Rheological Behaviour of Some Dilute Polymer Solutions

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ABSTRACT   Rheological characteristics of dilute aqueous solutions of three types of commercial polymer were investigated using a rotational viscometer.

The polymer concentrations were varied between 500 ppm and 3000 ppm at a temperature range between 20°C and 65°C. Shear rate ranged between 5.41 S^{-1} and 692.48 S^{-1}.

A new proposed correlation for the viscosity of dilute polymer solution as a function of temperature, shear rate and concentration has been suggested using a multiple linear regression program as

$$\eta = A_1 \left[\exp\left(B_1 / T\right)\right] \; \dot{\gamma}^{C_1} \left[\exp\left(D_1 C\right)\right]$$

The proposed correlation was found to fit the experimental data adequately. A coefficient of determination ranging between 0.98 and 0.99 is reported.

1. Introduction

For many simple fluids the study of rheology involves the measurements of viscosity. For such fluids the viscosity depends primarily upon the temperature and hydrostatic pressure. However, the rheology of polymers is much more complex because polymeric fluids show non-ideal and complex shear viscosity behaviour.

The subject of rheology is extremely important for polymers, since the flow behaviour is important in processing and fabricating such polymers in order to make useful objects[1]. It is also very important in injection molding, compression molding, blow molding, calendering, cold-forming, and in the spinning of fibers. Rheology is important also in the formulation of polymeric material in preparing them for fabrication processes[2]. Mill rolling and extrusion processes are typical examples.

Rheology is involved in many other aspects of polymer science. For example,

many polymers are made from emulsions of monomers in stirred reaction vessels. The resulting lattices flow through pipes and may end up as a paint which is applied to a surface by some processes in which the rheological properties of latex must be controlled carefully[2].

Polymer additives are used extensively to modify the rheological properties of solutions in a wide variety of industrial applications. An increasingly important application is also found in the field of enhanced oil recovery (EOR), principally as a means of increasing the viscosity of drive fluids in petroleum reservoirs. In EOR processes, the polymer solution flows through a complex network of fine pores. The in-situ viscosity is, therefore, a very important factor governing both the rate of flow and distribution of polymer solution and associated immiscible liquids in the reservoir porous media[3]. Concentrations of only a few hundred ppm of polymer in water can provide greatly increased viscosities[4]. However, the requirements for even a small EOR project are very large.

Polymer solutions are characterized as dilute or concentrated. It is difficult to distinguish between these two terms[5]. Many formulas describing the viscosity behaviour of dilute polymer solution are presented by Van Krevelen[6], Bird et al.[7], and Buchholz[8]. While for concentrated polymer solution, there are other correlations given by Nielsen[2], Lyonds and Tobolsky[9], Kulicke and Hass[10], and Van Krevelen[6].

Most well known expression describing the effect of temperature on the viscosity was proposed by Eyring[11] as

$$\eta = K_1 \exp (E_0 / RT) \tag{1}$$

However, Amin and Maddox[12] have reviewed most common correlation used for the prediction of liquid viscosity as function of temperature.

A number of proposed empirical equations describing the effect of shear rate on liquid viscosity may be found in, Bird and Sadowski[13], Bouldin et al.[14], Nielsen[2], and Van Krevelen[6]. The most popular equation represents the so-called power law model formulated by Ostwald and Waele was given as[7]

$$\eta = K \dot{\gamma}^{n-1}$$

or as

$$\tau = K \dot{\gamma}^{n} \tag{2}$$

Recently, Al-Fariss et al.[15] have propsed a correlation for the viscosity of waxy oils as a function of temperature and shear rate.

The purpose of this work is; first, to extend the above work by investigating experimentally the effect of polymer concentration on polymer solution rheology. Second, to develop a generalized correlation for the viscosity as function of temperature, shear rate, and polymer concentration.

2. Mathematical Modelling

Although many workers[14-18] have proposed expressions describing the depen-

dence of polymer solution viscosity on temperature and shear rate, yet literature lacks correlations which include the effect of polymer concentration as well as temperature and shear rate in one general formula.

Due to the sensitivity of the viscosity of polymer solutions to temperature, shear rate and concentration, a large amount of data is needed to characterize the flow behaviour of these solutions.

According to Eyring equation (1), the temperature dependence of viscosity of Newtonian fluids was given as

$$\eta \; \alpha \; \exp{(E_0 / RT)} \tag{3}$$

While the effect of shear rate on viscosity may be expressed according to the power law as

$$\eta \; \alpha \; \dot{\gamma}^{n-1} \tag{4}$$

Thus from (3) and (4), the correlation relating viscosity temperature and shear rate can be written as[1]

$$\eta \; = \; A_1 \; \exp{(B_1 / T)} \; \dot{\gamma}^{C_1} \tag{5}$$

In this work the effect of polymer concentration on the viscosity of polymer solution has been investigated experimentally. Different type of expressions for the effect of concentration were superimposed on equation (5) to fit the experimental data obtained. However, our proposed expression to predict the viscosity of the polymer solutions is

$$\eta \; = \; A_1 \; [\exp{(B_1 / T)}] \; \dot{\gamma}^{C_1} \; [\exp{(D_1 \, C)}] \tag{6}$$

where, A_1, B_1, C_1 and D_1 are constants, and
  $T \; = \;$ temperature in K
  $\dot{\gamma} \; = \;$ shear rate in s^{-1}
  $C \; = \;$ concentration of the polymer in ppm.

Statistical analysis of the suggested correlation (6) has been performed using the SAS package for the data points obtained experimentally. The analysis proved that equation (6) is best fitting. More details of the analysis can be found in reference[19].

3. Experimental Work

3.1 · Sample Preparation

Three different types of polymer solutions were prepared with different concentrations. Those polymers are PUSHER 700, ROHAGIT F 700 and FLOCON 4800 CT. For PUSHER 700 and ROHAGIT F 700 type polymer, six different concentrations of the polymer solutions were prepared, these concentraitons ranged from 500 to 3000 ppm. While four different concentrations were prepared of FLOCON 4800 CT between 1500 to 3000 ppm. Brief description of these polymers are given in the appendix.

The polymer solutions were prepared by gradual addition of small amounts of the pure polymer to a measured amount of distilled water. Continuous magnetic stirring and heating was necessary for the dissolution of the polymer during the addition process. The gradual addition of the polymer was necessary to avoid agglomeration of the polymer.

However, more time and higher temperature were needed for the dissolution of the polymers causing higher viscosity in the solution, for example; at 50-60°C, ten to fifteen hours were required by PUSHER-type polymer to dissolve depending on the required concentration. Meanwhile, for ROHAGIT samples the necessary time for dissolution was an average of six to nine hours at a temperature of 40-50°C. Finally, FLOCON samples took four to six hours to dissolve. In this case stirring alone proved to be satisfactory for dissolution.

3.2 Shear Stress-Shear Rate Measurements

The viscometer used in this study to measure the shear stress versus shear rate of the polymer solutions was a HAAKE ROTO-VISCO Model RV-12, a rotating bob type coaxial cylinder viscometer. The outer stationary cylinder (cup) is surrounded by a temperature controlled water jacket. Inside the cup there is an inner cylinder (bob) of smaller diameter which rotates to shear the polymer solution in the gap between cup and bob. Details of the experimental set up and technique are given in reference [19].

Shear stress and shear rates were measured at 10 different temperatures 20-65°C (293-338 K) by 5°C increment.

4. Results and Discussion

The rheological behaviour of three different polymer solutions was investigated. For a given temperature and concentration the values of the shear rate ($\dot{\gamma}$) and the shear stress (τ) were determined experimentally. For PUSHER 700 and ROHAGIT F 700 polymer solutions the temperature was varied stepwise between 20-65°C (293-338 K) for every concentration of the polymer solutions in the range 500-3000 ppm. The concentrations of the FLOCON 4800 CT polymer solutions were varied between 1500 and 3000 ppm. Using the same temperatures as for the first two polymer solutions. In each experiment, the shear rate was changed from 5.41 to 692.48 s^{-1}.

The consistency index K and the flow behaviour index n in the power law (equation 2) have been determined experimentally by the regression analysis of each set of data obtained for a given temperature and concentration. The data of log τ versus log $\dot{\gamma}$ were fitted to a straight line. From the slope of this line the value of n was obtained, while the value of K was determined from the intercept.

The flow behaviour index n is a measure of the non-Newtonian behaviour. The value of n is less than unity for shear thinning substances. The consistency index K is a function of the viscosity of the solution.

The coefficient of determination R^2 was calculated by fitting the viscometric data points to the power law. R^2 was found to be very close to one, which means that the power law is very adequate to describe the rheological behaviour of the polymer solutions used.

Tables 1, 2, and 3 show the rheological characteristics of the three polymers tested. It is clear that the value of K decreases with increasing temperature for a given concentration. This is expected since K is a direct function of the viscosity, while values of the flow behaviour index n is less than unity, *i.e.*, shear thinning behaviour. Typical graph for shear stress-shear rate behaviour for the polymer solution (PUSHER 700) is shown in Fig. 1. The solid line represents the power law model fit for the experimental data. Similar behaviour was noticed with the other two polymer solutions (ROHAGIT F 700 and FOLCON 4800 CT).

It is necessary to collect as many viscometeric data as possible to get a more precise formula that describes the viscosity of a polymer solution as a function of temperature T, shear rate $\dot{\gamma}$ and concentration C.

A correlation for the viscosity η as a function of T, $\dot{\gamma}$ and C of the following form was proposed as

$$\eta = A_1 \left[\exp \left(B_1 / T \right) \right] \dot{\gamma}^{C_1} \left[\exp \left(D_1 C \right) \right] \qquad (6)$$

TABLE 1. Rheological characteristics of PUSHER 700 polymer solutions.

Concentration of polymer, C = 2000 PPM.			
T (K)	n (–)	K (Pa. s^n)	R^2 (–)
293	0.3936	0.5635	0.997
298	0.4326	0.4034	0.997
303	0.4513	0.3487	0.999
308	0.4500	0.3425	0.999
313	0.4521	0.3334	0.999
318	0.4537	0.3254	0.999
323	0.4505	0.3216	1.000
328	0.4478	0.3179	0.999
333	0.4459	0.3137	1.000
338	0.4439	0.3098	0.999
Concentration of polymer, C = 3000 PPM.			
293	0.4086	0.9692	1.000
298	0.4077	0.9439	1.000
303	0.4055	0.9171	0.999
308	0.4005	0.9080	0.999
313	0.4042	0.8575	0.999
318	0.4107	0.8102	0.999
323	0.4083	0.7972	0.999
328	0.4105	0.7668	0.999
333	0.4174	0.7231	0.999
338	0.4249	0.6827	0.998

TABLE 2. Rheological characteristics of ROHAGIT F 700 polymer solutions.

Concentration of polymer, C = 2000 PPM.			
T (K)	n (–)	K (Pa. s^n)	R^2 (–)
293	0.7951	2.2978×10^{-2}	0.997
298	0.7925	2.2454×10^{-2}	0.999
303	0.8006	1.9666×10^{-2}	0.999
308	0.8230	1.6304×10^{-2}	0.999
313	0.8339	1.4211×10^{-2}	0.998
318	0.8580	1.1705×10^{-2}	0.999
323	0.8633	1.0907×10^{-2}	0.999
328	0.8878	9.2094×10^{-3}	0.999
333	0.8851	8.5956×10^{-3}	0.996
338	0.9052	7.0452×10^{-3}	0.997
Concentration of polymer, C = 3000 PPM.			
293	0.7086	6.2613×10^{-2}	0.999
298	0.7092	5.7820×10^{-2}	0.999
303	0.7158	5.4242×10^{-2}	0.997
308	0.7094	5.2213×10^{-2}	0.998
313	0.7195	4.7637×10^{-2}	0.997
318	0.7190	4.4719×10^{-2}	0.997
323	0.7240	4.1759×10^{-2}	0.997
328	0.7282	3.8564×10^{-2}	0.997
333	0.7456	3.2418×10^{-2}	0.998
338	0.7902	2.9400×10^{-2}	0.997

TABLE 3. Rheological characteristics of FLOCON 4800 polymer solutions.

Concentration of polymer, C = 2000 PPM.			
T (K)	n (–)	K (Pa. s^n)	R^2 (–)
293	0.7475	9.3728×10^{-3}	0.996
303	0.7782	6.7690×10^{-3}	0.996
313	0.7773	5.6497×10^{-3}	0.994
323	0.7879	4.7309×10^{-3}	0.995
333	0.7495	5.0065×10^{-3}	0.995
Concentration of polymer, C = 3000 PPM.			
293	0.6973	1.5879×10^{-2}	0.997
303	0.6926	1.3533×10^{-2}	0.995
313	0.6774	1.2218×10^{-2}	0.988
323	0.7064	9.2632×10^{-3}	0.999
333	0.7235	7.3044×10^{-3}	0.980

The optimum values of the model coefficients (A_1, B_1, C_1, and D_1) were deter-mined by using statistical analysis package SAS. The values of these coefficients are listed in Table 4.

From Table 4, it is clear that the exponent of the shear rate (C_1) can be changed
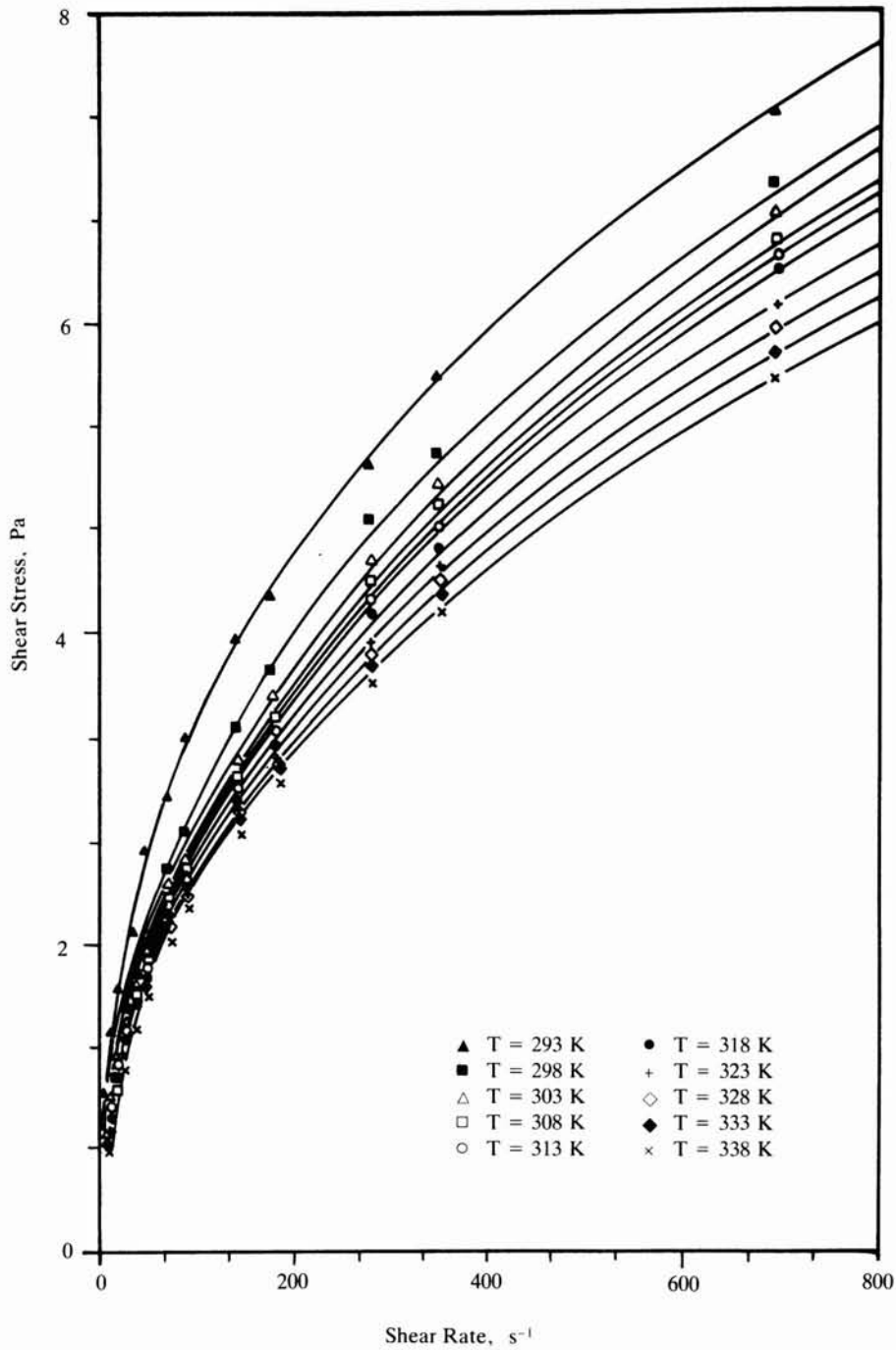
FIG. 1. Shear stress-shear rate curves for polymer solution (PUSHER 700 at 2000 ppm), where solid lines represent power law model fit.

TABLE 4. The optimum values for the coefficients of the proposed model (equation 6).

Polymer	$A_1 \times 10^2$ m. Pa. $s^{(C_1 + 1)}$	B_1 K	C_1 (-)	$D_1 \times 10^4$ (ppm^{-1})
PUSHER 700	436.9	957.5	- 0.5391	6.6262
ROHAGIT F 700	3.552	1477.9	- 0.1703	6.8618
FLOCON 4800 CT	3.591	1480.0	- 0.2731	2.9889

from zero to unity for pseusoplastic fluids and it indicates the degree of deviation from Newtonian behaviour. ROHAGIT F 700 and FLOCON 4800 CT type polymer solutions have the smallest value of C_1 while PUSHER 700 type polymer solution has the highest value of C_1 which indicates that it has more deviation from Newtonian behaviour than the other two polymer solutions.

Figure 2 shows the predicted and experimental values of the viscosity η versus the shear rate for different temperatures for PUSHER 700 polymer solution at 1500 ppm concentration. From this figure the following points are noticed:

a) For the same temperature and concentration the viscosity η varies exponentially with the shear rate.
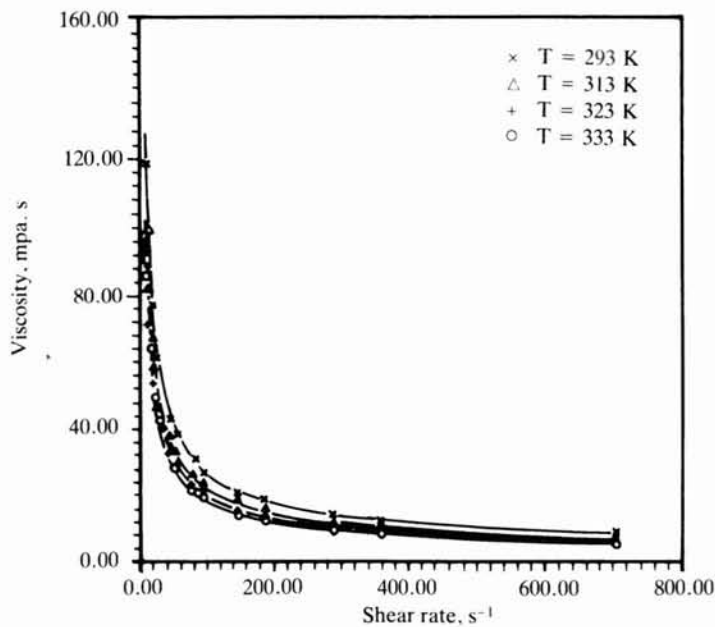

FIG. 2. Viscosity vs shear rate for polymer solution (PUSHER 700 at 1500 ppm), where solid lines represent the proposed correlation fit (equation 6).

b) The drop in viscosity η is very sharp as shear rate $\dot{\gamma}$ increases slightly at low levels of $\dot{\gamma}$. This sensitivity vanishes rapidly at the higher values of $\dot{\gamma}$.

c) The higher the temperature the lower will be the viscosity at the same shear rate.

The variation of viscosity with shear rate for different concentrations ranging between 1000 and 3000 ppm are illustrated on Fig. 3. Again viscosity varies exponentially with shear rate and sensitivity is maximum at lower levels of shear rate. For the same shear rate, it is seen that viscosity increases as the concentration increase too.
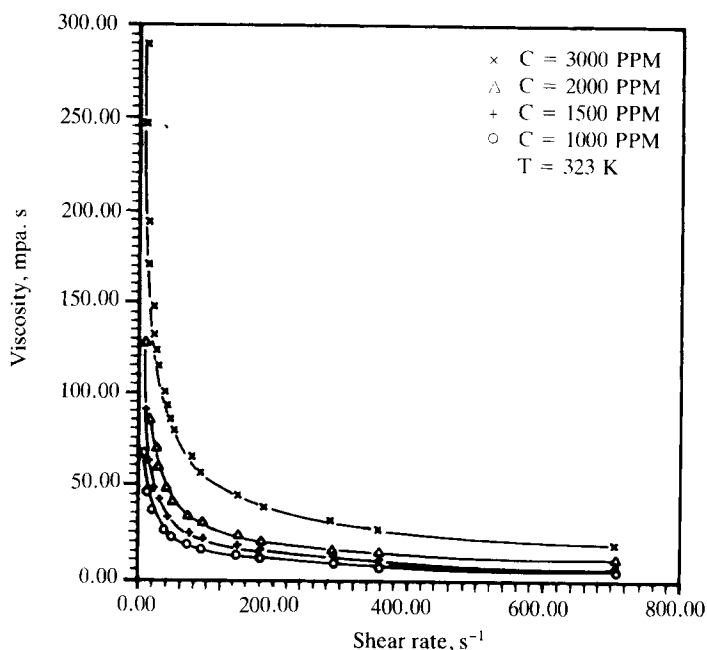

FIG. 3. Viscosity vs shear rate for polymer solution (PUSHER 700), where solid lines represent the proposed correlation fit (equation 6).

Similar curves have been plotted for the other two polymer solutions (ROHAGIT F 700 and FLOCON 4800 CT). Figures 4 and 5 are for ROHOGIT F 700 polymer solutions, while Fig. 6 and 7 are for FLOCON 4800 CT polymer solutions.

The same features outlined and discussed for the PUSHER 700 polymer solution are noticed in the two other polymer solutions.

However, to illustrate the basic difference between the behaviour of different polymer solutions under the same conditions of temperature, shear rate, and concentration the viscosity η has been plotted in Fig. 8 against $\dot{\gamma}$ for a fixed concentration and a fixed temperature. From this figure it is clear that polymer solution of PUSHER 700 has the highest viscosity followed by the ROHAGIT F 700, while the solution of FLOCON 4800 CT has the lowest viscosity under identical conditions.

PUSHER 700 polymer solutions show a value of 3.12% average error as a mean value for the whole data points which seems to be the smallest value than ROHAGIT F 700 and FLOCON 4800 CT polymer solutions. This is due to the high sensitivity of
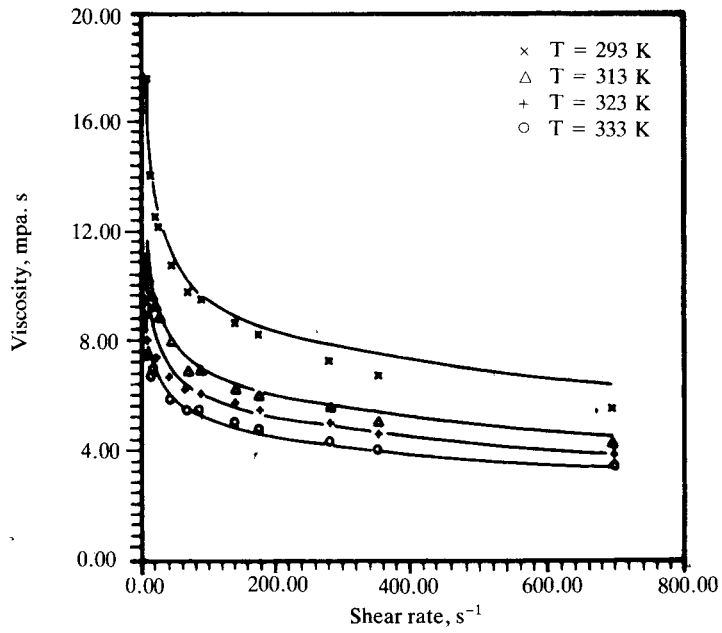
FIG. 4. Viscosity vs shear rate for polymer solution (ROHABIT F 700 at 2000 ppm), where solid lines represent the proposed correlation fit (equation 6).
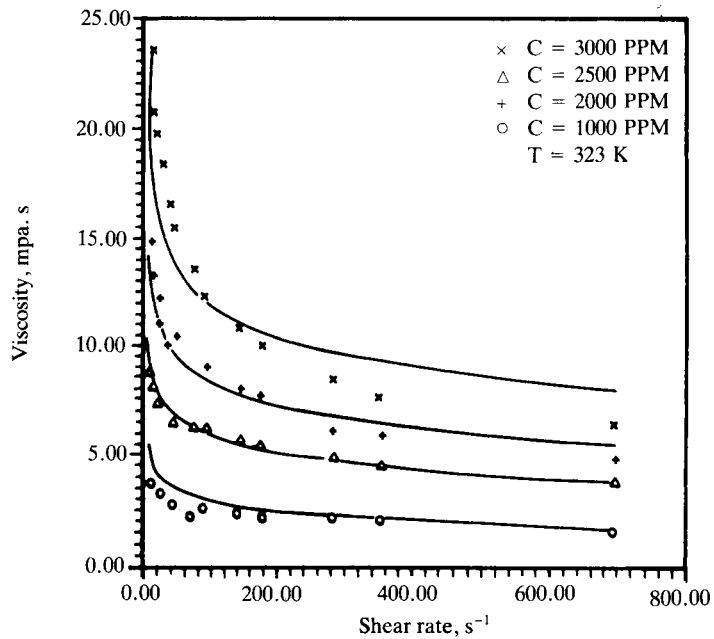

FIG. 5. Viscosity vs shear rate for polymer solution (ROHAGIT F 700), where solid lines represent the proposed correlation fit (equation 6).
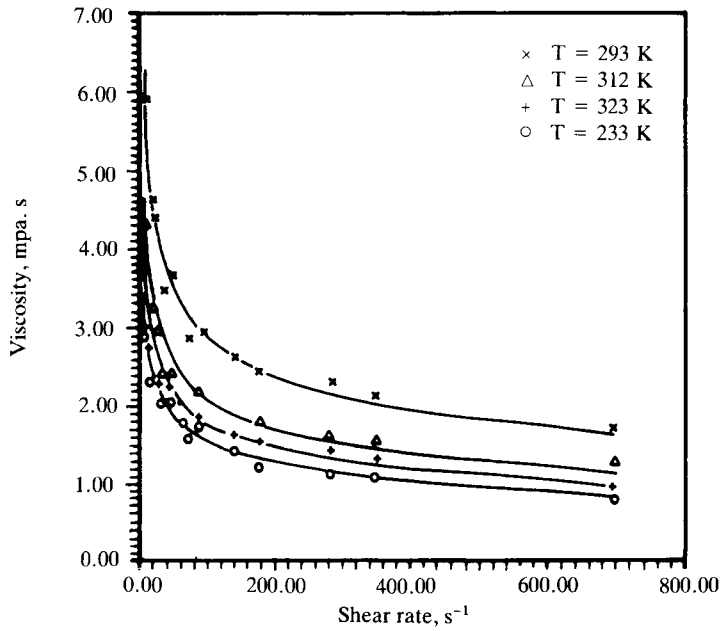
FIG. 6. Viscosity vs shear rate for polymer solution (FLOCON 4800 CT at 2000 ppm), where solid lines represent the proposed correlation fit.
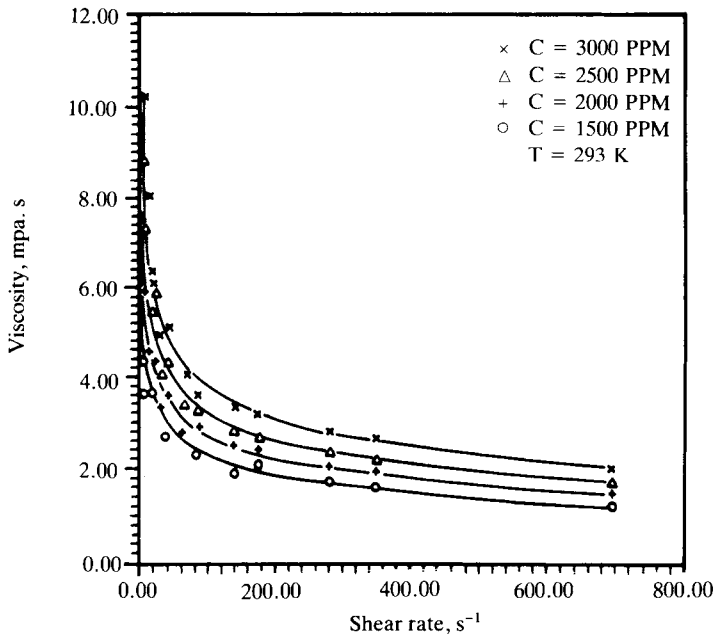

FIG. 7. Viscosity vs shear rate for polymer solution (FLOCON 4800 CT), where solid lines represent the proposed correlation fit (equation 6).
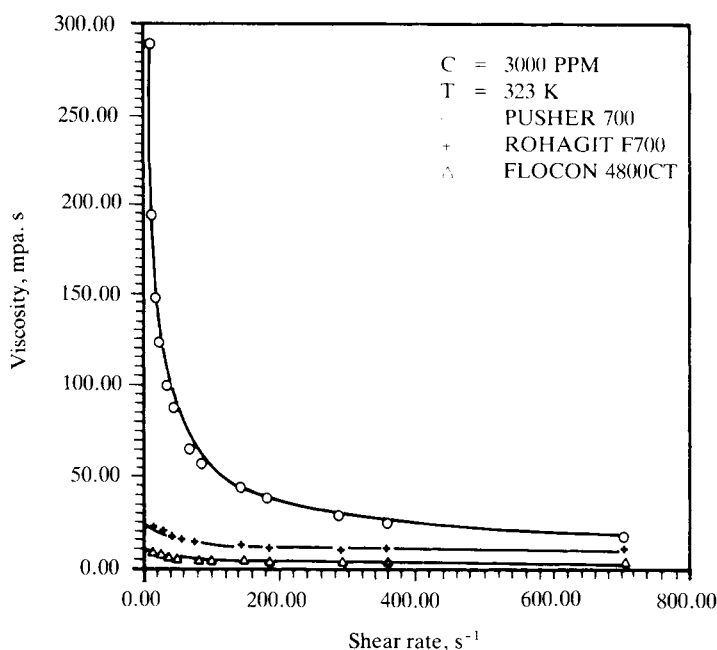
FIG. 8. Viscosity vs shear rate for different types of polymer solutions, where solid lines represent the proposed correlation fit (equation 6).

the viscometer to this type of polymer solutions (PUSHER 700). Meanwhile the average errors of ROHAGIT F 700 and FLOCON 4800 CT are 8.54 and 9.65% respectively.

5. Conclusion

A correlation has been proposed to predict the viscosity of three different polymer solutions as a function of temperature, shear rate, and concentration. The developed correlation can be used for both Newtonian and non-Newtonian liquids. It fits adequately the experimental data of polymer solutions tested. The proposed equation gives an average absolute errors of 3.12% for PUSHER 700, 8.54% for ROHAGIT F 700, and 9.65% for FLOCON 4800 CT, with coefficient of determination ranging from 0.98 to 0.99.

List of Symbols

A_1 Constant as defined in equation (5,6) (m. Pa. $s^{(C_1 \cdot 1)}$).
B_1 Constant as defined in equation (5,6) (K).
C Concentration of the polymer in the solution (ppm).
C_1 Constant as defined in equation (5,6) (–).
D_1 Constant as defined in equation (6) (ppm^{-1}).
E_0 Energy of activation (kJ/kg. mole).
K Consistency index (Pa. s^n).

K_1 Constant as defined in equation (1) (–).

n Flow behaviour index (–).

R_2 Coefficient of determination.

R Gas constant (m^3. Pa/kg. mol. K).

T Temperature (K).

t Time (s).

τ Shear stress (N/m^2).

$\dot{\gamma}$ Shear rate (dV/dy) (S^{-1}).

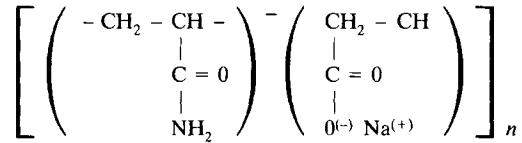μ Viscosity of polymer solution (m.Pa.s).

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Appendix

Brief Description of the Polymers Tested in this Study

1 – PUSHER 700

This type of polymer is polyacrylamide-CO sodium acrylate in the powder form. (Trade mark of the DOW Chemical Company). The molecular weight of PUSHER 700 is 14.07×10^4 while the repeating unit of the hydrolyzed polyacrylamide is

$$\left[\left(\begin{array}{c} - CH_2 - CH - \\ | \\ C = 0 \\ | \\ NH_2 \end{array} \right) - \left(\begin{array}{c} CH_2 - CH \\ | \\ C = 0 \\ | \\ 0^{(-)} \; Na^{(+)} \end{array} \right) \right]_n$$

2 – ROHAGIT F 700

ROHAGIT F 700 is a nonionic acrylamide-based polymer in the powder form. This type of polymer is manufactured by ROHM Company in Germany. It can be classified as water-soluble acrylic resins. The range of density of this polymer is (750-850 gm/cm³) while the pH value is $7+0.5$.

3 – FLOCON 4800 CT

FLOCON 4800 CT is a polysaccharide bio-polymer manufactured by Pfizer Chemicals Ltd. It is a 13% active aqueous solution of xanthan gum which has a molecular weight greater than one million.

الخــواص الانسيابيــة لبعض محاليل البلـمرات المخفــفة

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الريـــاض – المملكة العربية السعودية

المستخلص . تمت دراسـة ثلاثـة أنواع من محاليل البلمرات التجارية المخففة باستعمال جهاز قياس اللزوجة الدوراني ، وكانت تراكيز تلك المحاليل تتراوح بين ٥٠٠ و ٣٠٠٠ جزء بالمليون ، ودرجات حرارة بين ٢٠ و ٦٥ درجة مئوية ، ودرجة إجهاد القص تتراوح بين ٤١,٥ و ٤٥,٦٩٢ من الثانية .

وتم استحداث علاقة رياضية تربط بين لزوجة محاليل البلمرات المخففة ، إجهاد القص ودرجة الحرارة وتركيز البلمرات باستخدام برنامج حاسب آلي مطور على الشكل التالي

$$\eta = A_1 [\exp(B_1/T)] \ \dot{\gamma}^{C_1} [\exp(D_1 C)]$$

وأظهرت النتائج المختبرية تطابقًا معقولًا مع العلاقة الرياضية المقترحة في هذا البحث .