

# Research of polymer compositions rheological properties for oil production

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**Abstract.** In the present article the results of theoretical and laboratory researches for rheological performances of aqueous polymer solution, represented by hydrolyzed polyacrylonitrile and polymethacrylate (“Geopan” reagent), were considered. It was established that with increase of the polymer content in solution, the yield stress and, consequently, the plastic viscosity logarithmically increase. Repeatability of obtained laboratory data is confirmed by directly proportional dependence of the solution consistency coefficient on the polymer concentration. It was also found that with increase of the polymer content in solution, the flow index decreases according to a power law. With increase of a molecular weight, the polymer solution viscosity increases according to the power law, and the same behavior of curve is also observed for dependence of the molecular weight on the degree of hydrolysis. When the degree of hydrolysis increases, the molecular weight increases according to the power law. The results of the theoretical and laboratory researches shown in the present article may be used in modeling of such oil production processes as a polymer water-flooding and an in-situ water shutoff.

**Key words.** Hard to recover oil, polymer solution, rheological researches, effective viscosity, shear rate, shear stress.

## 1. Introduction

It is commonly known that currently a share of hard to recover oil reserves (HRR) in residual reserves grows steadily and it is associated with the active recovery of mobile oil reserves, the oil properties deterioration and the geologic aspects of the productive strata. In the work [1] according to data of oil reserves analysis in the Republic of Tatarstan (RT) and considering the usage of modern methods of oil production notes that the oil HRR account for 7.7% and the immobile oil reserves account for 61.4% of geologic reserves of oil. In general, the share of the oil HRR in Russian Federation is 78.7% as of 01. 01. 2013 [2]. Chemical reagents development for oil production objects, in particularly for the certain geology-physical

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conditions, is performed by carrying out of complex laboratory researches including the physical-chemical, rheological and filtration researches [3–8]. In this article we will consider the theoretical and practical part of the rheological researches of the polymer solutions and compositions, including those used for polymer water-flooding and in-situ water shutoff [9, 10].

## 2. Methodology

Determination of the effective viscosity of the polymer solutions was carried out according to [10] using Rheotest RN 4.1 general-purpose rotary viscometer having H2 cylindrical measurement system. Measurement method for the effective viscosity involves plotting of “viscosity curve” in controlled shear rate mode (CR test–Controlled Rate). Principle of the method is based on obtaining the dependence of the effective viscosity (shear stress) on shear rate (rotation frequency) at gradual increase of the last parameter from 0 up to 300 1/s (fluid viscosity curve).

## 3. Results of theoretical and practical research

As per to the flow and viscosity curves (dependence of the shear stress (Fig. 1, left part) and the effective viscosity (Fig. 1, right part) the polymer solutions relate to pseudoplastic fluids having yield strength according to [8–10]. The hydrolyzed polyacrylonitrile and polymethacrylate (the “Geopan” reagent) widely applicable in oil production was used as a target of research.

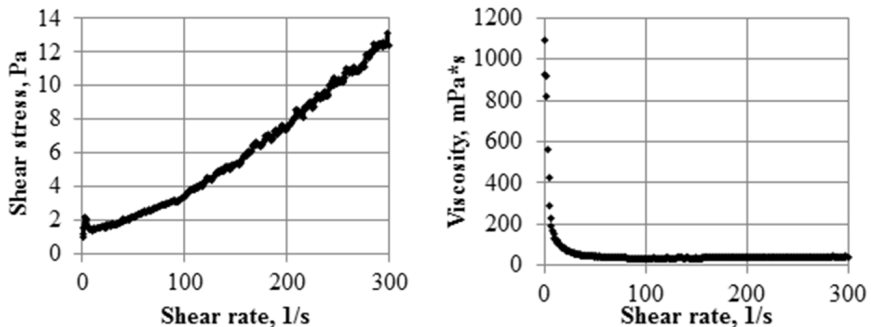


Fig. 1. Flow curve (left) and Viscosity curve (right) of 0.1% aqueous solution of the hydrolyzed polyacrylonitrile and polymethacrylate

Viscosity parameter ( $\mu$ ) of the polymer solutions can depend on minimum of 6 values, so that it can be represented as a function

$$\mu = f(S, T, P, D, t, EF). \quad (1)$$

According to the research results, the two molecular weights areas divided by

critical value  $M_c$  were determined:

$$\mu = a \cdot M^\alpha \text{ for } M < M_c, \mu = b \cdot M^\beta \text{ for } M \geq M_c. \quad (2)$$

Here,  $a$  and  $b$  are the specific constants of polymer-homologous range,  $\alpha$  is a value of the order of 1 (typically, more than 1) and  $\beta$  is a value close to 3.4–3.5.

In this work, the characteristic viscosity depends on the molecular weight as per formula [8]

$$M = 2.11 \cdot h^{0.75}. \quad (3)$$

where  $K$  is a constant, which depends on the nature of solvent, polymer and temperature and  $a$  is a constant determined by conformation of a macromolecule in solution (for flexible polymers:  $0.5 < a < 0.8$ ). A viscosity of polyesters melt depends on the degree of polymerization as per the following formula [10]

$$\ln \mu = \frac{A}{R} + \frac{B}{R} \sqrt{n} + \frac{C}{RT}, \quad (4)$$

where  $n$  denotes the degree of polymerization,  $T$  is the absolute temperature,  $R$  represents the universal gas constant and  $A$ ,  $B$ ,  $C$  are constants for the given polymer-homologous range.

Paper [9] provides the results for researches of the effective viscosity of the polymer solutions of different molecular weight and the degree of hydrolysis. On the basis of obtained data the dependences of  $\mu$  on  $M$  (Fig. 2) at different content of polymer in aqueous solution were plotted.

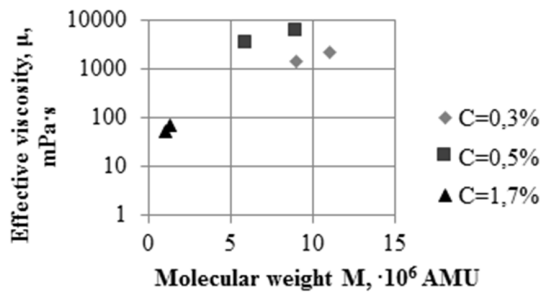


Fig. 2. Dependence of the effective viscosity of aqueous polyacrylamides solutions of different grades on molecular weights of PAA

With increasing the degree of hydrolysis of polyacrylamide the molecular weight increases according to the power law

$$M = 2.11 \cdot h^{0.75}. \quad (5)$$

In this case, the coefficient  $R^2 = 0.95$ .

The increase of molecular weight results in the increase in the effective viscosity. Consequently, with the increasing of value of  $h$ , the  $\mu$  value of PAA solutions increases.

The activation theory is associated with the activation energy  $E$  of fluid flow process which is described by the Arrhenius-Frenkel-Eyring (AFE) equation [9]

$$\mu = B \exp\left(\frac{E}{RT}\right), \quad (6)$$

where  $E$  is the activation energy of the flow process and  $B$  a constant.

When the value of  $B$ , which is weakly dependent on temperature, is specified, equation (6) can be rewritten as follows:

$$\mu = B \cdot T^{\frac{3}{2}} \exp\left(\frac{E}{RT}\right). \quad (7)$$

As per the free-volume theory, the temperature dependence of the viscosity is associated with a free volume. The Dependence of the free volume  $v_f$  on temperature can be shown by the M. Williams, R. Landel and J. Ferry formula

$$v_f = v_{f,g}(1 + \alpha_0(T - T_g)), \quad (8)$$

(8) where  $T_g$  is the glass transition temperature,  $v_{f,g}$  is the value of  $v_f$  at  $T = T_g$  and  $\alpha_0$  is the thermal expansion coefficient of the free volume.

Then the viscosity can be determined according to the researches A. Doolittle and T. Fox by formula

$$\mu = A' \cdot \exp\left(\frac{B_0 v}{v_f}\right), \quad (9)$$

where  $A'$  and  $B_0$  are constants.

G. Falcher and G. Tamman proposed a modification of the free-volume theory using formulas

$$\mu = A \cdot \exp\left(\frac{B}{T - T_0}\right), \quad B = \frac{b_0 v_0}{2.3 \alpha'_0}. \quad (10)$$

Summarizing the formulas applied in the activation theory and the free-volume theory, the viscosity can be determined by the following equation

$$\mu = A \cdot \exp\left(\frac{B}{T - T_0} + \frac{E_v^*}{RT}\right). \quad (11)$$

The empirical coefficients and the determinacy coefficients for the equations of dependence of the effective viscosity on temperature are listed in Table 1.

According to the results of the laboratory researches of the hydrolyzed polyacrylonitrile and polymethacrylate the following dependence of the effective viscosity of the "Geopan" aqueous solutions was established

$$\mu = A \cdot \exp(-BT), \quad (12)$$

where  $A$  and  $B$  are the empirical coefficients.

Table 1. The empirical coefficients and the determinacy coefficients for the equations of dependence of the effective viscosity on temperature

No.	Shear rate	Polymer content in the polymer solution (% wt)								
		0.1			0.5			1		
		A	B	R <sup>2</sup>	A	B	R <sup>2</sup>	A	B	R <sup>2</sup>
1	0.1	1320	0,010	0.86	44713	0.030	0.96	119634	0.025	1
2	1	459	0.010	0.95	5908	0.018	0.96	15465	0.016	1
3	10	160	0.011	0.99	781	0.007	0.94	1999	0.007	0.99
4	50	76	0.011	0.99	240	0.003	0.96	528	0.001	0.92
5	100	41	0.011	0.96	153	0.003	0.98	318	0.002	0.76
6	200	41	0.011	0.96	121	0.008	0.92	228	0.004	0.79
7	300	34	0.011	0.96	121	0.011	0.98	221	0.009	0.99

The influence of pressure on viscosity of polymer systems is poorly studied [9]. In the same work an exponential relationship between initial viscosity and pressure in the low values area is specified

$$\mu_P = \mu_A \exp^{\delta P}, \quad (13)$$

where  $\mu_P$  is the viscosity value at pressure  $P$ ,  $\mu_A$  denotes the the viscosity at the atmospheric pressure and  $\delta$  is a constant coefficient (which has a value of the order of several thousands of reciprocal bars).

As previously stated, the dependence of the viscosity on shear rate predetermines the behavior of non-Newtonian fluid. The issue regarding the viscosity changing depending on shear rate (viscosity curve) and on shear stress for the polymer solutions was quite well studied [4, 9] and so on.

For example, in the works of Vinogradov and Malkin the empirical formulas are given which describe the changing of viscosity depending on shear rate and on shear stress.

According to the results of our researches the power-law relations (Fig. 3) between the effective viscosity and the shear rate  $D$

$$\mu = \mu_0 + \frac{a}{D^b}, \quad (14)$$

where  $a$  and  $b$  are empirical coefficients,  $\mu_0$  is the «initial» viscosity, corresponding to the yield strength  $\tau_0$ .

From the formulas of the dependence of the effective viscosity on the shear rate which are represented in the theoretical part of the article, the Herschel-Bulkley model is one of the most completely models describing the results obtained. The values of the empirical coefficients and the plastic viscosity of 0.1, 0.5 and 1 % aqueous solutions of the hydrolyzed polyacrylonitrile and polymethacrylate are summarized in Table 2.

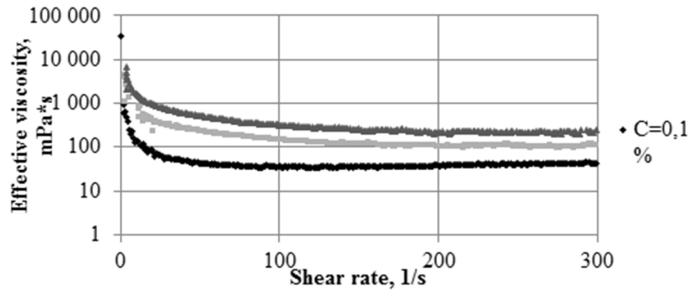


Fig. 3. Dependence of the effective viscosity of the polymer solutions with different concentration on the shear rate

Table 2. The empirical coefficients and the plastic viscosity of 0.1, 0.5 and 1 % aqueous solutions of the "Geopan" as per the Herschel-Bulkley model

No.	Polymer content $C$ in the polymer solution (% wt)	«Initial» viscosity corresponding to yield strength $\tau_0$ (plastic viscosity) $\mu_0$ ( $\mu_p$ )	Consistency factor $K$	Flow index $n$
1	0.1	892	366	0.551
2	0.5	4339	2806	0.382
3	1	6527	6267	0.374

As a result of the analysis of the rheological performances of the "Geopan" aqueous solution, the following is revealed that:

1) With increase of the polymer content in solution the yield strength increases and, correspondingly, the plastic viscosity increases logarithmically. Moreover, the solution consistency coefficient is directly proportional to the polymer concentration, and it indicates the repeatability of the obtained laboratory data.

2) With increase of the polymer content in solution the flow index decreases according to the power law.

## 4. Conclusion

The results of the laboratory and theoretical researches obtained in the present study are important for modeling of such oil production processes as the polymer water-flooding and the in-situ water shutoff. When performing the process activities associated with flooding of the polymer solution into stratum, it is necessary to obtain the reliable values of the viscosity depending on geology-physical conditions of the stratum. In the absence of taking into account of the influence of the physical parameters reviewed above on the viscosity and its incorrect determination it can result in the negative results, for example, the uncontrolled formation of high-conductive crack.

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