Development of a novel model to predict HPAM viscosity with the effects of concentration, salinity and divalent content

Abdullah Al-Hamairi¹ · Waleed AlAmeri¹

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Abstract

Polymer flooding has been established as an effective enhanced oil recovery (EOR) technique and can be utilized in large-scale field expansions. With high success rates and efficiency, polymer flooding operates by increasing the viscosity of water, promoting greater sweep efficiency and resulting in higher oil recovery beyond conventional waterflooding. Predicting viscosity has been established by numerous researchers as an essential tool to study polymers behavior under varying conditions. Previous model has proven a link between polymer viscosity and zero shear rate viscosity, relaxation time, hardness, and many other factors. This research initially reviews different types of polymers that can be applied successfully in EOR, demonstrate conditions that can alter polymer viscosity in porous medium, and analyze models that predict polymer bulk and in situ viscosity. The research then discusses a novel modification of the power law model to predict HPAM (SAV10) viscosity in a wide range of shear rates based on polymer concentration, fluid salinity, and divalent content. A polymer rheology study was carried out on SAV10 at various concentrations (750–5000 ppm) and brine salinities (43–210 k ppm). Results show the effectiveness of the model and the ability to predict viscosity accurately in low to medium shear rates, while in high shear rate, a slight deviation was noticeable.

Keywords Enhanced oil recovery · EOR · Polymer · SAV10 · HPAM · Rheology · Viscosity · Model · Power law

Introduction

Numerous methods have been established in secondary and tertiary recoveries to enhance oil production after waterflooding, namely water injection, thermal methods, and miscible and immiscible gas injection. One of the proved techniques nowadays is polymer flooding which increases the viscosity of water and promotes higher sweep efficiency by decreasing the mobility ratio between water and oil resulting in additional oil recovery (Sorbie 1991).

In this paper, a selection of polymers that can be utilized in polymer flooding and the factors affecting their viscosity based on previous researches have been outlined. However, the main aspect of our work is to present a novel model

based on a modification of the power law that predicts polymer viscosity in a wide range of shear rate and compare it with well-established models such as Carreau, Ellis, Meter, and other power law modifications.

Objective

The purpose of this paper is to introduce a comprehensive rheological model that predicts polymer viscosity under different shear rate values, based on polymer concentration, brine salinity, and divalent content. The model suggested differs from previous models with the inclusion of all three parameters and the reduction of the number of coefficients (a, b, c, d, f) which resulted in the lack of over-parameterization and ease of use. The study also compares between a number of models and explains briefly the requirement of each to be conducted successfully and how it compares to the new model suggested.

✉ Abdullah Al-Hamairi
abdullah.alhamairi@ku.ac.ae
Waleed AlAmeri
waleed.alameri@ku.ac.ae

¹ Petroleum Engineering Department, Khalifa University, SAN Campus, P.O. Box 2533, Abu Dhabi, United Arab Emirates

Polymers selection

Some of the frequently used polymers include synthetic polymers and biopolymers. Common ones are partially hydrolyzed polyacrylamide (HPAM), a synthetic polymer, and biopolymers namely Xanthan and Schizophyllan. Polyacrylamide (Sheng et al. 2015) is type of synthetic polymers that contains acrylamide in one of its monomers (Pakinat et al. 2011) with a molecular weight ranging from 10^5 to $>10^7$.

Non-hydrolyzed polyacrylamide (PAM) is nonionic; subsequently, there is no effect of salinity on it (Levitt and Pope 2008). PAM is thermally stable, and by-products of PAM such as salt tolerant polymer (KYPAM) and acrylamide methyl propane sulfonates (AMPS) have higher viscosity in saline water than other types of polymers, electrically conductive, and has good ionic exchange (Sheng et al. 2015; Luo et al. 2006). PAM polymers are strongly adsorbed into the minerals surface and hydrolyzed with the increase in temperature and/or pH. Hydrolysis occurs to the amide moiety resulting in an acrylate moiety and the formation of ammonium ion as Fig. 1 represents (Sheng 2013).

Result of PAM hydrolysis produces commercially used partially hydrolyzed polyacrylamide (HPAM) suitable for chemical EOR techniques for its low cost, good viscosifying water properties, and relative ease of implementation on large-scale production (Sheng 2013). Modified types of HPAM are thermally stable and produce higher injectant viscosity in porous media than other types of polymers (Yeramilli et al. 2013).

One distinct drawback of HPAM is the sensitivity to salinity with multivalent cations having stronger effect than monovalent cations and the possibility of precipitation if water

contained Ca^{2+} or Mg^{2+} (Abidin et al. 2012). In temperatures higher than 120°C and presence of oxygen, commercially viable HPAM suffers from thermal (Levitt and Pope 2008) and chemical degradation; studies (Sheng et al. 2015) suggest the use of oxygen scavenger, while makeup water and dissolution equipment should be kept in a nitrogen blanket.

Biopolymers are biologically produced polysaccharides, with excellent performance in high-salinity environments (Abidin et al. 2012). Previous studies concluded that schizophyllan, a biopolymer structured as a triple helical as demonstrated in Fig. 2, has excellent viscosifying properties and thermal stability up to 120°C (Quadri et al. 2015), while

Fig. 2 Schizophyllan structure

Fig. 1 Hydrolysis of PAM

Fig. 3 Xanthan structure

biopolymer Xanthan shown in Fig. 3 obtains a desirable shear thinning behavior and mechanical shear tolerance. Biopolymers in general are not retained on rock surfaces and relatively compatible with most surfactant making it suitable for polymer injection in tertiary recovery (Abidin et al. 2012). However, biopolymers cost more than HPAM, very susceptible to biological degradation, and certain types such as Xanthan may not tolerate high temperature. Other biopolymer issues include poor filterability and plugging in porous media caused by organic material (Al-Shalabi 2018).

Polymer economics

In an economic comparison between different types of polymers by Cenk et al. (2017), the prices of biopolymers were found to be double than HPAM polymers per kg. With additional cost of laboratory tests, mobilization, pumping, and supervision have a part in choosing an economically feasible polymer that can provide higher oil recovery for an extended period of time.

Therefore, one of the main causes of favoring alternative EOR techniques over polymer flooding is the difficulty of finding a suitable type of polymer that effectively delivers a positive outcome after implementation over extended periods of time.

Polymer stability

Polymer flooding focuses on the increase in water viscosity resulting in high sweep efficiency and enhancing oil recovery. Viscosity of a polymer can be affected by different factors causing it to change drastically depending on polymer type and degree of exposure to that certain factor. In this part, causes of polymer viscosity changes are discussed from previous researches for the types of polymers mentioned earlier.

Some of the factors affecting viscosity include:

- Chemical factors.
- Mechanical factors.
- Biological factors.
- pH.
- Salinity.
- Temperature.

Chemical stability

Polyacrylamide hydrolysis causes the backbone of polymer chains to interact with negative charges causing it to repel each other and stretching polymer chains. When electrolytes such as NaCl are added to the solution, the repulsion force is shielded by a double layer of electrolytes, causing a

Fig. 4 Salinity effect on HPAM viscosity (from Levitt and Pope 2008)

Fig. 5 Divalent effect on HPAM viscosity (from Melo et al. 2017)

reduction in viscosity (Sheng 2013). Levitt and Pope (2008) indicated that HPAM viscosity stabilizes after a certain salinity as Fig. 4 represents. Divalent cations have higher effect on HPAM than monovalent (Melo et al. 2017) with small amounts causing a greater reduction in viscosity as Fig. 5 illustrates. Sheng et al. (2015) suggests that formation water salinity should be less than 50,000 ppm and divalent content should not exceed 100 ppm for effective polymer deployment. The use of salt-tolerant biopolymers in high-salinity reservoirs is also suggested. In polymer modeling, specifically UTCHEM model, divalent and monovalent effect is taken into consideration due to its influence on HPAM viscosity.

Another polymer is Xanthomonas campestris, commercially known as Xanthan is a biopolymer shaped as a helix (Sorbie 1991) and an alternative for HPAM in polymer flooding. Delamaide (2018) reported the stability of Xanthan in temperatures up to 80 °C in moderate to high salinity and pH conditions. Figure 6 demonstrates the performance of HPAM and Xanthan mixture in high-salinity water, showing the stability of the mixture in high divalent and monovalent brine (Delamaide 2018). Whereas Fig. 12 demonstrates the experimental and predicted HPAM viscosity match using modified power law correlation (Hashmet et al. 2014b). Xanthan high

Fig. 6 Viscosity versus concentration of HPAM+Xanthan (GX) mixture in 17.1 g/l brine with 260 mg/l of $[Ca]^{(2+)}$ and 280 mg/l of $[Mg]^{(2+)}$ (from Delamaide 2018)

viscosity is attributed to the helical conformation and stabilized by the formation of hydrogen bonds between the backbone and side chains. Due to the charge shielding effect, Xanthan viscosity drops when a small amount of salt is added. However, the addition of more salt does not significantly further decrease the viscosity (Xu et al. 2013). The biopolymer faces a filtration issue caused by the micro-gels and insoluble materials that form in the manufacturing process. Biodegradation is more prevalent in biopolymers also; hence, Abidin et al. (2012) recommend the addition of effective biocide to reduce microbial degradation.

Schizophyllan is a biopolymer that performs well in extreme conditions of high salinity/temperature. It is produced by a fungus during fermentation process of glucose (Delamaide 2018). Schizophyllan obtains a triple helical structure stabilized by an interchain hydrogen bond giving it excellent viscosifying properties. The nonionic nature and the absence of a functional group in Schizophyllan give it high stability and resistance in high-salinity brine (Quadri et al. 2015). A field test of (0.5–1%) active polymer was reported in Bockstedt field, Germany, where temperature reached 54 °C and salinity 186 g/L. Results displayed a loss of polymer due to biodegradation although precautions were made by adding biocide (Delamaide 2018).

Thermal stability

Several researchers Gaillard et al. (2010), Levitt and Pope (2008), and Sheng et al. (2015) indicated that thermal degradation of HPAM polymers in high temperature up to 120 °C is noticeable, caused by the instability of acrylic backbone resulting in the reduction of viscosity over time and possible precipitation of the polymer. Seright et al. (2010) stated that HPAM retained half of its viscosity for more than 8 years at 100 °C in low-salinity, oxygen-free, and divalent-free environment and for 2 years at temperatures of up to 120 °C. Delamaide (2018)

Table 1 HPAM pilot test in high temperature conditions (Delamaide 2018)

Field	Country	Temperature (°C)	Outcome
Northeast Hallsville Crane	USA	109	Successful
Hitts Lake Unit	USA	99	Successful
Sanand	India	85	Successful
Mangala	India	85	Successful
Caracara Sur	Colombia	86	Not provided
West Salym	Russia	83	Successful

reviewed a number of polymer flooding pilot tests presented in Table 1 and reported the successful implementation of HPAM in all of them. The temperatures ranged from 65 to 109 °C; however, for the 65 °C test, polymer was heated to 85 °C prior to injection and reported a 15–20% loss in viscosity.

Xanthan molecules have a double helix structure in low temperature, but in high temperatures, the structure is distorted and converted into a disordered coil (Kamal et al. 2015). Therefore, Xanthan polymer does not obtain thermal stability. The maximum temperature the polymer was deployed in is 70 °C in Wangchang field in china and reported to be successful (Sheng 2010). Other studies (Lambert and Rinaudo 1985; Kierulf and Sutherland 1988) indicate thermal stability to 90 °C in high salinity conditions but a drop in Xanthan viscosity can take effect if the salinity drops due to the loss of molecule structure mentioned previously. Generally, Xanthan polymer is stable for temperatures < 90 °C.

The triple helical structure of Schizophyllan produces strong thermal stability up to 135 °C in short term and up to 110 °C long term. Leonhardt et al. (2014) reported a long-term stability test on Schizophyllan, results established Schizophyllan stability for temperatures from 54 to 135 °C for several years and a half-life partially exceeding 10 years. Stability test was done in anaerobic condition to minimize biodegradation effect.

Shear effect

HPAM polymers exhibit shear thinning behavior in rheometers caused by elongational viscosity, as opposed to porous media where it tends to experience shear thickening due to more dominant extensional viscosity. Based on Green and Willhite (1998), shear thickening is a porous media flow property and cannot be observed in rheological measurements of HPAM. Skaug et al. (2016) illustrate the viscoelastic behavior of HPAM in Fig. 7; at (a), the polymer is in zero shear rate region having the highest viscosity, while the interactions between polymer coils are not changed exhibiting a Newtonian behavior. Increasing the shear rate forces apart the polymer coils reducing by that the viscosity and

Fig. 7 Typical HPAM viscosity curve (Skauge et al. 2016)

Fig. 8 Viscosity versus shear rate of Schizophyllan (from Leonhardt et al. 2014)

exhibiting a non-Newtonian behavior at (b–c), this part of the viscosity curve is the shear thinning area where the polymer viscosity drops while shear rate increases. At high shear (d–f), polymer enters extensional flow region and a noticeable increase in polymer viscosity takes effect until strain reaches maximum point (f) where carbon–carbon binding is disrupted and polymer length reduces. The viscosity drops after that (g) until reaching brine viscosity. Hence, HPAM polymer displays both shear thinning and thickening behavior, while the latter is more dominant in porous medium.

Xanthan produces better rheological properties and shear resistance in comparison to HPAM in high-salinity environment. At room temperature, Xanthan reacts in a non-Newtonian manner showing a shear thinning behavior with the increase in shear rate. The presence of salts causes negative molecules to wrap around the main chain forming a rigid rod structure; the rigid structure obtains Xanthan resistance to mechanical and shear degradation (Xu et al. 2013).

Schizophyllan viscosity drops down when shear rate increases, demonstrating a typical shear thinning profile both in laboratory and porous medium. Figure 8 from Leonhardt

et al. (2014) illustrates the behavior of Schizophyllan in different concentrations measured in a rotational rheometer at temperature of 54 °C, conforming the expected shear thinning behavior.

Polymer modeling

Polymer rheology has been extensively studied to explain the non-Newtonian polymer behavior at different flow conditions. Several models such as Carreau, Viscoelastic, Ellis, and Power law are developed and modified to explain different phenomenas, namely shear thinning, shear thickening, and viscoelastic behavior, giving an idea of the polymer general performance under variable shear rate. In this part, different bulk and in situ viscosity models are explained and compared from previous researches.

Carreau model

Developed by Carreau et al. (1968), Carreau model represents a reference point for polymers that exhibit shear thinning behavior in low, intermediate, and high shear rates. Carreau equation is the following:

$$\mu_p = \mu_\infty + (\mu_0 - \mu_\infty) [1 + (\lambda \dot{\gamma})^2]^{(n-1/2)} \quad (1)$$

where μ_p is the viscosity at any shear rate $\dot{\gamma}$, μ_∞ is infinite viscosity in which the polymer reaches solvent viscosity and known as the Newtonian lower plateau for shear thinning polymers, μ_0 is zero shear rate viscosity and known as the upper Newtonian plateau for shear thinning polymers, λ is the maximum relaxation time or time constant, and n is the power law constant.

Carreau model is an effective tool to model biopolymers or any polymer that exhibit shear thinning behavior but lacks the accuracy for HPAM polymers that tend to exhibit shear thickening behavior in porous media. In addition, the model fails to establish a link between viscosity and polymer concentration or brine salinity. It is, however, recommended for modeling of bulk rheology.

Ellis model

The previous research Masuda et al. (1992) applied Ellis model and concluded that it is an effective tool for shear thinning polymers and obtains an advantage of excluding μ_∞ from its parameters as opposed to Carreau. However, the model overestimated the breakthrough saturation and underestimated the recovery efficiency of oil at breakthrough compared to experimental data. Additionally, Ellis model does not take in consideration salinity of the brine or the porous medium properties, making it applicable only for

bulk rheology modeling for shear thinning polymers. Ellis equation is the following:

$$\mu = \frac{\mu_0}{1 + \left(\frac{\tau}{\tau_{1/2}}\right)^{\alpha-1}} \quad (2)$$

where μ is fluid viscosity, μ_0 is zero shear rate viscosity, τ is shear stress, $\tau_{1/2}$ is the shear stress at which $\mu = \mu_0/2$, and α is an empirical model constant.

Viscoelastic model

Viscoelastic model was presented by Delshad et al. (2008), Masuda et al. (1992), and Lotfollahi et al. (2016), specifically designed for HPAM polymers that exhibit contrasting types of viscosities in rheometers and porous medium. The model includes two types of viscosities: shear viscosity dominant-type μ_{sh} which equates to the shear thinning region in a viscosity profile and represented by Carreau model, and elongational viscosity dominant-type μ_{el} represented by Deborah's number and equates to the shear thickening region:

$$\mu = \mu_{sh} + \mu_{el} \quad (3)$$

Shear thickening region

Elongational viscosity μ_{el} dominant region is represented by Deborah's number N_{Deb} , the ratio of the polymer's relaxation time t_r to the characteristic time for the flow t_{pr} . Table 2 shows the different forms of elongational viscosity equations proposed by multiple researchers:

As previously defined, Deborah's number is:

$$N_{Deb} = \frac{t_r}{t_{pr}} \quad (7)$$

Masuda et al. (1992) presented the characteristic time for the flow t_{pr} as the inverse of the apparent shear rate; that is,

$$t_{pr} = \frac{1}{\dot{\gamma}_a} \quad (8)$$

whereas Hirasaki and Pope (1974) and Durst et al. (1981) approximated t_{pr} to be the inverse of the rate of flow elongation and contraction in the reservoir rock ε , defined as:

Fig. 9 Viscosity versus shear rate for 200 ppm polyacrylamide (from Masuda et al. 1992)

$$\varepsilon = \frac{v}{d} = \frac{u_w}{(1 - \phi S_w) \sqrt{150 k k_{rw} / \phi S_w}} \quad (9)$$

Therefore, based on Delshad et al. (2008), viscoelastic model for shear thinning and thickening regions is defined as:

$$\mu = \mu_{\infty} + \left(\mu_p^0 - \mu_{\infty}\right) \left[1 + (\lambda \dot{\gamma}_a)^{\alpha}\right]^{(n-1)/\alpha} + \mu_{\max} \left[1 - \exp\left(-(\lambda_2 t_r \dot{\gamma}_a)^{n_2-1}\right)\right]$$

where the high shear rate viscosity μ_{∞} reaches water viscosity μ_w , $\dot{\gamma}_a$ is the apparent shear rate, λ , λ_2 , and n_2 are empirical model constants, and α is generally taken to be 2. $\mu_{\max}$ is the shear thickening plateau which is computed as a function of polymer concentration C_p and effective salinity C_{SEP} , as such:

$$\mu_{\max} = \mu_w \left[1 + \left(A_{p11} C_p + A_{p22} C_p^2\right) C_{SEP}^{Sp}\right] \quad (10)$$

where A_{p11} and A_{p22} are model coefficients.

Predictions from (Masuda et al. 1992) for the fractional flow curves, oil recovery, and recovery efficiency of oil were all better for the viscoelastic model compared to Ellis model. Additionally, Fig. 9 illustrates the match between polymer viscosity and viscoelastic model in the high shear rate region compared to Ellis model due to the shear thickening factor. However, calculated histories of

Table 2 Proposed equations for elongational viscosity

Model	Equation	Description
Hirasaki and Pope (1974)	$\mu_{el} = \mu_{sh} / [1 - N_{Deb}]$ (4)	
Masuda et al. (1992)	$\mu_{el} = \mu_{sh} C_c (N_{Deb})^{m_c}$ (5)	C_c and m_c are empirical model constants
Delshad et al. (2008)	$\mu_{el} = \mu_{\max} \left[1 - \exp\left(-(\lambda_2 N_{Deb})^{n_2-1}\right)\right]$ (6)	λ_2 and n_2 are empirical model constants

Fig. 10 Viscosity versus shear rate for 1500 ppm Flopaam 3630S (from Delshad et al. 2008)

pressure drop for both models did not agree with experimental data. Delshad et al. (2008) results were similar to Masuda et al. (1992) reporting a successful match between HPAM apparent viscosity and viscoelastic model as Fig. 10 reveals, with another simulation indicating a close prediction between coreflood results and the viscoelastic model for the oil cut, pressure drop, and oil recovery.

Flory–Huggins and meter

The modified version of Flory–Huggins equation developed by Flory (1953) utilizes the chemical concentration to obtain polymer viscosity; that is:

$$\mu_p^0 = \mu_w \left[1 + \left(A_{p1} C_p + A_{p2} C_p^2 + A_{p3} C_p^3 \right) C_{SEP}^{Sp} \right] \quad (11)$$

where μ_p^0 is polymer viscosity at zero shear rate (cP), μ_w is water viscosity (cP), C_p is polymer concentration, C_{SEP} is effective polymer salinity, A_{p1} , A_{p2} , A_{p3} , and Sp are empirical model constants.

In general, C_{SEP} takes into consideration the effect of salinity and hardness on polymer viscosity, defined as:

$$C_{SEP} = \frac{C_{51} + (\beta_p - 1)C_{61}}{C_{11}} \quad (12)$$

Specifically, the salinity that C_{SEP} considers is the effect of anion and divalent cations concentration in C_{51} and C_{61} (Eq/l), respectively, C_{11} is the aqueous phase water concentration, β_p is a constant model parameter, and Sp is the slope of the power line in a log–log plot for $\frac{(\mu_p^0 - \mu_w)}{\mu_w}$ versus C_{SEP} .

Obtaining μ_p^0 from Flory–Huggins equation can be utilized in finding the apparent polymer viscosity using Meter's equation (1964), as such:

$$\mu = (g_{1D} MW + g_{2D} DOH_D + g_{3D} C + g_4) \gamma^{(h_1 MW_D + h_2 DOH_D + h_3 C_D^2 + h_4 C_D + h_5) - 1} \quad (17)$$

$$\mu_p = \mu_\infty + \frac{\mu_p^0 - \mu_\infty}{1 + (\dot{\gamma}/\dot{\gamma}_{1/2})^{P_a - 1}} \quad (13)$$

where μ_p^0 is from Flory–Huggins equation, μ_∞ is polymer viscosity at infinite shear rate or the lower Newtonian plateau viscosity (approximated to water viscosity μ_w), $\dot{\gamma}_{1/2}$ is the shear rate at which polymer viscosity $\mu = \frac{\mu_p^0 + \mu_w}{2}$, and P_a is an empirical model constant. Modeling of apparent shear rate $\dot{\gamma}$ is accomplished using modified Blake Kozeny capillary bundle equation (Sorbie 1991), that is:

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right)^{\frac{n}{n-1}} \frac{4C|\vec{u}_w|}{\sqrt{k} k_{rw} \phi S_w} \quad (14)$$

where n is the power law exponent, u_w is Darcy velocity, $\bar{k}$ is the effective permeability, k_{rw} is the relative permeability of water phase, and S_w is water saturation.

Simplified by (Delshad et al. 2000),

$$\dot{\gamma} = 3.94C \frac{|\vec{u}_w|}{\sqrt{k} k_{rw} \phi S_w} \quad (15)$$

In the above equation, C is the shear rate coefficient that depends on porosity and permeability; different values for C ranging between 1 and 6 have been reported (Kulawardana et al. 2012; Cannella et al. 1988; Zheng et al. 2000; Al-Shalabi 2018).

The implementation of Flory–Huggins model on a wide range of polymers showed accuracy concerning viscosity values and effective shear rate for Al-Shalabi (2018), while Delshad et al. (2008) reported less accuracy for oil recovery, pressure drop, and oil cut compared to other models. One of the model drawbacks is that it contains a large set of parameters. In addition, the value of the coefficient C varies from one paper to another without sufficient reasoning.

Power law model

Based on power law, few models were developed that correlate different polymer parameters to flow consistency index (n) and flow behavior index (k).

$$\mu = k \dot{\gamma}^{n-1} \quad (16)$$

A power law modification was developed by Hashmet et al. (2014a) to predict polymer viscosity. The modification accounts for four parameters (polymer concentration, degree of hydrolysis, molecular weight, and shear rate); such that:

where $g_1, g_2, g_3, g_4, h_1, h_2, h_3, h_4$, and h_5 are model coefficients obtained by nonlinear regression analysis of experimental data, and D stands for dimensionless. Two types of HPAM were tested, and the results were correlated by the previous model and showed consistency at low to medium

similar for the molecular weight as well. However, polymer concentration effect on k is linear, but on n is quadratic.

Another model by Hashmet et al. (2014b) combines the effect of salinity, hardness, and shear rate to predict polymer viscosity using a modified power law equation, such that:

$$\mu = (e_1 \text{salinity}^{e_2+1} + e_3 \text{hardness}^{e_4+1} + e_5) \dot{\gamma}^{((f_1 \text{salinity}^2 + f_2 \text{salinity} + f_3 \text{hardness} + f_4) - 1)} \quad (18)$$

shear rates. At high shear rate, the polymer exhibited a Newtonian behavior and the model was not able to predict viscosity precisely as Fig. 11 illustrates. The model also does not offer a representation of brine salinity. Results indicate a linear relationship between degree of hydrolysis and k and n ,

where $e_1, e_2, e_3, e_4, e_5, f_1, f_2, f_3$, and f_4 are model coefficients obtained by nonlinear regression analysis of experimental data. The match between experimental and predicted data using the model gave R^2 values of 0.999 and 1.000 for the two polymer samples. The maximum relative error values were 13.02% and 9.2%, indicating a good match up for viscosity predictions as Fig. 12 represents.

Divers et al. (2017) reported the limitation of this model to good solvent quality and failure in predicting polymer viscosity in high divalent content and provided a modification by replacing salinity with TDS (total dissolved salt (wt%)) and hardness with TDC (total divalent cations (wt%)), as such:

$$\mu = (e' \text{TDS}^{(a+1)} + e'' \text{TDC}^{(b+1)} + e''') \dot{\gamma}^{((f' \text{TDS}^2 + f'' \text{TDS} + f''' \text{TDC} + f''') - 1)} \quad (19)$$

where $e, e', e'', a, b, f, f', f'',$ and f''' are model coefficients determined by nonlinear regression analysis of experimental data. The model was a good match as Fig. 13 illustrates for values up to $R+ = 0.1$ for all the polymers, but the adjustment failed to match the experimental data for $R+ = 0.15$. Furthermore, the modification has a large set of parameters

Fig. 11 Experimental and predicted HPAM viscosity match using modified power law correlation (from Hashmet et al. 2014a)

Fig. 12 Experimental and predicted HPAM viscosity match using modified power law correlation (from Hashmet et al. 2014b)

Fig. 13 Experimental data modeling using power law adjustment for 2000 ppm in alternating R^+ and salinity (from Divers et al. 2017)

and lacks in introducing a link between viscosity and polymer concentration.

Experimental procedure

In this section, the material and equipment used will be outlined. Furthermore, rheological measurement and fluid preparation will be explained.

Material

Partially hydrolyzed polyacrylamide commercially known as SAV10 and produced by SNF Floerger containing *N*-vinylpyrrolidone with high temperature resistance of up to 120°

was used. The molecular weight range is 2–4 million Daltons and concentration is 5000 ppm to 500 ppm. Four synthetic brines were prepared with different salinities ranging from 220,000 to 43000 ppm.

Equipment and measurements

Polymer viscosity was measured using Modular Compact Rheometer (MCR302) equipped by a cone-plate geometry from Anton Paar. Temperature was set to 25 °C in the cone plate, and shear rate ranged from 0.1 to 1000 s⁻¹.

Table 3 Composition of brines

Ions	210,000 ppm	167,000 ppm	105,000 ppm	43,000 ppm
Sodium	66,024	52,952	33,012	13,072
Calcium	9789	9250	4894.5	539
Magnesium	3029	1446	1514.5	1583
Potassium	1242	744	621	498
Chloride	126,239	102,722	63,119.5	23,517
Sulfate	3298	0	1649	3298
Divalent content	12,818	10,696	6409	2122

Table 4 Curve fitting results

Salinity	Concentration	Salinity	TDC	A	b	c	d	F	R ²
210,000	3000	21	1.2818	4.75091	0.36326	1.49837	0.09316	0.06119	0.73083
210,000	1500	21	1.2818	1.77985	0.37755	1.38982	0.08221	0.06409	0.91588
210,000	750	21	1.2818	1.79549	0.17091	-2.25004	1.00006	0.1246	0.7924
167,000	5000	16.7	1.0696	19.0262	0.29048	1.9485	0.14108	0.03893	0.97467
167,000	3000	16.7	1.0696	5.42041	0.40913	1.67944	0.09791	0.07122	0.89237
167,000	2000	16.7	1.0696	2.49354	0.42267	1.5129	0.09523	0.11611	0.81456
105,000	5000	10.5	0.6409	17.62662	0.3249	2.30151	0.17988	0.06464	0.89927
105,000	1500	10.5	0.6409	1.59553	0.4594	1.70989	0.0953	0.23301	0.79582
105,000	1000	10.5	0.6409	0.75664	0.49179	1.72369	0.06562	0.33295	0.70613
43,000	5000	4.3	0.2122	12.56381	0.41699	3.41046	0.25378	0.1812	0.74874
43,000	4000	4.3	0.2122	0.72608	0.36056	4.33487	0.0675	0.25415	0.97177
43,000	3000	4.3	0.2122	3.82769	0.47202	3.22752	0.12565	0.31444	0.837

Fluid preparation

Four types of synthetic brines were prepared based on the composition of the salts in Table 3. Brines then went through a filtration process to remove any particulates or impurities using a 0.5 µm filtration paper. Polymer solutions were prepared in a glove box on API standards (RP63 1990). Brine was stirred on high speed to form a vortex; polymer powder was then poured slowly on the edge of the vortex until a thick and homogenous mixture formed. The mixture was left for 10 min, and the speed was gradually reduced to the lowest setting. Mixture was then left overnight in the stirrer. Polymer solution was prepared in a glove box to minimize oxidation and viscosity loss (Sheng et al. 2015).

Viscosity modeling and results

A novel model to predict polymer viscosity was established based on a modification of Ostwald–de-Waele relationship:

$$\mu = k\dot{\gamma}^{n-1} \quad (16)$$

where k is the fluid consistency index and n is the flow behavior index. The model predicted viscosity based on fluid salinity, divalent content, and polymer concentration.

Viscosity vs Shear Rate of SAV10 in 105k Brine

Fig. 14 Effect of SAV10 concentration on viscosity

It also focused on reducing the number of coefficients used in nonlinear regression analysis, where

$$k = (a + \text{Con} + (\text{Sal}^c)d + (\text{DC})f) \quad (20)$$

$$n = (b + (\text{DC}^c)d + (\text{Sal}) * f * \text{Con}) \quad (21)$$

Combining the two equations gives the full model for predicting viscosity, such that:

$$\mu = (a + \text{Con} + (\text{Sal}^c)d + (\text{DC})f)\dot{\gamma}^{((b+(\text{DC}^c)d+(\text{Sal}) * f * \text{Con})-1)} \quad (22)$$

Fig. 15 Effect of salinity on SAV10 viscosity

where a , b , c , d , and f are model coefficients, Con is the polymer concentration, Sal is fluid salinity, and DC is the divalent content. The model matched the experimental data with less error and a better fit compared to Divers et al. (2017). Lowest R^2 value was 0.70613, and the remaining corresponding coefficients are in Table 4. Incorporation of polymer concentration was important as Fig. 14 represents; viscosity drops with the decrease in concentration indicating a direct relationship between the two parameters. In contrast, salinity had an opposite effect on viscosity as Fig. 15 illustrates, and a drop in salinity would result in an increase in polymer viscosity. Finally, as discussed earlier, divalent cations presence has detrimental effect on polymer viscosity; therefore, it was necessary to include it in the model. These three parameters control the viscosity interchangeably, and by means of nonlinear regression analysis, we were able to link it to our model successfully as results from OriginPro in Fig. 16 indicate.

Prior research indicates two methods of modeling the data, the first is to model one data set and produce a number of coefficients that predict the rest of the results with different input parameters. The second is to produce different set of coefficients for each data set and test the match between the bulk rheology and the model produced. We have chosen the second method which has been established by numerous researchers (Delshad et al. 2008; Quadri et al. 2015; Yerramilli et al. 2013).

Effect of salinity and hardness

In deionized water, polymer chains stretch as the negative forces form a repulsive force causing an increase in viscosity. The introduction of monovalent and divalent cations decreases the forces of repulsion and coils up polymer chains resulting in a drop in polymer viscosity (Hashmet et al. 2014b; Sorbie 2013). To test the validity of our equation in regard to monovalent and divalent cations, we kept the concentration constant and modeled the bulk data in a

range of salinities starting by 43,000 up to 220,000 ppm. Results in Fig. 16a, e, m highlight the accuracy of the model in predicting viscosity in different salinities for 3000 ppm of SAV10 concentration.

Effect of polymer concentration

It is well established that increasing polymer concentration causes a rise in viscosity; our results also confirm that in the range of 500–5000 ppm. The model provided quiet a good fit in high polymer concentrations. However, for lower polymer concentration as can be seen in Fig. 16c, the data scattering was too large and the range of viscosity decreased. Hence, difficulties came across in predicting viscosity in low concentrations and high shear rates. Nevertheless, the model still managed to provide an acceptable fit for the data provided.

Models comparison

Carreau

Carreau model is an effective tool to predict polymer viscosity in the shear thinning region; however, Carreau does not incorporate any of the parameters we obtain in our model (Con, DC, Sal) but uses another set of parameters (μ_0 , μ_∞ , λ). While μ_0 and μ_∞ can be acquired easily from bulk rheology data, the relaxation time λ or time constant cannot as it requires certain laboratory tests; therefore, Carreau model could not be applied.

Ellis

Based on (Shenoy 2013), Ellis model is a simple yet effective way of modeling polymer viscosity in the low to medium shear rate range. However, it does not take fluid salinity or divalent content in consideration, both of which has a drastic effect on viscosity. Ellis model is not recommended in the high shear rate, whereas our model can predict viscosity even in the high shear rate of up to 1000 s^{-1} as Fig. 16a, b shows.

Viscoelastic model

As discussed earlier, the model consists of two parts, Carreau model and its drawbacks have been outlined, and an empirical model that correlates viscosity with Deborah's number. It is aimed at HPAM polymers that exhibit shear thickening behavior in the reservoir, whereas our model is concerned with modeling of bulk rheology. Additionally, the model suggested in this paper only requires basic parameters to predict viscosity on a wide range of shear rates;

Fig. 16 Results obtained from Originpro non-linear regression analysis

Fig. 17 Comparison between Flory–Huggins and the new model

however, viscoelastic model needs some core flood data to be applicable.

Flory–Huggins and meter

Flory–Huggins equation was used to obtain zero shear rate viscosity; then, Meter equation was used to predict the viscosity of 2000 ppm of SAV10 data. As Fig. 17 indicates, the model diverges from the bulk data in medium to high shear rate range, whereas our model predicts viscosity accurately in medium shear rate range but slightly deviates from the data in the end of the high shear rate range. Therefore, it can be concluded that our model overall shows better accuracy compared to Meter's Model.

Power law modifications

The equation formulated by Hashmet et al. (2014b) was modeled using Originpro but was not valid as the fit did not

converge as results in Fig. 18 represent. The reason was due to the mutual dependencies that exist between the parameters. The solution proposed to over-parameterization of the fitting function was to eliminate salinity and divalent content from the equation as an input and add it as a coefficient to be estimated too.

Concluding remarks

A novel modification to power law has been developed to model polymer viscosity under various salinities, divalent content, and polymer concentrations. Rheological measurement on a wide number of polymer solution was conducted to establish the model and investigate its validity. Conclusion of results obtained is:

- Accuracy of the model in low to medium shear rate and slight deviation from the bulk data at extreme shear rate.
- The model produced a good fit for all types of salinities in a fixed polymer concentration.
- The fit was acceptable for low concentration polymer solution with noticeable deviation at low and high shear rates caused by the scattering of the laboratory measurement.
- At high polymer concentration, the suggested model provided excellent results across all salinities.
- Reduction of number of coefficients in comparison to other modifications assisted in the lack of over-parameterization and coexistence of mutual dependencies.
- The novel model was proved to be a contender for other established models and proved its accuracy in predicting polymer viscosity under a wide range of variables.

Fig. 18 Results of a power law modification for SAV10 data

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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