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RHEOLOGICAL PROPERTIES OF POLYMER-GEL DRILLING FLUIDS AT HIGH TEMPERATURE AND PRESSURE

Hai Bu,[1,2] Jinsheng Sun,[2] Chengbiao Wang,[3] and Ping Bu[3]

Free-radical polymerization in solution was used to synthesize a terpolymer consisting of acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, and styrene sulfonate. Drilling fluids based on the terpolymer were prepared for use in high-temperature and high-pressure wells. The rheological properties of the drilling fluids based on the terpolymer were analyzed by the regression method. We found that the rheological properties of the drilling fluids at high temperature and high pressure can be described by the Casson model. A mathematical model is proposed for predicting the downhole viscosity of drilling fluids containing the terpolymer at high temperature and high pressure.

Key words: *drilling fluids, water-soluble polymer, rheological model, apparent viscosity, multivariate statistics*.

Drilling fluids are mainly suspensions of bentonite in water [1]. These fluids perform the following functions: transporting rock cuttings to the surface, lubricating the drill bit, applying hydrostatic pressure to the wellbore to ensure safe operation of the well, and minimizing fluid loss in high-permeability layers [2].

In connection with deep well drilling, the number of high-temperature and high-pressure wells has grown in recent years [3]. The rheological properties of drilling fluids affect the mechanical drilling speed, hole cleaning, and wellbore stability [4]. These properties of the drilling fluid are difficult to control. Today we observe a trend toward replacing natural fluid loss control additives which can be used only at a temperature below 180°C (modified cellulose, humic acid, lignin) with synthetic products [5]. Chromium salts are often included in additives used at high temperature. Cr^{6+} and Cr^{3+} ions form complexes with polymeric fluid loss control additives having many functional groups [6]. In order to ensure the safety of deep and ultra-deep drilling, the rheological properties of the drilling fluids must be controlled during drilling [7]. In this work, we have studied the rheological properties of water-based drilling fluids containing polymer gels.

Temperature-independent electrostatic attractive forces arise between the metal complexes and clay particles. As a result, the clay particles can adsorb the chains of the polymer additives even at high temperature, which makes it easier to maintain a constant concentration of the small clay particles in the aqueous bentonite suspension [8]. A permeable clay mudcake is formed on the walls of the borehole. However, using additives based

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[1] School of Engineering & Technology in China University of Geosciences, Beijing. [2] Research Institute of Drilling Engineering, CNPC, Beijing. [3] School of Business Administration in China University of Petroleum, Beijing.
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on chromium salts may have serious environmental consequences. It is very important to develop new synthetic fluid loss reducers which make water-based drilling fluids stable at high temperatures and pressures.

A binary copolymer or terpolymer containing 2-acrylamido-2-methylpropanesulfonic acid (AMPS) plays an important role in these polymer additives. Literature data, in particular [9], indicate that pyrrolidone and sulfonate segments are resistant to high temperature and are salt tolerant. Therefore drilling fluids which contain copolymers having pyrrolidone and sulfonate groups can be used under hostile conditions. To date, there have been no studies of the application of sulfonated polymers as fluid loss reducers in suspensions of bentonite in water [10].

Analysis methods. Fourier transform IR spectroscopy (FTIR) was performed on a Nicolet NEXUS-470 (USA) FTIR spectrometer. Thermogravimetry was carried out on a TA5000-DSC2910 (USA) analyzer in a nitrogen atmosphere, raising the temperature at a rate of 10 degrees per minute from 50°C to 800°C. The rheological properties of the drilling fluids were studied using a Fann50SL HT-HP viscometer (US Fann Company). The maximum working pressure was 5 MPa; the maximum temperature was 260°C; the shear stress was measured within the range from 0 to 1022 s^{-1}.

Synthesis of the polymer. Styrene sulfonate was distilled at reduced pressure and stored before use in a refrigerator at a temperature of 4°C. Acrylamide was recrystallized from chloroform and dried under vacuum. 2-Acrylamido-2-methylpropanesulfonic acid was used without preliminary purification.

Weighed amounts of styrene sulfonate, acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, and distilled water were added to a 500-mL four-necked flask equipped with a stirrer, thermometer, and reflux condenser. The flask was flushed with nitrogen for 30 minutes to remove oxygen. A molecular weight regulator and an initiator were added to the flask contents at a temperature of 60°C. The reaction was run at constant temperature for several hours, and the target product (the polymer) was obtained. The equation for the reaction is given below.

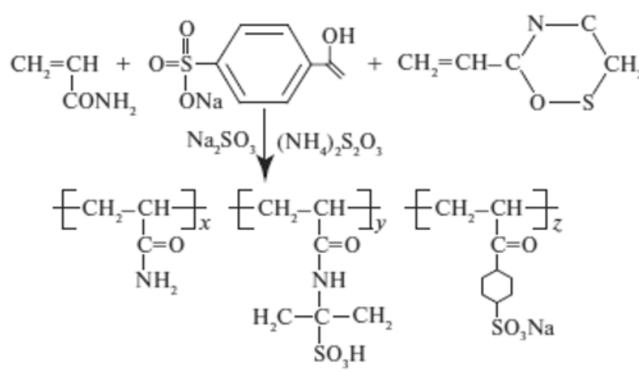

Table 1

Components	Content, g/L, in drilling fluid		
	1	2	3
Water	777.8	777.8	777.8
Bentonite	15.6	15.6	15.6
Polymer	70.0	87.8	87.8
Sulfonated asphaltenes	23.3	0	23.3
Potassium hydroxide	11.7	11.7	11.7
Potassium chloride	62.2	62.2	62.2
Barite	1000.0	1000.0	1066.7

Sequence of procedures for studying the effect of temperature and pressure on the rheological properties of the drilling fluids [11]. First the drilling fluid, containing the synthesized polymer, was stirred for an hour at low stirrer speed. The cell temperature required for studying the sample was established. When the cell temperature became constant, the drilling fluid was added to the cell and heated for an hour until the required sample temperature was reached. Then the drilling fluid was stirred at a speed of 1022 s^{-1} for 30 minutes. Then the pressure in the system was raised to 5 MPa, and the rheological properties of the drilling fluid were measured at different temperatures and shear rates. Measurements were made similarly at constant temperature and different pressures and shear rates.

Table 1 gives the composition of the drilling fluids prepared using the synthesized polymer. The density of drilling fluids *1* and *2* was 1850 kg/m^3; for drilling fluid *3*, 2000 kg/m^3.

Structure of the polymer. Fourier transform IR spectroscopy (FTIR) is most often used for analysis of the functional groups in a compound [12]. The IR spectrum of the synthesized polymer is shown in Fig. 1. The absorption band in the 3420 cm^{-1} region corresponds to the —NH_2 group; 3207 cm^{-1} corresponds to the —NH group; 2920 cm^{-1}, the asymmetric stretching vibration of the —CH_3 group; 2900 cm^{-1}, the stretching vibration of the —CH_2— group in the polymer chain; 1650 cm^{-1}, the stretching vibration of the = bond in the acyl group; 1460 cm^{-1}, the asymmetric bending vibration of the methylene units; 1040 and 1220 cm^{-1}, the symmetric and asymmetric vibrations of the —SO_3 group; 699 cm^{-1}, the substituents on the benzene ring; 627 cm^{-1}, the stretching vibration of the C—S bond.

Thermal stability of the polymer. The thermogravimetric curves for the polymer are presented in Fig. 2. The thermal stability of the polymer reaches 330°C. From Fig. 1, we see that the polymer contains a sulfonate

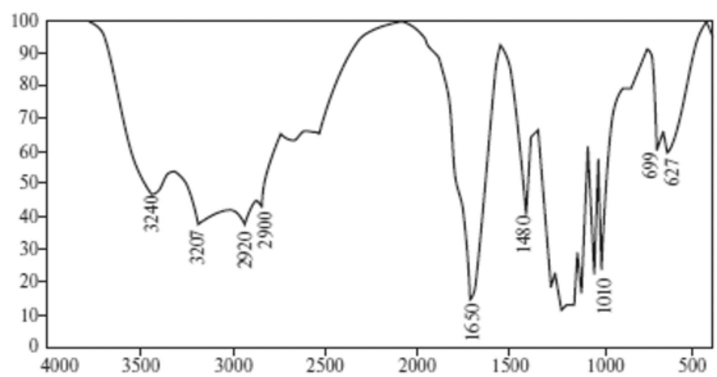

Fig. 1 IR spectrum of synthesized polymer.

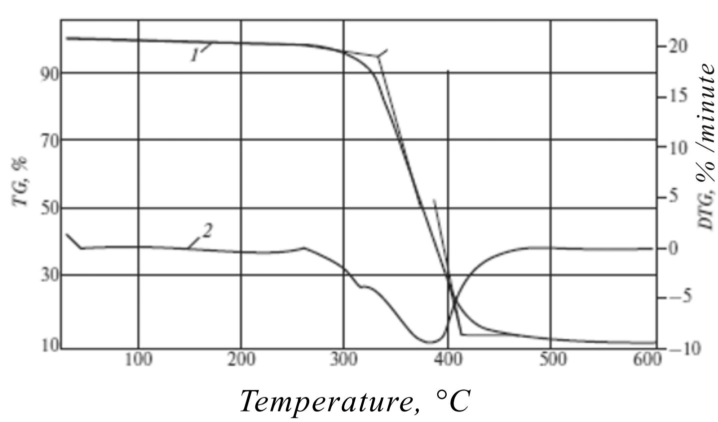

Fig. 2 Thermogravimetric curves for polymer: 1) TG; 2) DTG.

group —SO_3, which retains its mobility at high temperature. Stronger bonds as a result of the functional groups not only ensure high adsorption capacity but also can lead to a change in the polymer conformation [13].

*Rheological properties of drilling fluids at different temperatur*es. Fig. 3 shows the shear stress vs. shear rate for drilling fluid containing the polymer at different temperatures and at a pressure of 5 MPa. We see that the shear stress increases with shear rate. For the same shear rate, the shear stress decreases as the temperature increases. The minimum shear stress is observed at 210°C, and increases a little as the temperature is raised up to 240°C.

Rheological properties of drilling fluids at different pressures. Pressure has less of an effect than temperature on the rheological properties of water-based drilling fluids containing the polymer. High pressure may

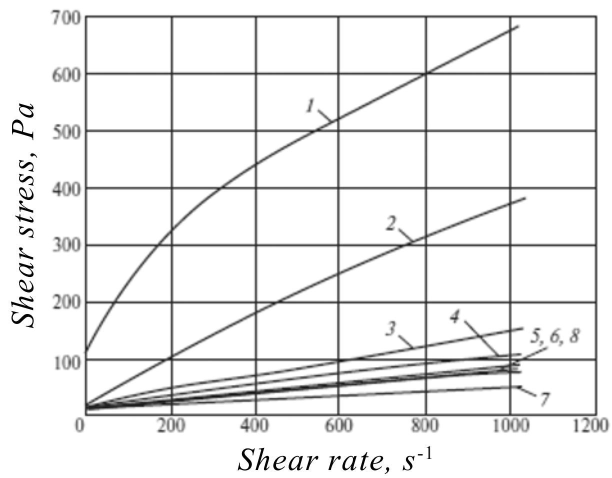

Fig. 3 Shear stress vs. shear rate for drilling fluid at pressure 5 MPa and temperature, °C: 1) 30; 2) 60; 3) 90; 4) 120; 5) 150; 6) 180; 7) 210; 8) 240.

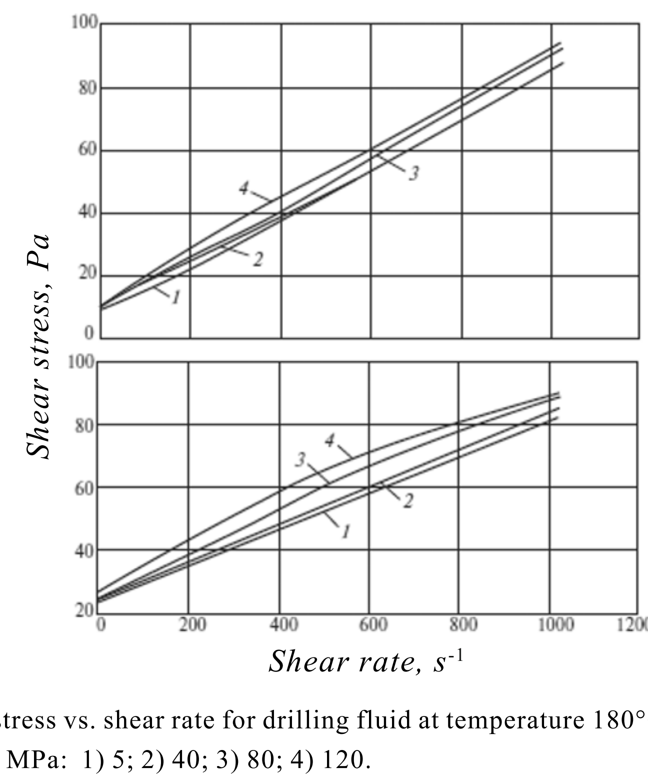

Fig. 4 Shear stress vs. shear rate for drilling fluid at temperature 180°C (a) and 240°C (b) and pressure, MPa: 1) 5; 2) 40; 3) 80; 4) 120.

only slightly reduce the volume of the fluid, which affects its density and viscosity [14]. Fig. 4a and Fig. 4b show the shear stress vs. shear rate at different pressures and at temperatures of 180°C and 240°C. As we see, due to the low compressibility of the drilling fluid, the pressure has only a slight effect on the shear stress. At the same temperature, the shear stress only slightly increases as the pressure increases. As the temperature rises from 180°C to 240°C, the effect of pressure on the shear stress is slightly enhanced.

Viscosity of the drilling fluid vs. temperature and pressure. From the experimental data, we calculated the apparent viscosity and the plastic viscosity of the drilling fluids containing the polymer at different temperatures (Fig. 5). As we see, the apparent viscosity and the plastic viscosity of the drilling fluid are reduced as the temperature rises. The temperature dependences of the apparent viscosity and the plastic viscosity have a similar appearance. In the temperature range 90°C-180°C, the viscosity shows a relatively strong decrease, then up to a temperature of 210°C the viscosity smoothly decreases, reaching the minimum value at 210°C. Above this temperature, the plastic viscosity and the apparent viscosity increase slightly.

A rise in temperature affects the molecular structure of the polymer. High temperature may induce oxidative degradation, conformational changes, or breaking of hydrogen bonds. This in turn leads to a decrease in the viscosity of the drilling fluid. At a temperature of 240°C, the apparent viscosity and the plastic viscosity of the drilling fluid containing the synthesized polymer are respectively greater than 20 and 15 mPa·s. As shown by the study in [15], the drilling fluid has a high capacity for transporting rock cuttings if it has an apparent viscosity and a plastic viscosity no lower than respectively 20 and 15 mPa·s. Based on this, the drilling fluid containing the synthesized polymer can be successfully used in high-temperature and high-pressure wells.

Rheological model for the behavior of the drilling fluid at high temperature and high pressure. The rheological properties of the drilling fluid can be described by the Bingham model ($\tau = \tau_0 + \eta\gamma$), a power-law model ($\tau = K\gamma^n$), the Casson model ($\tau = \tau_0^{1/2} + \eta_\infty^{1/2}\gamma^{1/2}$), and the Herschel—Bulkley model ($\tau = \tau_y + K\gamma^n$) [16]. In these equations, τ is the shear stress; γ is the shear rate; τ_0 is the yield stress; η is the plastic viscosity; K is the consistency index; n is the flow behavior index; η_∞ is the maximum shear stress; τ_y is the yield stress in the Herschel—Bulkley model.

We used linear regression to describe the experimental data on the rheological properties of the drilling fluids. The four equations indicated above led to a linear form. Then we calculated the coefficients of the regression equations by the least-squares method [17]. The regression equations obtained for calculating the shear stress of the drilling fluids at different temperatures are presented in Table 2, while the correlation coefficients for these equations are presented in Fig. 6.

From Fig. 6 we see that the experimental data are best described by the Casson model. The correlation coefficient at different temperatures is greater than 0.995, which confirms that it is possible to exactly

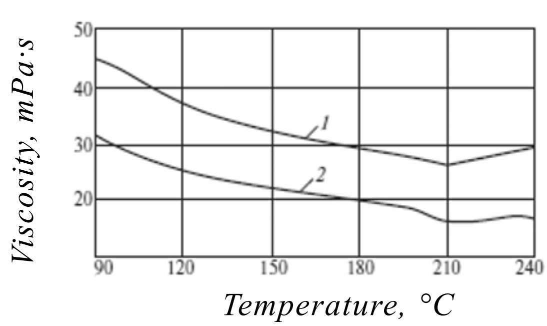

Fig. 5 Apparent viscosity (curve 1) and plastic viscosity (curve 2) of drilling fluid vs. temperature.

Table 2

Rheological model	Temperature, °C				
	120	150	180	210	240
Bingham	$\tau = 16.6012 + 0.0271y$	$\tau = 13.863 + 0.0226y$	$\tau = 10.5212 + 0.0188y$	$\tau = 8.2015 + 0.0184y$	$\tau = 14.1545 + 0.0284y$
Power-law	$\tau = 0.2135\tau^{08298}$	$\tau = 0.2491\tau^{07820}$	$\tau = 02752\tau\text{-}^{0.7626}$	$\tau = 0.2814\tau^{0.7264}$	$\tau = 0.2214\tau^{0.7864}$
Herschel–Bulkley	$\tau = 0.7762 + 0.1658\tau^{0.86737}$	$\tau = 0.7576 + 0.1193\tau^{0.8897}$	$\tau = 0.7175 + 0.0895\tau^{0.9146}$	$\tau = 0.5365 + 0.0764\tau^{0.9028}$	$\tau = 0.6365 + 0.0764\tau^{0.9028}$
Casson	$\tau^{1/2} = 0.4522^{1/2} + 0.0589^{1/2}y^{1/2}$	$\tau^{1/2} = 0.3958^{1/2} + .0483^{1/2}y^{1/2}$	$\tau^{1/2} = 0.3659^{1/2} + 0.0428^{1/2}y^{1/2}$	$\tau^{1/2} = 02983^{1/2} + 0.0330^{1/2}X\,y^{1/2}$	$\tau^{1/2} = 0.3983^{1/2} + 0.0460^{1/2}Xy^{1/2}$

Table 3

No. of drilling fluid (see Table 1)	Density, kg/m^3	*A*, °C	*B*, MPa^{-1}	Correlation coefficient
1	1850	74.1068	-0.1667	0.9916
2	1850	86.5324	-0.1815	0.9935
3	2000	90.6988	-0.2167	0.9947

Table 4

Temperature, °C	Apparent viscosity, mPa·s		Relative error, %
	measured	calculated	
90	45.2	44.8	0.94
120	37.1	36.4	1.77
150	32.7	32.2	1.51
180	29.6	29.7	0.21
210	25.5	27.0	5.23
240	28.4	28.8	1.27

calculate the rheological properties of the drilling fluid at high temperature. The correlation coefficients for the Herschel—Bulkley model, especially at high temperatures, are a little lower than for the Casson model. The Bingham model is not applicable for calculation of the rheological properties at high temperatures, since the correlation coefficient significantly decreases as the temperature rises. Of the four models, the power-law model most poorly describes the experimental data; the correlation coefficient is no greater than 0.99 over the entire studied temperature range. Thus the Casson model provides the highest accuracy in calculating the rheological properties of the drilling fluid containing the polymer at high temperatures.

Mathematical model for the apparent viscosity of the drilling fluid. In order to calculate the apparent viscosity of the drilling fluid downhole, we need to develop a mathematical model based on the known apparent viscosity of the fluid at the wellhead [19]. Based on the functional equation recommended by the API and describing the dependence of the apparent viscosity on temperature and pressure, a new mathematical model is proposed in [20]. The equation recommended by the API is described as follows:

$$\mu_e(T_2) = \mu_e(T_1)\mathbf{exp}\left[a\left(\frac{T_2 - T_1}{T_2 T_1}\right)\right] \quad (1)$$

$$\mu_e(T_2) = \mu_e(T_1)\mathbf{exp}\left[a\left(\frac{T_2 - T_1}{T_2 T_1}\right)\right] \; \mu_e(P_2) = \mu_e(P_1)\mathbf{exp}[\beta(P_2 - P_1)] \quad (2)$$

where $\mu_e(T_1)$ and $\mu_e(T_2)$ are the apparent viscosity at temperatures T_1 and T_2, mPa·s; a is the temperature constant; $\mu_e(P_1)$ and $\mu_e(P_2)$ are the apparent viscosity at pressures P_1 and P_2, mPa·s; b is the pressure constant.

Combining equations (1) and (2), we obtain an equation applicable for practical calculations. By simplifying, we obtain linear dependences of $\ln AV_{(p)}$ on $1/T$ and $\ln AV_{(T)}$ on P:

$$\mu_e(T_2) = \mu_e(T_1)\mathbf{exp}\left[a\left(\frac{T_2 - T_1}{T_2 T_1}\right)\right] \; \mathbf{ln}\, AV_{(T)} = cP + d \quad (3)$$

$$\mathbf{ln}\, AV_{(T,P)} = a / T + cP + e \quad (4)$$

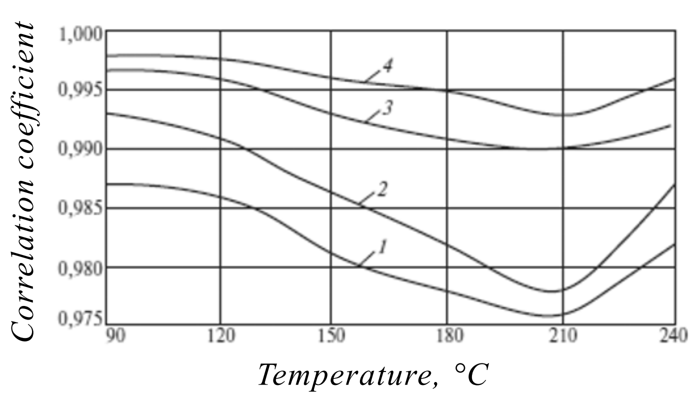

Fig. 6 Correlation coefficients for rheological models [1) Bingham; 2) power-law; 3) Herschel—Bulkley; 4) Casson] at different temperatures for the shear stress calculation.

where AV is the apparent viscosity; a, b, c, d are constants.

Combining equations (3) and (4), we obtain

$$\mu_e(T_2) = \mu_e(T_1)\mathbf{exp}\left[a\left(\frac{T_2 - T_1}{T_2 T_1}\right)\right] \quad AV_{(T,P)} = C\,\mathbf{exp}(A/T + BP) \tag{5}$$

$$AV_{(T,P)} = AC\,\mathbf{exp}(A/T + BP) \tag{6}$$

where A, B, e, C are constants.

In the fields, we need to predict the apparent viscosity of the drilling fluid at a certain depth from the known apparent viscosity at the wellhead. Obviously we need an equation relating the apparent viscosity downhole to the viscosity at the wellhead. In high-temperature and high-pressure wells, the drilling fluids returning to the wellhead have a high temperature. Therefore the apparent viscosity of the drilling fluid at 80°C was assumed to be equal to the apparent viscosity AV_0 of the fluid at the wellhead. In Eq. (6), the constant C can be replaced by AV_0. Then Eq. (6) takes on the form:

$$AV_{(T,P)} = AV_0\,\mathbf{exp}(A/T + BP) \tag{7}$$

where $AV_{(T,P)}$ is the apparent viscosity, mPa·s, at the downhole pressure and temperature; AV_0 is the apparent viscosity of the drilling fluid, mPa·s, at the temperature and pressure at the wellhead; P is the assumed pressure for the given fluid, MPa; A and B are the characteristic parameters of the drilling fluid.

The characteristic parameters A and B of the drilling fluid can be calculated by multiple linear regression. Table 3 gives the characteristic parameters of the prepared drilling fluids.

From Eq. (7) for known characteristic parameters, we calculated the values of the apparent viscosity of the drilling fluid *1* at different temperatures. The calculated and measured values of the apparent viscosity at a pressure of 5 MPa are compared in Table 4. We see that the largest relative error is 5.23%. The accuracy of the apparent viscosity measurement is affected by stirring time, stirring speed, shear stress, shear rate, and other factors. The relative error of the apparent viscosity measurement is about 10%, and the correlation coefficient of the mathematical model is greater than 0.99. Thus the mathematical model provides a calculation of very high accuracy. When the composition of the polymer in the drilling fluid is similar to that of the polymer we synthesized, the mathematical model obtained can be used to calculate the apparent viscosity of drilling fluids downhole [21].

The coefficients of the model (the temperature constant A and the pressure constant B) quantitatively characterize the dependence of the apparent viscosity of the drilling fluid on temperature and pressure, and show the change in rheological properties of the fluid with temperature and pressure. Analysis of the mathematical model lets us draw the following conclusions:

- The constant A shows that the effect of temperature on the apparent viscosity of the drilling fluid is determined by its composition;
- the constant B indicates that at constant temperature, the pressure has an insignificant effect on the apparent viscosity of the drilling fluid;
- the model obtained is applicable to calculation of the apparent viscosity of the drilling fluids containing the polymer at any depth, for known parameters A and B and the apparent viscosity of the fluid at the wellhead.

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