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Empirical Correlations for Viscosity of Polyacrylamide Solutions with the Effects of Concentration, Molecular Weight and Degree of Hydrolysis of Polymer

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Abstract: In this study, an extensive experimental work has been conducted to develop a set of correlations to predict the viscosity of partially hydrolyzed polyacrylamide solutions. These correlations account for the individual as well as combined effects of four major parameters; namely, shear rate, concentration, molecular weight and degree of hydrolysis, on polymer solution viscosities. Viscosities of various polymers solutions have been measured. The power law model for the viscosity has been modified to accommodate these four major parameters on which the polymer viscosity is dependent. Non-linear regression analyses on the experimental data were performed to develop the correlations presented in this study. These correlations can be integrated into any reservoir simulator and also for the initial screening for the selection of the polymer for enhanced oil recovery processes.

Key words: Viscosity, enhanced oil recovery, polyacrylamide solution

INTRODUCTION

In majority of oil reservoirs, a significant amount of oil is still left after water flooding. Water being more mobile will flow the path of least resistance and hence water channeling occurs resulting the oil to be by passed and left trapped in the porous media. Polymer is injected in the reservoir to viscosify the injected brine and to reduce its mobility and the viscosity contrast between the reservoir saline and the crude oil, thereby to improve the sweep efficiency (Wang and Caudle, 1970; Chatterji and Borchardt, 1981; Lee *et al.*, 2009).

The conventional polymer such as partially hydrolyzed polyacrylamide (HPAM) is commonly used in the Enhanced Oil Recovery (EOR) processes to control the mobility ratio and to improve the sweep efficiency (Myagchenkov and Kurenkov, 1991; Lee *et al.*, 2009). HPAM is a synthetic polymer consisted of straight chains of acrylamide monomers some of which has been hydrolyzed. A typical property of polymers used in the Chemical Enhanced Oil Recovery (CEOR) is their shear thinning (pseudoplastic) behavior. This feature allows these polymers to be injected without excessive pressure

drop. However, at the same time this property is a weakness in displacing the bypassed oil from the porous media. This is because when the polymer solution passes through the high permeability zone or flow at high rates, the mechanical degradation may occur, thereby decreasing the viscosity of polymer solution. The viscosity of the polymer solutions exhibiting shear thinning behavior can be modeled by a simple power-law (Nouri and Root, 1971; Mungan, 1972; Teeuw and Hesselink, 1980; Cannella *et al.*, 1988; Nasr-El-Din *et al.*, 1991; Delshad *et al.*, 2008):

$$\mu = k\gamma^{n-1} \quad (1)$$

where, μ is the viscosity (Pa.s), k is the flow consistency index (Pa.sⁿ), n is the flow behavior index (unitless) and γ is the shear rate (1 sec).

The concentration of the polymer has a pronounced effect on the apparent viscosity of the solution. With the increase in the concentration of polymer, the viscosity will be increased. Due to the increased number of polymer molecules in the solution, the interaction between the polymer chains will be more. The molecular weight of the polymer has a drastic effect on the polymer solution

viscosity. The higher molecular weight polymers will have higher hydrodynamic radius and charge density per molecule.

The objective of this study is to provide a set of correlations to predict viscosity of polymer solutions that account for the individual effects of four major parameters; namely, shear rate, concentration, molecular weight and degree of hydrolysis, as well as the combined effects of all these four parameters on polymer solutions. For this purpose, an extensive experimental work has been conducted to measure the viscosity of polymer solutions as a function of the above mentioned parameters.

MATERIALS AND METHODS

Chemicals and equipment: The details of the properties of polymers used in this study are described in Table 1. The equipment required to prepare polymer solutions include; weighing balance, magnetic stir plates, magnetic bars, breakers and filter press unit.

Fluid preparation procedure: Solutions of polyacrylamide powders were prepared as a stock solution and were then diluted to the required test concentrations. Vigorous agitation was necessary for the initial dispersion of the dry powder. As soon as the entire polymer has been added, the stirrer was adjusted to a low speed that just keeps the solid particles from settling to the bottom. The lowest possible speed was used to avoid mechanical degradation of the polymer solution. The stirring of the solution was continued at low speed for 2 or 3 hours and was left to stand overnight. Solutions were then ready for desired dilution by gently mixing the required amount of concentrate and deionized water. All the solutions were prepared according to the API standard.

A fully hydrated polymer solution was then filtered through cellulose filter study, under 15 psi at a relatively constant rate. The polymer solutions with the filtration ratio of less than 1.2 were only used for the viscosity measurement (Delshad *et al.*, 2008).

Viscometric experiments: The OFITE M-1100 HPHT viscometer was used to measure bulk viscosities over the range of shear rates. The OFITE M-1100 viscometer can measure viscosities at shear rates as low as 0.01 1 sec⁻¹ to 10001 sec⁻¹. All the solutions were tested at 25°C and the solutions were prepared in distilled water.

To develop the correlations to be discussed in the next section, total of nine polymer solutions were prepared, details are given in Table 2 and then for each

Table 1: Polymers and their molecular weight and degree of hydrolysis used in this study

Polymer name	Molecular weight (X 10 ⁶)	Degree of hydrolysis (%)
3630-S	20	30
3530-S	16	30
3430-S	12	30
3330-S	8	30
1630-S	16	20

Table 2: Polymer solution names and their concentrations used in the study

3630 S		1630 S		3330 S	
Solution name	Concentration (ppm)	Solution name	Concentration (ppm)	Solution name	Concentration (ppm)
3630	4000	1630	4000	3330	4000
A-SS	3000	A-SS	3000	A-SS	3630
A-1		A-1		A-1	
3630	2000	1630	2000	3330	2000
A-2		A-2		A-2	

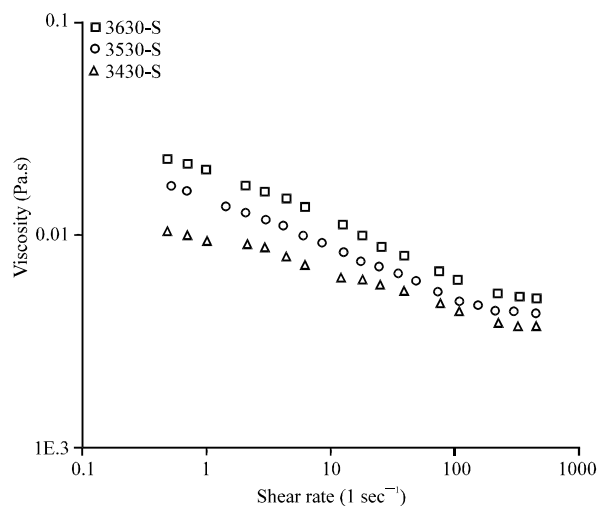


Fig. 1: Impact of molecular weight on the viscosity of three different polymer solutions

polymer solutions, viscosity was determined at fourteen different values of the shear rate in the range from 1 to 1000 1 sec⁻¹. Polymer 3330-S was taken as the reference polymer in this study except for the correlation of viscosity as a function of molecular weight and shear rate, where 3430-S was taken as reference polymer. Polymers having highest or lowest molecular weight can be taken as reference polymers; however, in this study polymer having lowest molecular weight was selected as reference polymer. Additional experimental values of viscosity vs. shear rate for polymer solutions named as 3630, 3530 and 3430-S, were provided to by SNF Floerger, France. The experimental data for these polymer solutions are presented in Fig. 1. The reason for considering these additional data is to show that the correlations provided in this study are valid in the presence and absence of salinity and hardness.

RESULTS AND DISCUSSIONS

This section discusses the correlation developed in this study to predict the viscosity of the polymer solution.

Effect of shear rate: The polymer used in this study showed shear thinning behavior as shown in Fig. 2-4. The change in viscosity of the polymer solution due to variation of shear rate can be modeled with power law as stated in Eq. 1.

By performing the non-linear regression on the data for all polymer solution, the best fit parameter estimates (k and n) of power law are presented in Table 3. The last column of Table 3 presents the values of the coefficient of determination (R-squared). As can be seen, the coefficient for all the cases almost identical to unity, indicating that the power-law model approximates the experimental data quite well.

Effect of concentration of polymer: As the concentration of the polymer solution increases, the viscosity of the polymer solution increases (Ghannam and Esmail, 1998; Yang, 2001). The repulsion between the negative charges on the polymer chains will be increased with the increase in polymer concentration.

Here a dimensionless parameter, called as the dimensionless concentration (C_D) is used to define a base case and to quantify the amount of vertical and horizontal shift due to the change in the concentration of a given polymer solution. It is defined by:

$$C_D = (C_{test} - C_{ref}) / C_{ref} \tag{2}$$

where, C_{test} is the testing concentration (ppm) and C_{ref} is the reference concentration (ppm).

By keeping all the other parameters constant and only changing the concentration of polymer solution, the values of the parameters k and n in the power law changes. The change in the parameter k with respect to the concentration of the polymer solution was found linear in nature as shown in Fig. 5. On the other hand the change in the parameter n with respect to the concentration of the polymer solution was found quadratic in nature as shown in Fig. 6. The 4000 ppm concentration was taken as the reference concentration in Eq. 2 to compute the dimensionless concentration plotted in Fig. 5 and 6. As 4000 ppm solutions were prepared as stock solutions for all polymers used in this study, it was more practical to consider this concentration as a reference concentration to quantify the effect of concentration on the viscosity of polymer solution. Variation in concentration of polymer affected the k and

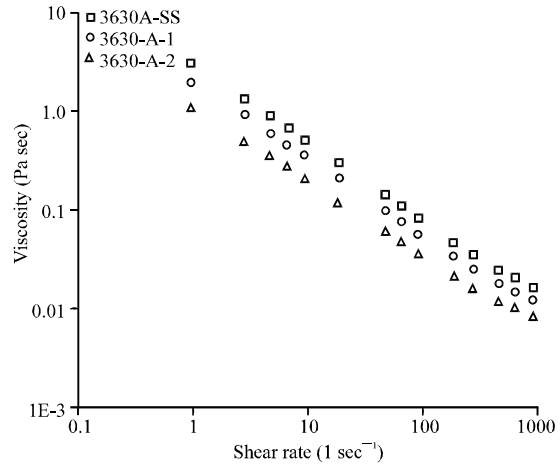


Fig. 2: Effect of shear rate on the viscosity of the polymer solutions of 3630-S

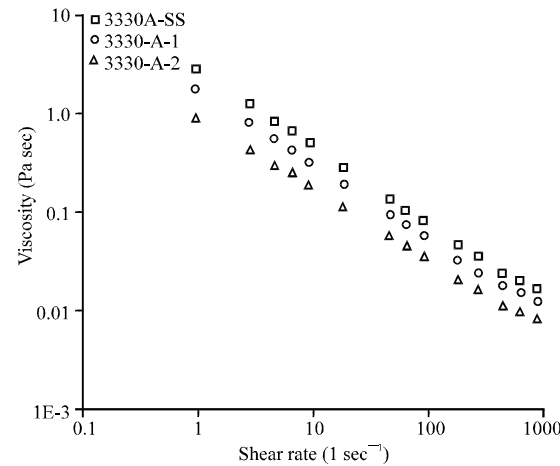


Fig. 3: Effect of shear rate on the viscosity of the polymer solutions of 3330-S

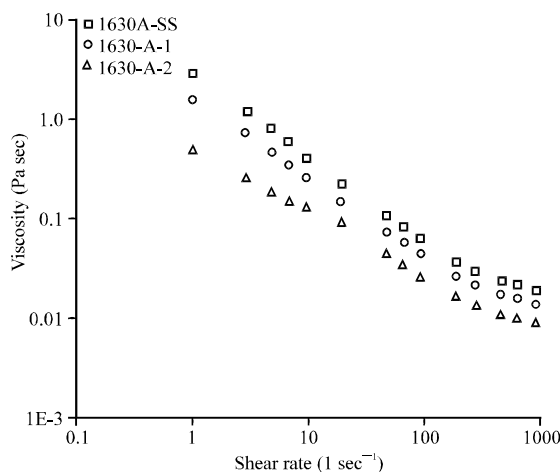


Fig. 4: Effect of shear rate on the viscosity of the polymer solutions of 1630-S

Table 3: Power law model parameters estimates for different polymer solutions given in Table 2

Solution name	Parameter	Estimate	R-squared	Solution name	Parameter	Estimate	R-squared
3630 A-SS	k	3.153	1.000	3330 A-2	k	0.911	1.000
	n	0.224			n	0.306	
3630 A-1	k	2.102	1.000	1630 A-SS	k	2.981	1.000
	n	0.248			n	0.176	
3630 A-2	k	1.104	1.000	1630 A-1	k	1.622	0.999
	n	0.281			n	0.240	
3330 A-SS	k	2.795	1.000	1630 A-2	k	0.500	0.999
	n	0.252			n	0.399	
3330 A-1	k	1.845	1.000	n	0.259		

Table 4: Parameter estimates of the correlation for viscosity as a function of concentration and shear rate of Eq. 5

Parameters	Estimate ----- 3630-S	Estimate ----- 1630-S	Estimate ----- 3330-S
a ₁	4.103	4.727	3767.912
a ₂	3.146	2.941	2792.192
b ₁	0.221	1.557	0.369
b ₂	-0.006	0.275	0.075
b ₃	0.228	0.184	0.253
R-squared	1.000	0.985	1.000

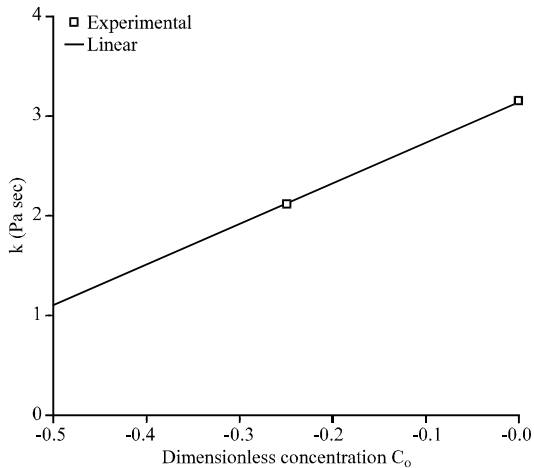


Fig. 5: Effect of dimensionless concentration on k for the polymer solutions of 3630-S

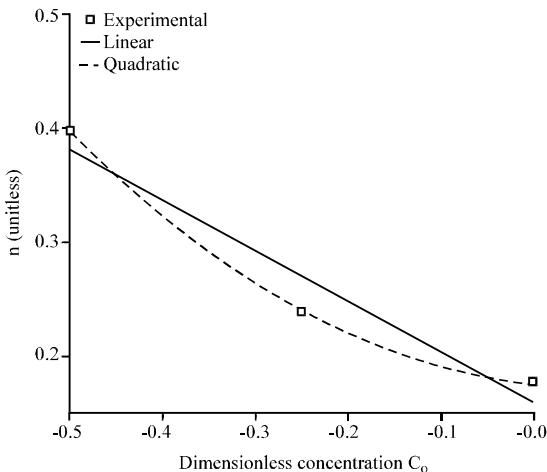


Fig. 6: Effect of dimensionless concentration on n for the polymer solutions of 1630-S

n parameters of power-law. So, we can propose a power-law model where k and n can be represented as a function of the dimensionless concentration, as given by Eq. 3 and 4, respectively:

$$k = a_1 C_D + a_2 \tag{3}$$

$$n = b C_{1D}^2 + b C_{2D} + b_3 \tag{4}$$

Then, a modified version of power law model can be used to account for the simultaneous effect of concentration of polymer and shear rate is obtained by using Eq. 3 and 4 in the right-hand side of Eq. 1 as:

$$\mu = (\alpha C + \alpha) \gamma (b C_D^2 + b C_D + b_3) - 1 \tag{5}$$

where, a₁, a₂, b₁, b₂ and b₃ are the coefficients determined by non-linear regression analysis of the experimental data of viscosity with the model of Eq. 5. The estimated parameters of the above equation for the polymers 3630-S, 1630-S and 3330-S are given in Table 4. A total of 42 data points were used to determine 5 coefficients of Eq. 5 for each polymer. Figure 7-9 shows the matches obtained between the experimental values and predicted values of viscosity by using Eq. 5. The polymer solutions of 1630-S shows high shear Newtonian region above shear rate of 500 1 sec⁻¹, due to which there is some deviation in the predicted and experimental values of viscosity.

With the increase in the concentration of the polymer in the solution the number of monomers of the polymers increases. From results, it seems that this increase will be reflected more on the value of k in a more or less linear way as represented by Eq. 5.

Effect of molecular weight: The molecular weight of polymer also affects the viscosity of the polymer solution. With the increase in the molecular weight of the polymer the viscosity of the polymer solution increases at the same fixed conditions. The data used to study the effect of molecular weight on the polymer solution are shown in Fig. 1.

A dimensionless Molecular Weight (MW_D) is used here to construct the base case and to quantify the

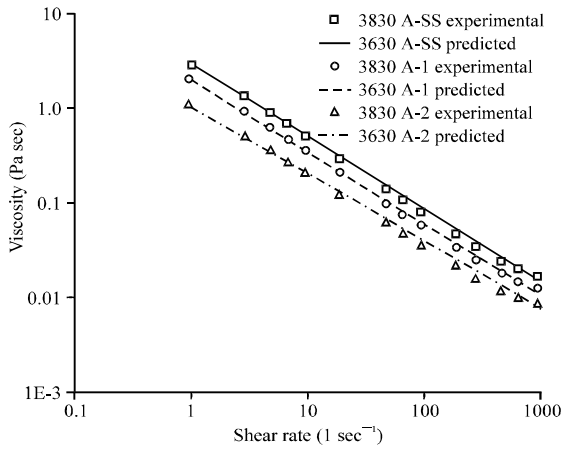


Fig. 7: Matches between the experimental and predicted data for 3630 polymer solutions using the correlation given by Eq. 5

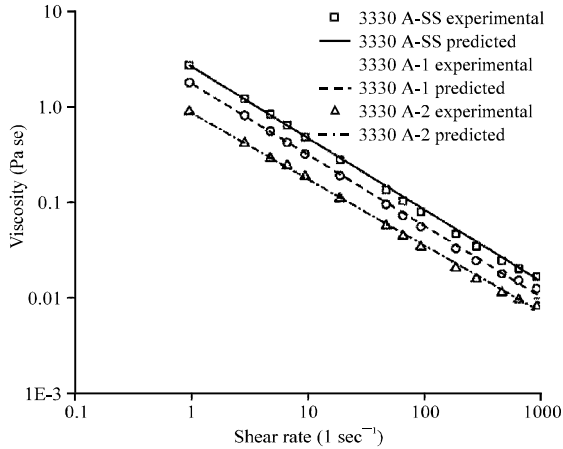


Fig. 8: Matches between the experimental and predicted data for 3330 polymer solutions using the correlation given by Eq. 5

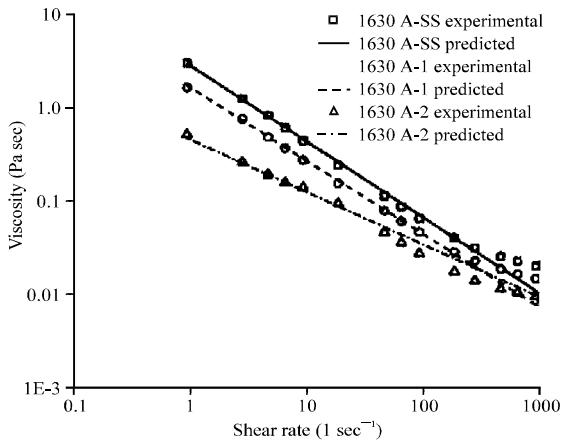


Fig. 9: Matches between the experimental and predicted data for 1630 polymer solutions using the correlation given by Eq. 5

amount of vertical and horizontal shift due to change in the molecular weight of polymer solution. The MW_D is defined by:

$$MW_D = (MW_{test} - MW_{ref}) / MW_{ref} \quad (6)$$

where, MW_{test} is the molecular weight of testing polymer (Daltons) and MW_{ref} is the molecular weight of reference polymer (Daltons).

Although, the results are not shown here, the parameters in the power law i.e., k and n were studied as a function of molecular weight of the polymer. It was found out that the parameter k and n is a function of molecular weight in linear manner. Hence, based on this analysis, equations for k and n as a function of molecular weight are presented below:

$$k = c_1 MW_D + c_2 \quad (7)$$

$$n = d_1 MW_D + d_2 \quad (8)$$

The correlation for the viscosity of the polymer solution as a function of molecular weight and shear rate in the form of power-law model can be given by:

$$\mu = (c_{1D} MW + c_2) \gamma^{(d_1 MW_D + d_2) - 1} \quad (9)$$

where, c_1 , c_2 , d_1 and d_2 are the coefficients determined by non-linear regression analysis. A total of 58 data points were used to estimate these four coefficients. The best fit parameter estimates for the coefficients of Eq. 9 are presented in Table 5. Figure 10 shows the matches between the experimental and predicted values of viscosities vs. shear rate by using the correlation provided by Eq. 9 for three different polymers. As can be seen from Fig. 10, the matches obtained by using Eq. 9 are quite good.

As is well known, the molecular weight of the polymer is increased by increasing the amount of the monomers. So, based on these results, it seems that the effect of the molecular weight on the value of k and hence on the viscosity can be represented well in a linear manner, as predicted by Eq. 9 quite well.

Combined effect of molecular weight, degree of hydrolysis and shear rate: A dimensionless degree of hydrolysis (DOH_D) is used here to construct the base case and to quantify the amount of vertical and horizontal shift due to change in the degree of hydrolysis of polymer solution. The DOH_D is defined by Eq. 10:

$$DOH_D = (DOH_{test} - DOH_{ref}) / DOH_{ref} \quad (10)$$

Table 5: Parameter estimates of the correlation for viscosity as a function of molecular weight and shear rate of Eq. 9

Parameters	Estimate
c ₁	0.016
c ₂	0.1
d ₁	-0.102
d ₂	0.825
R-squared	0.994

Table 6: Parameter estimates of correlation for Viscosity as a function of molecular weight, DOH and Shear rate of Eq. 11

Parameters	Estimate
e ₁	0.186
e ₂	0.078
e ₃	2.795
f ₁	-0.076
f ₂	0.086
f ₃	0.252
R-squared	1.000

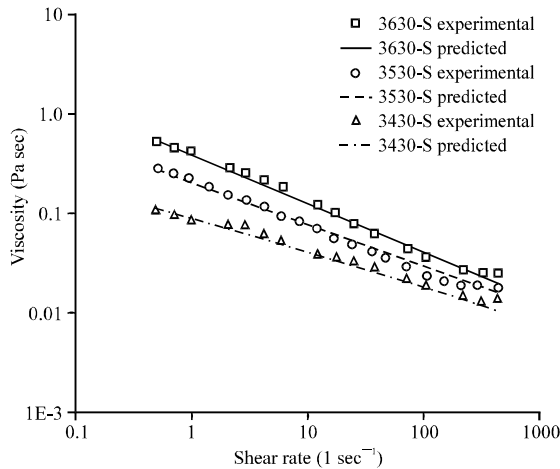


Fig. 10: Matches between the experimental and predicted data for different polymer solutions using the correlation given by Eq. 9

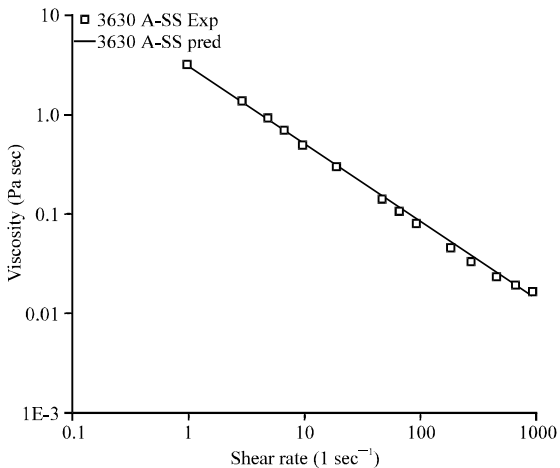


Fig. 11: Match between the experimental and predicted data of 3630 A-SS polymer solutions using the correlation given in Eq. 11

where, DOH_{test} is the degree of hydrolysis of testing polymer (%) and DOH_{ref} is the degree of hydrolysis of reference polymer (%).

Based on the analysis of variation of k and n due to change in the degree of hydrolysis of polymer, it was found that the impact of DOH_p on the parameter k and n of Eq. 1 is linear in nature. So, the modified form of power law equation containing three independent parameters on which the viscosity of the polymer solution is dependent can be given by:

$$\mu = (e_1 MW_D + e_2 DOH_D + e_3) \gamma^{(f_1 MW_D + f_2 DOH_D + f_3) - 1} \quad (11)$$

where, e₁, e₂, e₃, f₁, f₂ and f₃ are the coefficients estimated from experimental data by using nonlinear regression analysis. The estimates obtained for the coefficients of Eq. 11 are presented in Table 6. A total of 42 data points were used to estimate these six coefficients in Eq. 11. Excellent matches were obtained between the predicted and experimental values for all polymer solutions used in nonlinear regression. For example, Fig. 11 shows the match obtained for the experimental data of 3630 A-SS polymer solution.

Combined effect of molecular weight, degree of hydrolysis, concentration of polymer and shear rate on viscosity of polymer solution: The modified form of power-law equation for polymer viscosity that takes into account the combined effects of molecular weight, degree of hydrolysis, concentration and shear rate is presented in this section. These four parameters affect the viscosity of the polymer solution and can be combined in one equation to predict the viscosity of the solution at the required conditions.

Based on the analysis of the individual effects of polymer concentration, molecular weight and the degree of hydrolysis of the polymer and shear rate, the modified form of power-law equation that combines the effect of all these four parameters is presented below:

$$\mu = (g_1 MW_D + g_2 DOH_D + g_3 C_D + g_4) \gamma^{(h_1 MW_D + h_2 DOH_D + h_3 C_D^2 + h_4 C + h_5) - 1} \quad (12)$$

where, g₁, g₂, g₃, g₄, h₁, h₂, h₃, h₄ and h₅ are the coefficients determined from non-linear regression analysis of the experimental data. Three polymers of different MW and different DOH were used. A total of 98 data points corresponding to seven polymer solutions were used to estimate these nine coefficients. Two polymer solutions (3630 A-1 and 1630 A-1, Table 2) corresponding to 28 data points were used for validation. The data points used for validation were excluded from the set of data used for

Table 7: Parameter estimates of correlation for viscosity as a function of concentration, molecular weight, DOH and shear rate of Eq. 12

Parameter	Estimate	Parameter	Estimate
g_1	0.179	h_1	-0.012
g_2	0.934	h_2	0.036
g_3	4.277	h_3	0.442
g_4	2.928	h_4	0.020
		h_5	0.232
R-squared			0.997

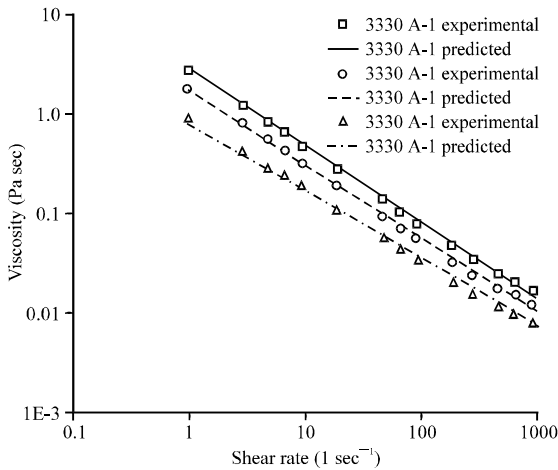


Fig. 12: Matches between the experimental and predicted data for different polymer solutions using the correlation given by Eq. 12

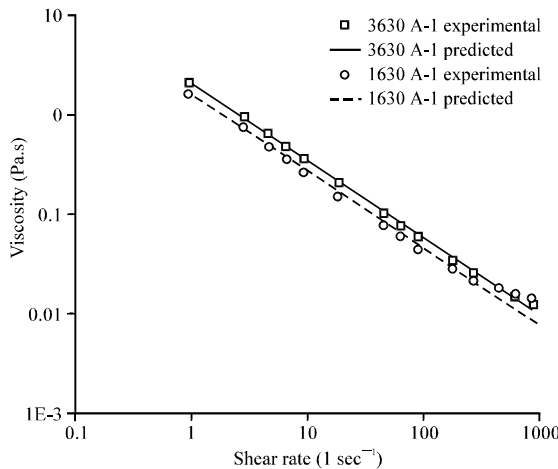


Fig. 13: Validation of Eq. 12

nonlinear regression. The parameter estimates of the above equation are presented in Table 7. As can be seen from the value of R-squared given in Table 7, the match obtained with experimental data by using Eq. 12 is quite good. For example, Fig. 12 shows the matches obtained for the experimental data of 3330-S polymer solutions. Figure 13 show further validation of the correlation proposed by Eq. 12 for the polymer solution 3630 A-1 and 1630 A-1. Both matches are very good,

except that the match is poor at high shear rates for 1630 A-1. In fact, this is expected because for polymer 1630 A-1, a Newtonian behavior is observed at shear rates above 500 l sec^{-1} .

CONCLUSION

A set of power-law type correlations has been developed for three different partially hydrolyzed polyacrylamide polymers. An extensive experimental work has been conducted to develop these correlations that should prove useful for reservoir simulation modeling and initial screening criteria of polymers. The correlations presented in this study accounts four major parameters (molecular weight, degree of hydrolysis, concentration and shear rate) that affect the viscosity of polymer solution. Based on the results of this study, the following specific conclusions are warranted:

- The flow consistency index (k) and flow behavior index (n) in power law equation are function of the concentration, molecular weight and degree of hydrolysis in addition to shear rate
- The impact of molecular weight on k and n is linear in nature
- The impact of degree of hydrolysis on k and n is linear in nature
- The concentration of polymer affects k in a linear, whereas it affects n in a quadratic manner

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NOMENCLATURE

- API = American petroleum institute
- CD = Dimensionless concentration, (dimensionless)
- Cref = Polymer concentration of the reference solution, (ppm)
- Ctest = Polymer concentration of the testing solution, (ppm)
- DOH = Degree of hydrolysis, (%)
- DOH_D = Dimensionless degree of hydrolysis, (dimensionless)
- DOH_{ref} = Degree of hydrolysis of reference polymer, (%)

DOHtest	= Degree of hydrolysis of testing polymer, (%)
k	= Consistency index factor, (Pa.s ⁿ)
MW	= Molecular weight of polymer, (Daltons)
MW _D	= Dimensionless molecular weight, (dimensionless)
Mwref	= Molecular weight of reference polymer, (Daltons)
Mwtest	= Molecular weight of testing polymer, (Daltons)
n	= Flow behavior index, (unitless)
R-squared	= Coefficient of determination, (unitless)
μ	= viscosity, (Pa.s)
μ ₀	= Low shear Newtonian region viscosity, (Pa.s)
μ _∞	= High shear Newtonian region viscosity, (Pa.s)
γ	= Shear rate, (1 sec ⁻¹)
λ	= Polymer specific constant, (unitless)
α	= constant

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