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Rheological Properties Of Some Surfactant-Based Fracturing Fluids

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ABSTRACT
The paper presents the rheological behavior study of some cationic surfactant-based aqueous solutions that can be used as fracturing fluids. It was followed the influence of salt type and concentration, as well as that of temperature by setting the dependence between the shear stress τ and the shear rate $\dot{\gamma}$. The analysis of dependence between τ and $\dot{\gamma}$ demonstrates that all the studied solutions have non-Newtonian behavior with flow behavior index smaller than 1.
Keywords - apparent viscosity, non-Newtonian behavior, surfactant

I. INTRODUCTION

Hydraulic fracturing is a well stimulation process used to maximize the extraction of underground resources. It refers to the procedure of creating fractures in rocks and rock formations by injecting a fracturing fluid into the cracks to force underground to open further. The main functions of a fracturing fluid are to open the fracture and to transport propping agent along the length of the fracture [1-5].

The ideal fracturing fluid should: be able to transport the propping agent in the fracture, be compatible with the formation rock and fluid, generate enough pressure drop along the fracture to create a wide fracture, minimize friction pressure losses during injection, be formulated using chemical additives that are approved by the local environmental regulations and exhibit controlled-break to a low-viscosity fluid for cleanup after the treatment [6,7]. Many types of fracturing fluids were used in oil field, such as polymer solution, crosslinked polymer, foam, viscoelastic surfactant (VES), combination between a single phase microemulsion and a gelable polymer [1].

To optimise fracture operations that increase porosity in the underground strata around the well, the fracturing fluid's viscosity must be high enough under low shear conditions to suspend and carry proppant to the smallest crevices in the fractured rock. In addition, its viscosity must be low enough under high shear rates so that adequate flow to these newly fractured strata is obtained and the proppant is released [6].

Surfactant-based fracturing gels are considered as clean gels due to the absence of insoluble residues in their composition. This kind of fluid has been developed to minimize or eliminate damages to fractures [2, 8-10].

The composition of viscoelastic surfactant fluids is fresh water, salt and VES product (typically a quaternary ammonium salt of a long-chain fatty acid). In some cases, an organic counter ion is used to improve the thermal stability of the VES micelle structures. When the aqueous environment contains an optimum concentration of salts (usually potassium or ammonium chloride solutions), the micelles assume a rodlike shape. If the surfactant is present in a sufficient concentration (usually > 1% by volume) the micelles associate with one another. The resulting hindered movement causes the fluid to become both viscous and elastic. If the micelles are disrupted owing to shear, they will quickly reaggregate and recover when shear ceases [6,11].

II. EXPERIMENTAL

2.1. Materials and methods

The surfactant used for the preparation of viscoelastic type fluids is of cationic type, with an active substance content of 30%. The main characteristics of this product are given in Table 1.

The aqueous surfactant solutions also contain sodium salicylate (NaSal) (1÷5%) and potassium or ammonium chloride (0÷4%). The salts content is chosen so the sum of the percentages of the two types of salt (organic and inorganic) is always 5%. All the salts were purchased from Merck.

The samples preparation was done at room temperature (25˚C), by dispersing the cationic surfactant in the aqueous solution containing organic and inorganic salts. It was used a stirrer with

diameter 45 mm which provides an intense stirring (Re = 5×10^4) corresponding to a peripheral velocity of 3.5 m s^{-1}. The composition of the samples with surfactant content is presented in Table 2.

2.2. Rheological measurements

The rheological characterization of the samples was carried out under thermostatic conditions (temperature range 25÷45ºC), using a rotation viscometer Rheotest-2 with the system vat-drum S/S$_1$, suitable for the viscosity range of these fluids and higher sensibility. The device allows the measurement of the torsion moment appeared thanks to the ring-shaped substance layer placed between a fixed cylinder and a rotating one with known revolution. The torsion moment is correlated with the shear stress. The revolution and the ring-shaped layer thickness determine the shear rate. Shear rate values were changed in the range 9÷729 s^{-1}. The samples were analysed after one day of preparation.

III. RESULTS AND DISCUSSIONS
3.1. Effect of temperature

The influence of temperature on the rheological behavior was determined for all the analysed samples. In Fig. 1, dependence $\tau = f(\dot{\gamma})$ is shown, at three temperature values, for solution F$_{5-2}$ (3% NH$_4$Cl) and B$_{5-2}$ (3% KCl).

Nonlinear dependences $\tau = K \cdot \dot{\gamma}^n$ obtained for all the analysed samples indicate the non-Newtonian behavior similar to the real plastic fluids (flow behavior index n < 1). Also, it is noted that there is a point of inflection of $\tau = f(\dot{\gamma})$ curves, especially at the lower temperature values. For this reason, the rheological equations have been established on different ranges of shear rate, thus determining the shear rate value at which the inflection takes place (the value of transition $\dot{\gamma}_{ch}$).

The obtained rheological equations are presented in Table 3.

It is observed that the shear stress values, at the same shear rate value, are slightly lower for the sample containing added ammonium chloride. Also, for both samples, the temperature increasing leads to an increase in the shear rate transition value.

From the graphical representation of apparent viscosity (calculated as the ratio between the shear stress and the shear rate) evolution as a function of shear rate for samples F$_{5-2}$ and B$_{5-2}$ (Fig. 2) it is observed that at 25ºC the samples viscosity has a pronounced decrease with the shear rate increasing, by an average of 93%. At higher temperatures and low values of the shear rate, the apparent viscosity of both samples increases with the increasing shear rate, followed by a decrease of it to the further increase of the shear rate. The decrease is more pronounced at

35ºC (by an average of 67% from the maximum value) and lower at 45ºC (by 29%).

3.2. Effect of inorganic salt concentration and of the cation type

For the solutions having in composition cationic surfactant, sodium salicylate and, respectively, different concentrations of potassium chloride, at 45ºC, $\tau = f(\dot{\gamma})$ dependences are presented in Fig. 3. It can be noticed that the addition of potassium chloride leads to a slight decrease in the shear stress and, respectively, in the apparent viscosity compared to standard sample (B5-0% KCl). On increasing the amount of potassium chloride, the shear stress values become higher than the values of the standard sample and increase with increasing the amount of salt. The solutions with added ammonium chloride present similar behavior. The rheological equations obtained for the entire shear rate range (16.2÷ 729 s^{-1}) are presented in Table 4.

At 25°C, in the case of both sets of samples, the increasing of salt content leads to the decrease of the shear rate transition value ($\dot{\gamma}_{ch}$), Fig. 4.

The influence of the cation type of inorganic salt on the rheological properties of the fracturing fluid is shown in Fig. 5. It is found that at the same salt concentration the samples containing potassium chloride have a higher apparent viscosity than those containing ammonium chloride. The difference is more visible at higher salt concentrations and lower shear rate values.

The temperature increase leads to microdrops mobility intensification which influences the activation energy of the system. The phenomenon can be explained by Arhenius type equations applied to the cumulative effect described by the shear stress:

$$\tau = A' \cdot e^{\frac{E_a}{R \cdot T}} \qquad (1)$$

where E$_a$ is the viscous flow activation energy, J mol^{-1}; R is the gas general constant, J mol^{-1} K^{-1}; T is absolute temperature and A' represents the material constant, Pa s.

The study of the influence of temperature on the flow activation energy of the system was done for the samples with different ammonium chloride concentrations (F$_{5-4}$, F$_{5-2}$ and F$_{5-1}$). Dependence lnτ=f(1/T) was graphically represented, as obtained from the logarithmic form of eq. (1), for shear stress values corresponding to the three chosen values of the shear rate. Particular expressions of eq. (1) for these solutions are presented in Table 5.

The characterization of liquids flow in ring-shaped spaces and the establishing of the type of hydrodynamic regime can be expressed using the Taylor-Reynolds number (Ta$_{Re}$) which depends on the geometry of the ring-shaped space (radii of the

inner and outer cylinder, r_i and r_o), the inner cylinder revolution n and the fluid properties (density ρ and apparent viscosity η_a), eq. (2)   [12-14]:

$$Ta_{Re} = \frac{2 \cdot \pi \cdot n \cdot r_i \cdot (r_e - r_i) \cdot \rho}{\eta_a}$$

(2)

The critical value of this number, indicating the transition between laminar and intermediate regime, is $Ta_{Re} = 60$. For the system vat-drum S/S1 the geometric dimensions of the ring-shaped space are: $r_o = 19.5$ mm and $r_i = 18.5$ mm.

In Fig. 6a and 6b are represented the values of Taylor-Reynolds number and, respectively, of the activation energy of viscous flow depending on the content of inorganic salt (NH_4Cl, KCl) in solution, at 25°C. The size of Ta_{Re} number was calculated for the transition value of the shear rate ($\dot{\gamma}_{ch}$), analytically determined. The values of the activation energy correspond to the shear rate $\dot{\gamma} = 27$ s^{-1}.

It is noted that increasing the proportion of inorganic salt in the surfactant solution leads to a decrease in the Ta_{Re} value, in accordance with the increase of apparent viscosity. Also, the obtained values indicate the placement of the flow of analysed solutions in laminar regime ($Ta_{Re} < 60$). The values of viscous flow activation energy do not change significantly with the salt content.

IV.   CONCLUSIONS

The analysed samples have non-Newtonian behavior with flow behavior index smaller than 1 on the entire temperature range used, regardless of the type and concentration of the added salt.

At lower temperature values, the dependences of the rheological curves have a point of inflection characterized by the transition value of the shear rate at which the inflection occurs. Increasing temperature leads to the increase of the shear rate transition value or even to the disappearance of inflection.

The increase of the shear rate determines the decrease of the activation energy of viscous flow, respectively the increase of Taylor-Reynolds number.

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V.   FIGURE AND TABLE CAPTIONS

Figure captions
Figure 1: Shear stress vs. shear rate for samples F_{5-2} and B_{5-2}
Figure 2: Apparent viscosity vs. shear rate for samples F_{5-2} and B_{5-2}
Figure 3: Shear stress vs. shear rate for samples B5, B_{5-1}, B_{5-2}, B_{5-4} at 45°C
Figure 4: Shear rate transition values vs. inorganic salt content at 25°C
Figure 5: Apparent viscosity vs. shear rate for samples B_{5-4}, B_{5-1}, F_{5-4} and F_{5-1} at 35°C
Figure 6a: Ta_{Re} number vs. inorganic salt content
Figure 6b: The activation energy vs. inorganic salt content

Table captions
Table 1: The properties of cationic surfactant
Table 2: The composition of the samples
Table 3 Rheological equations for samples F_{5-2} and B_{5-2}
Table 4 Rheological equations for the analysed samples at 45°C
**Table 5** Particular forms of eq. (1) for samples with NH_4Cl content
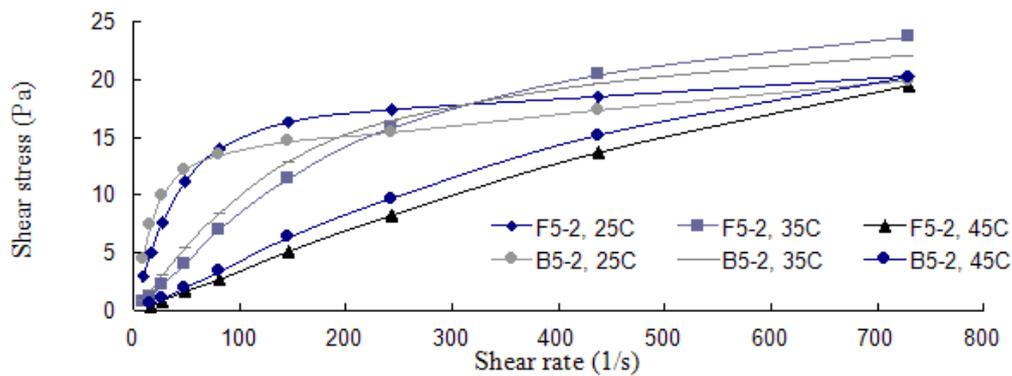

Figure 1: Shear stress vs. shear rate for samples F_{5-2} and B_{5-2}
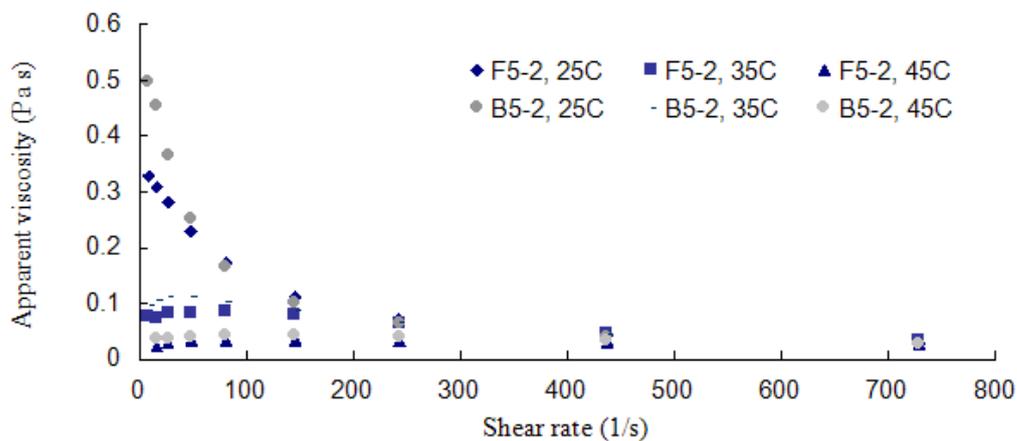
Figure 2: Apparent viscosity vs. shear rate for samples F_{5-2} and B_{5-2}
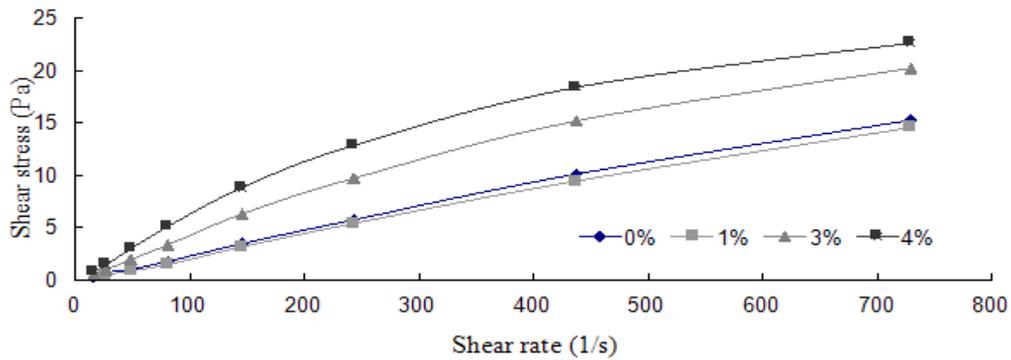
**Figure 3:** Shear stress vs. shear rate for samples B_5, B_{5-1}, B_{5-2}, B_{5-4} at 45°C
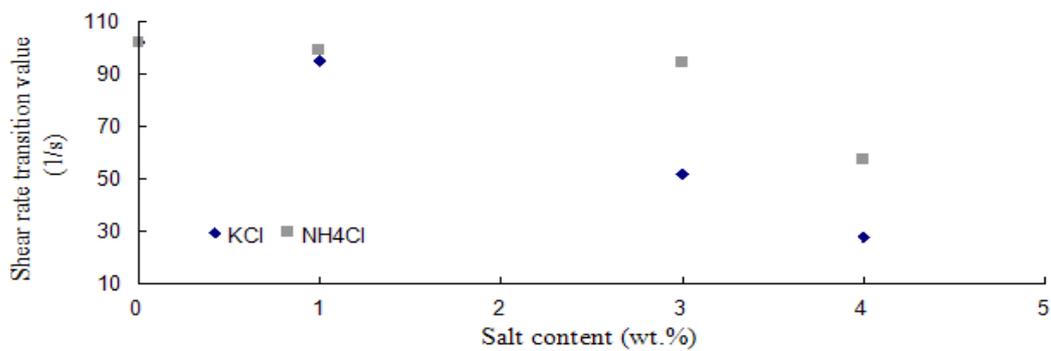
Figure 4: Shear rate transition values vs. inorganic salt content at 25°C
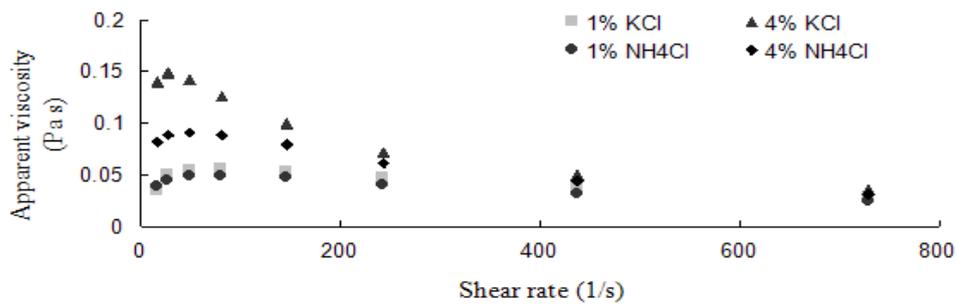
Figure 5: Apparent viscosity vs. shear rate for samples B_{5-4}, B_{5-1}, F_{5-4} and F_{5-1} at 35°C
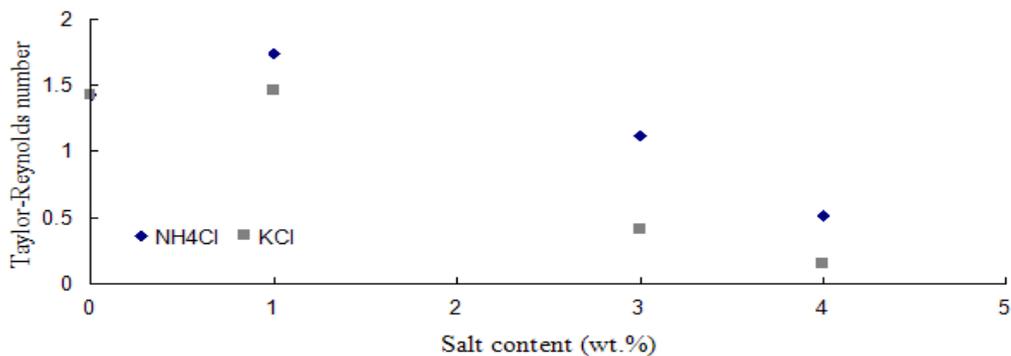

**Figure 6a:** Ta_{Re} number vs. inorganic salt content
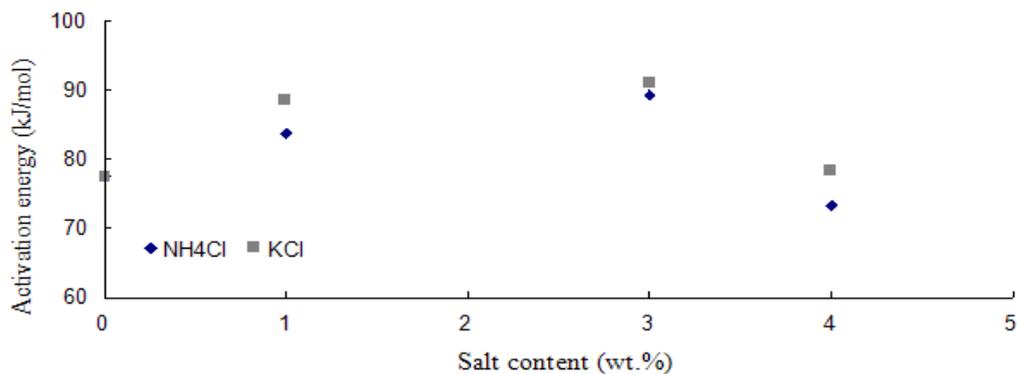
Figure 6b: The activation energy vs. inorganic salt content

Table 1: The properties of cationic surfactant

Property	Conditions of admissibility/Value
Molecular weight, g/mol	319.5
Aspect/odor	Clear liquid, odorless
pH of aq. sol. 1%	$6.5 \div 8$
Solubility in water	Slightly soluble
Density (25°C), kg/m^3	1000
Dynamic viscosity (25°C), mPa s	10.1
Surface tension*, N m^{-1}	38.4

* for the solution with concentration 0.05 mol/L

Table 2: The composition of the samples

Sample	Composition, wt.%				
	Surfactant	Sodium salicylate	KCl	NH$_4$Cl	Water
B$_5$		5	-	-	
B$_{5-1}$		1	4	-	
B$_{5-2}$		2	3	-	
B$_{5-4}$	5	4	1	-	90
F$_{5-1}$		1	-	4	
F$_{5-2}$		2	-	3	
F$_{5-4}$		4	-	1	

Table 3: Rheological equations for samples F$_{5-2}$ and B$_{5-2}$

Sample	Temp., °C	Eq. $\tau = K \cdot \dot{\gamma}^n$	R^{2*}	$\dot{\gamma}_{ch}$, s^{-1}
F$_{5-2}$	25	$\tau = 0.87 \cdot \dot{\gamma}^{0.621},\ \dot{\gamma} \in (9 \div 145.8)s^{-1}$	0.9616	94.4
		$\tau = 7.18 \cdot \dot{\gamma}^{0.158},\ \dot{\gamma} \in (81 \div 729)s^{-1}$	0.9703	
	35	$\tau = 0.082 \cdot \dot{\gamma}\ ,\ \dot{\gamma} \in (9 \div 145.8)s^{-1}$	0.9957	106.5
		$\tau = 0.57 \cdot \dot{\gamma}^{0.585},\ \dot{\gamma} \in (81 \div 729)s^{-1}$	0.9798	
	45	$\tau = 0.026 \cdot \dot{\gamma}^{1.031},\ \dot{\gamma} \in (9 \div 729)s^{-1}$	0.9906	-
B$_{5-2}$	25	$\tau = 1.38 \cdot \dot{\gamma}^{0.553},\ \dot{\gamma} \in (9 \div 81)s^{-1}$	0.9544	51.8
		$\tau = 6.24 \cdot \dot{\gamma}^{0.171},\ \dot{\gamma} \in (48.6 \div 729)s^{-1}$	0.9808	
	35	$\tau = 0.14 \cdot \dot{\gamma}^{0.9},\ \dot{\gamma} \in (9 \div 243)s^{-1}$	0.9847	161.9
		$\tau = 2.57 \cdot \dot{\gamma}^{0.33},\ \dot{\gamma} \in (145.8 \div 729)s^{-1}$	0.9759	
	45	$\tau = 0.046 \cdot \dot{\gamma}^{0.952},\ \dot{\gamma} \in (16.2 \div 729)s^{-1}$	0.9907	-

*the correlation coefficient

Table 4: Rheological equations for the analysed samples at 45°C

Salt content, wt.%	KCl		NH₄Cl	
	Eq. $\tau = K \cdot \dot{\gamma}^n$	R^{2*}	Eq. $\tau = K \cdot \dot{\gamma}^n$	R^2
0	$\tau = 0.035 \cdot \dot{\gamma}^{0.923}$	0.9977	$\tau = 0.035 \cdot \dot{\gamma}^{0.923}$	0.9977
1	$\tau = 0.028 \cdot \dot{\gamma}^{0.951}$	0.9973	$\tau = 0.029 \cdot \dot{\gamma}^{0.925}$	0.9964
3	$\tau = 0.046 \cdot \dot{\gamma}^{0.952}$	0.9907	$\tau = 0.026 \cdot \dot{\gamma}^{1.031}$	0.9906
4	$\tau = 0.318 \cdot \dot{\gamma}^{0.655}$	0.9815	$\tau = 0.089 \cdot \dot{\gamma}^{0.82}$	0.9939

[*] the correlation coefficient

Table 5: Particular forms of eq. (1) for samples with NH₄Cl content

$\dot{\gamma}$, s⁻¹	Eq. $\tau = A' \cdot \exp(E_a / R \cdot T)$		
	1 % NH₄Cl	3 % NH₄Cl	4 % NH₄Cl
27	$\tau = 7.9 \cdot 10^{-15} \cdot \exp(10\,090 / T)$	$\tau = 1.6 \cdot 10^{-15} \cdot \exp(10745 / T)$	$\tau = 1.2 \cdot 10^{-12} \cdot \exp(8820 / T)$
81	$\tau = 1.3 \cdot 10^{-12} \cdot \exp(8810 / T)$	$\tau = 5.0 \cdot 10^{-11} \cdot \exp(7870 / T)$	$\tau = 8.4 \cdot 10^{-7} \cdot \exp(4940 / T)$
243	$\tau = 1.8 \cdot 10^{-6} \cdot \exp(4730 / T)$	$\tau = 3.0 \cdot 10^{-5} \cdot \exp(4000 / T)$	$\tau = 2.4 \cdot 10^{-4} \cdot \exp(3345 / T)$