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TÍTULO DO TRABALHO:

RHEOLOGICAL STUDY OF CATIONIC POLYACRYLAMIDE AND COMPARISON WITH ANIONIC HPAM

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Abstract

The rheology of cationic polyacrylamide (CPAM) was studied using shear rheology and viscoelastic tests, and its behavior was compared to that of an anionic partially hydrolyzed polyacrylamide (HPAM). Despite the rare use of cationic polymers in Enhanced Oil Recovery (EOR) projects, they can be a promising alternative for positively charged reservoirs, such as carbonates.

All shear rheology tests were performed at ambient temperature (23ºC), using polymer concentrations ranging from 50 to 5000 ppm in brine with 110,000 ppm NaCl, which represents a high-salinity environment. The critical concentration (C*), which separates the semi-dilute and the dilute regions in a graph of the apparent viscosity versus polymer concentration, was obtained as a function of the shear rate. This way, the range of concentrations for which the solutions are more pseudoplastic, with less addition of polymer, were determined. Finally, the elastic and viscous moduli, G' and G", respectively, were used to evaluate the elasticity of the 5000 ppm polymer solution.

The cationic polyacrylamide solutions showed pseudoplastic behavior for all polymer concentrations. Solutions with higher polymer content were more shear thinning. Furthermore, the CPAM (5-6 g/mol) was compared to an anionic HPAM (8-10 g/mol) from the literature with similar molecular mass and under the same salt concentration and temperature. At 1000, 2000, and 5000 ppm, both polymers showed virtually the same viscosity and shear thinning nature, evidencing the thickening capability of the CPAM in brine with high salinity. The values for CPAM's critical concentrations lied between 524.8 to 558.7 ppm, for shear rates ranging from 7.847 to 233.57 s^{-1}, against considerably higher values displayed by the anionic HPAM (1860.52 to 1905.39 ppm). Nevertheless, there was no clear trend between C* and the shear rate, as suggested in the literature. Lastly, the viscous modulus G" was dominant for the polymer solution with 5000 ppm, and its value (0.315 Pa) was, roundly, the double of the elastic module G' (0.154 Pa) within the Linear Viscoelastic Region.

The results show that CPAM bulk rheology behavior was comparable to that of an anionic HPAM for the same experimental conditions and that the critical concentration is lower for the CPAM, despite the same salinity of the solutions.

Introduction

Polymer flooding is the most applied Chemical Enhanced Oil Recovery (CEOR) method (Sheng, Leonhardt, and Azri, 2015). It enhances the oil recovery by reducing the mobility ratio between the displacing solution and the displaced oil, decreasing the Injected Pore Volume (IPV), and by diminishing the effects of viscous fingering (Standnes and Skjevrak, 2014). The expectation is to obtain 15 to 20% incremental recovery over the conventional water flooding (Kamal et al., 2015).

Partially Hydrolyzed Polyacrylamides (HPAM) are used in most of the polymer flooding projects (Alsofi et al., 2017; Saleh et al., 2017). Anionic polyacrylamides are preferred for application in Sandstones since the repulsion between their negative charges and the anions present on the rock surface minimizes effects such as adsorption and loss of viscosity (Yen, Coscia, and Kohen, 1989). In addition, several authors have reported that the viscosity of polymers also decreases with increasing salinity, temperature and shear rates (Jung et al., 2013; Bennetzen et al., 2014; Gao, 2015; Quadri, Shoiab, Al Sumaiti, and Al Hassan, 2015; Silveira, Lopes, and Moreno, 2016; Tahir et al., 2017; Alafazazi, Al-Ameri, and Hashmet, 2018).

Carbonate rocks, which hold approximately half of the oil in the world, are a challenge in CEOR because the interaction between the cations present on their pore walls, especially Ca^{2+}, and the negative charges of anionic polymers leads to a loss of viscosity and adsorption of the polymer onto the rock surface (Wang et al., 2017). Kamal et al. (2015) suggest that Cationic Polyacrylamides (CPAM) should be considered for lab-scale investigation since they may be applied in carbonate reservoirs due to their positive charges. These types of polymers are extensively used in water treatment, mineral processing, and control water production (Fernandez, 2005), but applications in CEOR are very scarce since their

positive charges would probably suffer repulsion from the divalent ions present in negatively charged rocks such as Sandstones (Kamal et al., 2015).

Divers (2017) studied the rheology of several acrylamide-based polymers, including anionic and cationic polyacrylamides. They concluded that the high molecular weight CPAMs (23.4 and 26 MDa) were the most efficient viscosifiers because of their enhanced salt tolerance, which was attributed to their positive charges.

Studying the rheology of this type of polymer is the first step to predict if it is a suitable candidate for Polymer Flooding projects. For this reason, the rheology of a cationic polyacrylamide was assessed in this work using shear rheology and viscoelastic tests to evaluate its behavior in comparison with an HPAM used in the literature.

Methodology

Preparation of Polymer Solutions

The polymer used in this project was a cationic polyacrylamide, FO 4550 SH, provided by SNF Floerger, with 5-6 x 10^6 g/mol of molecular mass, and charge density of 45 mol % (Meszaros, Barany, and Solomentseva, 2009). All the tests were conducted at 23ºC in a brine prepared using deionized water and NaCl at 110,000 ppm, with polymer concentrations ranging from 50 to 5000 ppm.

The preparation of the polymer solutions followed the recommended practices of the standard API RP63 (1990). Firstly, a stock solution with a concentration of 5,000 ppm was prepared using the brine and the polymer powder. The powder was slowly added to the brine, which was placed on a magnetic stirrer. Following, the rotation of the stirrer was reduced to avoid mechanical degradation of the polymer and the solution was left to mix for 3 hours. After this period, the stirrer was turned off and the solution was left still for 24 hours to complete the homogenization. Six solutions were prepared by diluting the stock solution in brine, with concentrations of 50, 100, 200, 500, 1,000, and 2,000 ppm.

Shear rheology test

A Haake Mars III rheometer was used to evaluate the viscosity of all the solutions at 23ºC, with shear rates ranging from 0.1 to 1000 s^{-1}. The concentric-cylinders geometry was chosen to perform the tests.

The flow curves were fitted with the Power Law model given by **Equation 1** below:

$$\eta = K\dot{\gamma}^{n-1} \qquad \textbf{Eq. 1}$$

Where K is the flow consistency index and n is the behavior exponent. The curves of shear stress versus shear rate were used to obtain K and n.

Afterwards, the viscosity was plotted versus the polymer concentration in a log-log graph to obtain the critical concentrations (C*). This parameter is given by the intersection between the trend lines of the dilute and semi-dilute regions, which were modeled using a Power Law, given by **Equation 2:**

$$\eta = a.c^b \qquad \textbf{Eq. 2}$$

Viscoelastic tests

The viscoelastic tests were performed using the stock solution (5000 ppm). An Amplitude Sweep Test (AST) and a Frequency Sweep Test (FST) were implemented to evaluate the viscoelastic behavior of the polymer.

Results and Discussion

Flow Curves

Figure 1 shows the flow curves for seven polymer concentrations.

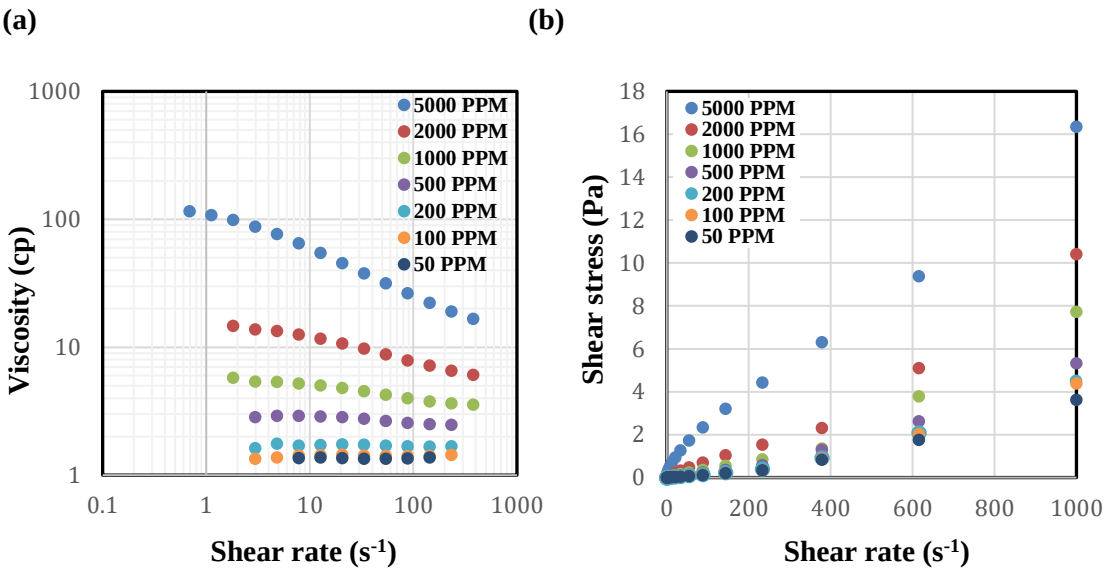

Figure 1: (a) Viscosity and (b) shear stress versus shear rate for different polymer concentrations at 110,000 ppm NaCl and 23°C.

The cationic polyacrylamide solutions displayed shear thinning behavior for all concentrations. A Power Law was used to fit the shear stress vs. shear rate curves and the rheological parameters (K and n) obtained for each concentration are summarized in **Table 2**.

Table 2: Rheological parameters of the Power Law model.

Polymer concentration	K	n	R^2
ppm	(Consistency index)	(Behavior exponent)	
5,000	0.1185	0.6717	0.998
2,000	0.0173	0.8268	0.999
1,000	0.0062	0.9053	1.000
500	0.0031	0.9599	1.000
200	0.0017	0.9982	1.000
100	0.0014	0.9991	1.000
50	0.0014	0.9992	1.000

The Power Law model provided a satisfactory fit for the flow curves, as indicated by the high correlation coefficient (R^2 > 0.99). The behavior exponent decreases with increasing polymer concentration, showing that highly-concentrated solutions are more sensitive to the effects of shear, leading to the steeper flow curves observed in **Figure 1**. This result agrees with previously published work (Jung et al., 2013; Gao, 2015; Silveira et al., 2016; Tahir et al., 2017; Alfazazi et al., 2018).

When the concentration decreases, the viscosity of the solutions tends to the viscosity of the solvent. Also, the viscosities and shear stresses are very similar for the 50 and 100 ppm data, as well as K and n. The inaccuracy of the rheometry to evaluate the properties of low-viscosity fluids may be responsible for this similarity (Ewoldt et al., 2015).

Figure 2 shows a comparison between the flow curves presented in this work and the results obtained by Bento (2015) for polymer concentration of 1,000, 2,000, and 5,000 ppm. He used an anionic

HPAM (Flopaam AN110 SH), at 23ºC and with a salt concentration of 110,000 ppm NaCl, which are the same conditions implemented in this work.

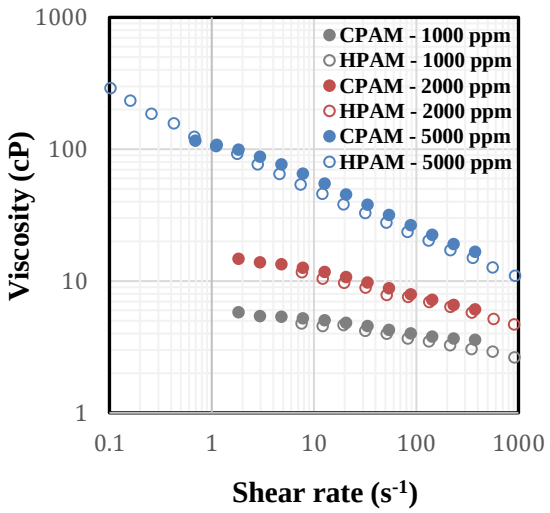

Figure 2: Viscosity vs. shear rate of CPAM and HPAM at different concentrations.

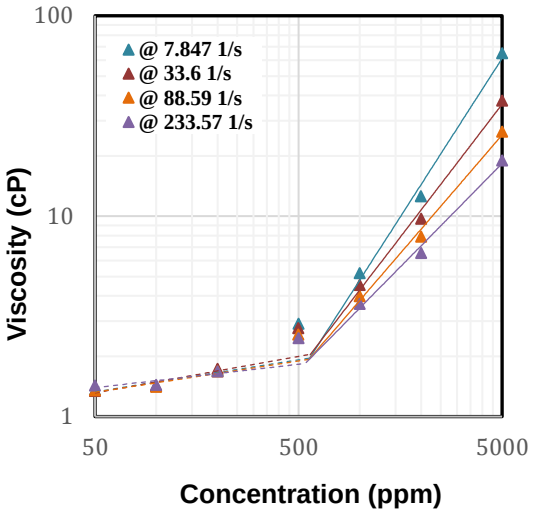

Figure 3: Viscosity vs. concentration of CPAM for different shear rates.

Note that the viscosities in both cases are very similar for the polymer concentrations considered, and follow the same shear-thinning trend. However, the HPAM has a higher molecular weight (8-10 x 10^6 g/mol) in comparison with the cationic polyacrylamide (5-6 x 10^6 g/mol), while its viscosity is virtually the same. This indicates that the CPAM shows better viscosifying ability for the same conditions. This is in line with the results found by Divers (2017), who suggests that CPAMs are more resistant to the effects of the salinity due to its positively-charged structure.

Critical Concentrations

Figure 3 shows the viscosity of the CPAM solutions as a function of the polymer concentration for a range of shear rates. The graph indicates that the viscosity increases with the concentration, as expected. However, two linear trends are observed. The first trend characterizes the dilute region, in which the intermolecular interaction is minimal, leading to lower viscosity of the solution (Yen et al., 1989). The second trend, on the other hand, represents the semi-dilute region, for which these interactions are more prominent and entanglement effects appear, making the viscosity rise sharply when the concentration is increased (Al Hashmi et al., 2013). A critical concentration (C*) separates these regions, which is found by the interception of the trend lines in the graph. For the shear rates considered, C* is located slightly above 500 ppm. **Table 3** presents the coefficients of the trend lines adjusted by a Power Law for the dilute and semi-dilute regions and the critical concentrations for each shear rate.

Table 3: Parameters of the trend lines for the dilute (dashed-line) and semi-dilute (continuous line) regions and the respective values of C*.

Shear Rate (s^{-1})	Trend Line 1 (Dashed)			Trend Line 2 (Continuous)			C* (ppm)
	a	b	R^2	a	b	R^2	
7.847	0.7129	0.1593	0.886	9E-5	1.5812	0.993	552.02
33.6	0.6434	0.1822	0.91	5E-4	1.3254	0.994	524.81
88.59	0.7171	0.1564	0.886	0.0011	1.1808	0.994	558.67
233.57	0.8831	0.1167	0.783	0.0028	1.0316	0.993	538.62

* Adjusted by the potential trend line: $\eta = a.c^b$

The data does not indicate a clear trend between the critical concentration and the shear rate since the values oscillate when this parameter changes. Papanagopoulos et al. (1998), Lopes et al. (2014), and Silveira et al. (2016) observed that C* increases with the shear rate. This trend is attributed to the deformation of the chains, which must cause difficulties in their interpenetration in solution (Papanagopoulos et al., 1998). Bento (2015), differently, observed the opposite relationship between these parameters. **Table 4** shows values of C* for the CPAM and the HPAM used by Bento (2015).

Table 4: Comparison of C* for CPAM and HPAM.

Shear Rate (s^{-1})	C* - CPAM (ppm)	C* - HPAM (ppm)
7.847	552.02	1905.39
33.6	524.81	1901.77
88.59	558.67	1873.98
233.57	538.62	1860.52

As indicated in the Table, the critical concentration is considerably lower for the cationic polyacrylamide. The comparison between the two polymers suggest that for the same temperature, salt concentration, and shear rates, the CPAM enhances the viscosity of the solution more effectively than the HPAM by changing the regime from dilute to semi-dilute at a lower polymer concentration.

Viscoelasticity

Initially, an Amplitude Sweep Test (AST) was carried out using ω = 1 Hz to determine the elastic and the viscous module (G' and G", respectively) versus the shear stress. The results are presented in **Figure 4 (a)**. Afterwards, the Frequency Sweep Test (FST) was implemented using shear stress of 0.1 Pa, within the Linear Viscoelastic Region (LVR), as displayed in **Figure 4 (b)**.

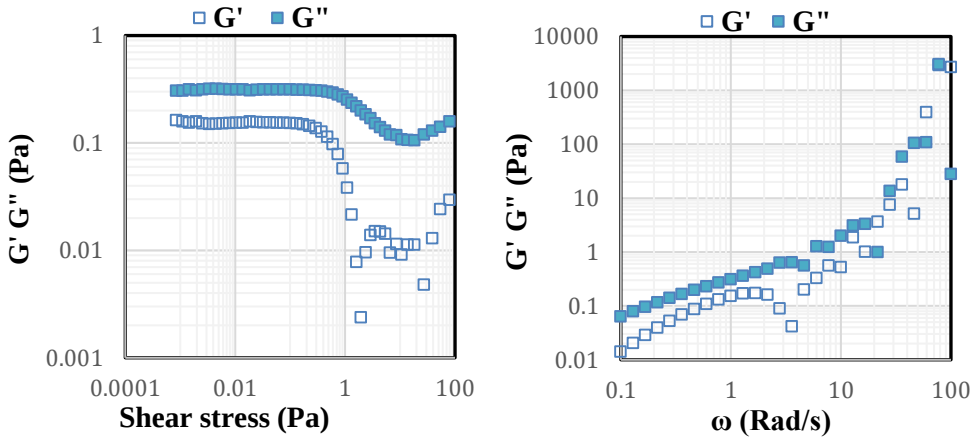

Figure 4: (a) AST and (b) FST for the 5000 ppm solution.

The Figure shows that the viscous module is predominant for this polymer. Its value (0.315 Pa) is approximately the double of the elastic module (0.154Pa) within the LRV. The tests were performed only for the stock solution because for solutions with lower concentrations, the elastic behavior is even less prominent since it decreases when the concentration of the polymer is lower (Hernández et al., 2018). The LVR ends at a shear stress of 0.2 Pa, approximately. After this point, the network formed by the polymers is deformed by the shear and the curves for G' and G" diverge from the plateau. These results are consistent with the literature for solutions with high salt concentrations (Silveira et al., 2016; Zhang et al., 2017; Hernández et al., 2018).

Conclusions

Laboratory tests were performed using a cationic polyacrylamide at 23ºC and 110,000 ppm NaCl. A rheometer was used to evaluate the effects of shear and polymer concentration on the viscosity of the solutions. AST and FST were also implemented to assess the viscoelastic behavior of the polymer.

The flow curves showed that the polymer displays a pseudoplastic behavior for the shear rates considered. Also, the effects of shear were more pronounced for high-concentration solutions. Furthermore, the CPAM was comparable to the anionic polyacrylamides regarding its ability to increase the viscosity of the brine.

The viscosity was plotted against the polymer concentration to obtain C*. There was no clear trend between C* and the shear rate, as suggested by other authors. The CPAM displayed substantially lower critical concentration than the anionic HPAM selected from the literature when conditions were the same. Additionally, the viscoelastic tests showed that the viscous module is dominant for the cationic polyacrylamide at 5000 ppm.

In brief, the results suggest that cationic polyacrylamides may be an interesting option for polymer flooding projects due to their promising ability to enhance the viscosity of aqueous solutions and possible better resistance to the salinity when compared to anionic polymers.

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