aggregation in asphaltene-resinous oils.

In the studied range of shear rate change from shear stress for nonlinear-viscous-plastic oils Muradkhanly and Sangachal-deniz, three areas can be distinguished (Figure 10):

- 1 - limit shear stress (static shear stress or limit of fluidity) -  $\tau_0$ ;
- 2 - transitional region in which the phenomenon of creep is observed;
- 3 - limit of dynamic shear stress -  $\tau_d$ .





**Figure 10.** Areas of static (1), transient (2), and limiting dynamic (3) shear stress at a temperature of 298 K, respectively, for Muradkhanly and Sangachal-deniz

The first characterizes the strength of the oil structure and is numerically equal to the shear stress at which the oil begins to flow from the equilibrium position. At shear stresses  $\tau < \tau_0$ , viscoplastic oils (Figure 9) behave like a solid with no flow [6]. In the stress range  $\tau < \tau_d$ , the flow of the oils under consideration occurs with a static shear stress and a very high viscosity. At stresses  $\tau > \tau_d$ , destruction occurs in the oil system, the viscosity decreases sharply, and the flow occurs with a lower viscosity and stress of fluidity  $\tau_d$ . For the oils under consideration, the shear stresses are respectively:

- Muradkhanly oil: static - 6.16 Pa and limiting dynamic - 14.81 Pa;
- Sangachal-deniz oil: static - 3.2 Pa and limiting dynamic - 6.39 Pa.

Changes in the properties of the mixture observed in the pipeline during the transportation of different types of oils, associated with the appearance of conditions for the occurrence of "incompatibility" and the onset of precipitation, were observed at relatively high contents of the heavy fraction. In the study of a mixture of different types of oils of the Azerbaijan oil region, no manifestations of singular and irrational properties of the mixture were found, arising from the dissociation of the associated molecules of one of the components of the mixture under the influence of another with a significant divergence of the natural composition of the oils. In the early stages of mixing, incompatibility is not a limiting factor. The structural-mechanical and thermodynamic aspects of miscibility dominate here. It should be noted that with the predominance of the influence of the Brownian motion of particles over the forces of external shear action or in the absence of such, the resulting limitation in the mobility of oil leads to an increase in coagulation processes, structural changes in the oil system.

#### 4. RESULTS

It is generally accepted that changes in a viscous oil system depending on temperature and oil flow rate are associated with structural changes occurring in it, and the destruction of particles of an oil dispersed system under the action of high shear rates is most likely due to their shear deformations. As can be seen from Figure 2, the dependence of the viscosity of the studied oils in the considered range of shear rates has a pronounced non-linear character. For the oils under consideration, due to the non-linearity of this dependence on the shear rate (Figure 2) and temperature (Figure 3), the determined quantities appear to be the apparent heats of activation of the flow. Since the effective viscosity  $\eta_{\text{eff}}$  is related to stress and shear rate, the changes in  $\eta_{\text{eff}}$  with temperature change are evaluated at constant stresses or shear rates. Approximation of nonlinear dependences  $\ln \eta$  on  $(1/T)$  in the range of shear rates  $20 \div 100 \text{ s}^{-1}$  by one linear function leads to large deviations from the experimental values. These experimental dependences of  $\ln \eta$  on  $(1/T)$  can also be approximated by several piecewise linear functions characterizing this dependence, which indicates the complex rheological behavior of the oil system. For any point of these experimental curves of dependence of  $\ln \eta$  on  $(1/T)$ , the calculated values of the activation energy will differ, and as the temperature decreases, these values will increase. Each of the points of the dependence of  $\ln \eta$  on  $(1/T)$  is informative in the study of the properties and behavior of processes within the studied temperature range.

Note that no intermediate, “special” temperatures characterizing, for example, phase changes for these oils have been found. In Figure 4, the break temperature of 283 K, as the middle of the temperature range under study, is chosen to illustrate the nonlinearity of the dependence and change in the values of activation energies on temperature. Such breaks take place over the entire temperature range under study with a difference in activation energies. In the temperature range under study, phase transitions in these SMSs are sensitive to temperature changes, especially in the highly solidifying paraffinic oils of Sangachal-deniz. The increase in activation energies with decreasing temperature (Figure 4) is most likely due to a change in the structure of oils.

With a decrease in temperature, most likely, a plurality of equilibrium states takes place. Under such conditions, the activation energy  $E_a$  retains its initial value  $E_{a0}$  [10]. The presence of a break in the dependences  $\ln \eta - 1/T$  is associated with phase changes in oils, in the composition of oil associates. Therefore, for each oil sample (Figure 4), the system is characterized by several, at least two values of activation energy.

Comparison of these characteristics with the group composition of the studied oils shows that with decreasing temperature, the viscosity of Muradkhanly oil increases significantly due to the high content of asphaltenes and resins. For Sangachal-Deniz oil, the investigated temperature range 293÷278 K coincides with the saturation temperature range (the temperature of nucleation and intensification of the crystallization process). For Sangachal-Deniz oil in the temperature range up to 283÷278 K, a sharp increase in viscosity is observed, which is caused by an increase in the phase transition occurring in oil, and the high content of paraffins and the presence of resins that hinder this process affect the rate of increase in viscosity.

The presence of a rather pronounced inflection on the dependences of  $\ln \eta$  on  $(1/T)$  for each of the oils, indicating a significant difference (almost two times) in the activation energies of the viscous flow  $E_1$  and  $E_2$  in the region of low ( $T < 283$  K) and high ( $T > 283$  K) temperatures. The presence of such an inflection in the dependence of  $\ln \eta$  on  $(1/T)$  for oils is not a new fact, since it is described in a number of works, for example, [15-18].

Figure 2 shows that for the studied oils, as the shear rate  $\dot{\gamma}$  decreases, the viscosity of the oils increases. So, at shear rates less than  $60 \text{ s}^{-1}$ , the viscosity change curve tends to a linear dependence, which indicates the convergence of the values of  $E_1$  and  $E_2$  of two neighboring viscous oil flow regimes. For oil from the Sangachal-deniz field, this leads to the successive disappearance of the inflection on the dependence of  $\ln \eta$  on  $(1/T)$  (Figure 3) and an increase in the phase transition of SMS at a temperature below 283 K. A similar pattern of change in flow regimes also takes place for oil from the Muradkhanly field, with the difference that, due to a lower saturation temperature of 275 K, the fluidity of oil deteriorates, and phase changes increase slightly.

The presence in the periodical literature of works with various methods for studying temperature transformations in SMS and calculating the thermodynamic parameters of the flow  $\Delta H$  and  $\Delta S$  determined the need to choose a method that gives the most reasonable and reliable results when they are determined by equation (4).

It was noted in [16, 17] that in most works the description of the effect of velocity  $v$  and shear stress  $\tau$  on the value of  $E = \Delta H$  and  $\Delta S$  remains unsatisfactory, there is no matching between two areas of SMS research: those based on rheological equations of type (1) and on equations of type (2). The authors of [16] consider it illegal to use the temperature dependence of  $\ln \eta$  on  $(1/T)$  to calculate the change in entropy  $\Delta S$ , since the expression for the value of  $A$  (Equation (3)), calculated from the experimental dependences of  $\ln \eta$  on  $(1/T)$ , in addition to  $\Delta S$  includes the constant  $B$ , namely:  $A = \ln B - \Delta S/R$ .

Also, the use of the expression  $B = hN / V_M$  obtained by Eyring, due to the uncertainty in the value of  $V_M$ , seems hardly acceptable for SMS, since the composition of SMS consists of components with molar masses differing by tens and hundreds of times. It is also noted that the results obtained when describing the temperature dependence of oil viscosity  $\eta$  in expression (3) by various empirical equations in order to find  $\Delta S$  have unsatisfactory accuracy [16]. In calculating the values of the parameters  $\Delta H$  and  $\Delta S$  for the studied

oil samples, algorithms taken from the literature [10,16,18,19] were used. The results of parallel calculations are presented in Table 4.

**Table 4.** Values of parameters  $\Delta H$  and  $\Delta S$  for oil samples from fields Muradkhanly and Sangachal-deniz

T, K	Algorithms of								
	[16]			[10, 19]			[18]		
	E, kJ/ mole	$\Delta S$ , J/ mole·K	$\Delta H$ , kJ/ mole	E, kJ/ mole	$\Delta S$ , J/ mole·K	$\Delta H$ , kJ/ mole	E, kJ/ mole	$\Delta S$ , J/ mole·K	$\Delta H$ , kJ/ mole
	For Muradkhanly field oil								
278	31.5	-122.3	31.5	46.2	-164.3	46.2	38.4	-142.1	38.4
	For oil field Sangachal-deniz								
278	77.9	-173.9	77.9	69.8	-186.1	69.8	58.1	-155.3	58.1

As shown in [10,13,19], the value of the energy barrier ( $E_a = W - A$ ) depends on the energy of vacancy formation ( $W$ ) and decreases due to the work of external forces ( $A = \tau \cdot v$ ) expended on the introduction of particles of volume ( $v$ ) into the formed vacancies.

Therefore, for the Muradkhanly asphalt-resinous oil, in which the sizes (volumes) of suprastructure particles (SSP) are slightly reduced due to the action of destructive friction, an increase in the activation energy of the viscous flow will be observed up to a certain limiting value  $W \sim 70-80$  kJ / mol. In oil from the Sangachal-deniz field, the SSP cores are strong paraffin microcrystals; therefore, during shear flow, their destruction almost does not occur ( $r \approx \text{const}$ ), and there will be no significant change in the activation energy of the viscous flow. Even a not very high paraffin content (8,2%) in Sangachal-deniz oil at a temperature below the oil saturation temperature with paraffins can lead to the formation of complex, strong spatial structures in the oil, which is confirmed by works [13,20] on the study of the rheological and thixotropic properties of heavy high-viscosity oil. With a decrease in temperature, the formation of solid paraffin particles increases, the structure of high-molecular components becomes harder and stronger, occupying an increasing volume in oil, which leads to a significant increase in its viscosity. With an increase in the shear rate, despite the effect of shear deformations at the phase transition temperatures of paraffins contained in oils, the difference between the activation energies  $E_1$  and  $E_2$  increases almost twofold. There is a multiple increase in the size of aggregates, particles in oils, but the effect of shear deformations turns out to be insignificant [10]. The activation entropy of the viscous flow of the studied oils of different types is the difference between the entropy of the activated and initial state. The negative value of the change in the entropy of activation of the viscous flow of these oils is explained by an increase in the orderliness of the oil system when shear stress is applied to it, by the dominance of orientation processes, accompanied by the formation of new ordered structures [6,13,15]. It follows from here that the entropy of the activated state must be less than the initial one, therefore, the entropy of activation of the viscous flow must be negative.

## 5. CONCLUSIONS

1. For waterless oils of the Muradkhanly and Sangachal-deniz fields, the temperature at which the studied systems show anomalies in properties is determined. The non-Newtonian behavior of oils is described with sufficient accuracy by the Bingham-Shvedov and Herschel-Bulkley rheological equations.
2. In the range of shear rates of  $20 - 100 \text{ s}^{-1}$  for the oils under consideration, the nonlinear dependences of  $\ln \eta$  on  $(1/T)$  are approximated by piecewise linear functions, on which the breaks are associated with phase transitions in oil samples. Dependences  $\ln \eta - 1/T$  for these systems are characterized by different activation energies. The increase in the activation energies of oils with decreasing temperature is explained by a change in the structure of oils.
3. With a decrease in temperature, starting from 293 K, conditions arise for phase transitions in Sangachal-deniz oil samples, which coincide with the saturation temperature range and, upon further cooling, can

cause precipitation of solid paraffins from the system. In the temperature range 278÷293 K for oil from the Muradkhanly field, due to a lower saturation temperature of 275 K, a deterioration in oil fluidity is detected.

4. Based on the use of the methodology described in the literature for studying the rheological viscosity-temperature properties of Muradkhanly asphaltene-resinous oil for various shear rates, the temperature of the beginning of structure formation was estimated at 282.83 K (9,83 °C) and the limiting dynamic shear stress equal to 17.96 Pa. For paraffinic oil Sangachal-deniz, the temperature of the beginning of structure formation is 297.23 K (24,23°C). Estimates of static and limiting dynamic shear stress are respectively equal: for Muradkhanly oil -3.2 and 6.39 Pa; for oil Sangachal-deniz - 6.16 and 14.81 Pa. It was found that when the critical shear rate is reached, the temperature of the beginning of structure formation decreases by 2.5 °. At speeds exceeding the critical shear rate, the temperature of the onset of structure formation remains constant.
5. Significant differences in the behavior of light and heavy oils are associated with rheological and thermophysical properties changing in the range of 293÷333 K. In this interval, as the temperature decreases, the structure of the studied commercial oils becomes more ordered. This follows from the dependence of the viscous flow activation energy (entropy) on temperature. For each sample of commercial oil at different shear rates of the piecewise linear approximation of the dependences  $\ln \eta$  on  $(1/T)$ , the activation energies of the viscous flow  $E_a$  were determined.
6. It has been experimentally confirmed that with a prolonged absence of movement (rest) of oils, due to underloading of the oil pipeline, the influence of the Brownian motion of particles and coagulation processes, structure formation at low temperatures increases. An increase in the oil flow rate, as well as the effect of surfactants, contributes to the crushing of associates of particles and macromolecules due to their destruction during a collision, and the fluidity of oil increases.
7. Curves of shear stress versus shear rate show a characteristic increase in shear stress with increasing flow rate, which indicates an increase in pressure losses due to hydraulic flow resistance during oil transportation through pipelines. It has been established that with an increase in the oil flow rate at the initial stage, a significant increase in viscosity occurs with further stabilization of the oil viscosity at all flow rates. It is shown that the most effective influence on the viscosity and, as a result, the improvement of rheological characteristics occurs with an increase in the temperature of the transported liquid. The results of the above rheological studies of oil from these fields can be used to predict their behavior during transportation through field pipelines.

## CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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