Flow behavior and thermal resistance of xanthan gum in formate brine

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Abstract

Drilling and completion operations in HP/HT environments demand the use of environmentally friendly fluids with suitable properties such as solid-free high-density and pseudoplastic behavior. Xanthan gum solutions in different brines may be an interesting alternative to ensure a suitable thermo-rheological behavior and biodegradability. Nevertheless, xanthan exposed at high temperature experiences thermal degradation that can modify the flow properties over time and limits the ceiling temperature of oilfield applications. To gain insight on this issue, this paper characterizes the flow behavior of low concentration XT solutions in calcium and potassium brines, evaluating the effect that potassium formate exerts on both the flow properties and the resistance to thermal degradation of xanthan solutions as a function of the biopolymer concentration. Xanthan in formate brine retains the pseudoplastic behavior up to 190ºC, however, low concentrate solutions undergo a thermal degradation that decreases the recovery of pseudoplasticity after being exposed to high temperature.

Keyword: xanthan gum, formate brine, flow behavior, thermal resistance

1. Introduction

Water soluble biopolymers are an interesting alternative in the oil industry to develop environmentally friendly fluids due to their biodegradability and harmless characteristics. Polysaccharide biopolymers are being used widely in the oilfield as viscosifiers for flooding and drilling operations due to their pseudoplastic behavior, at low concentrations and moderate temperatures, and their high resistance to shear degradation (Wei et al., 2014; Jang et al., 2015; Ghoumrassi-Barr and Aliouche, 2016). New drilling and completion of deeper wells, horizontal drilling and slim-hole operations demand the use of environmentally friendly fluids with selected properties such as solid-free high-density and suitable viscosity versus shear rate (Boul et al., 2017). These fluids can be formulated using biopolymer solutions in monovalent and divalent cation brines. High solubility salts (i.e. formate, chloride and bromide brines) are preferable to achieve the required density to compensate the formation pressure. High molecular weight biopolymers (i.e xanthan, guar, wellan, etc.) are selected to ensure a suitable thermo-rheological behavior, to carry and maintain in suspension the drilled cuttings, to resist thermal degradation at the temperature of the well, and to guarantee the biodegradability of the post-operations waste fluids (Caenn et al., 2017). Among biopolymers, xanthan gum (XT) may be preferable due to both its excellent solubility in water and brines and its satisfactory rheological properties at low concentrations, compared to others biodegradable polymers such as guar gum, wellan gum and scleroglucan (Howard et al., 2015). These characteristics cover a wide range of engineering requirements, from high viscosity at low shear rate, necessary when the flow is stopped, to low viscosity at high shear rate for easy pumping circulation (Asafa and Shah, 2014; Hermoso et al., 2015).

The thermo-rheological properties of XT in water solutions have been described in the literature with the help of both linear oscillatory shear (Choppe et al., 2010; Rochefort and Middleman, 1987; Whitcomb and Macosko, 1978) and viscous flow techniques (Dario et al., 2011; Marcotte et al., 2001). These properties have been explained on the basis of time-dependent structures. The most accepted structure for XT in solution is a partially ordered broken helix that undergoes a progressive order-disorder transition. In the ordered state, XT solutions show the rheological behavior of a weakly structured material, characterized by a tendency to reach a high value of the Newtonian viscosity, in the low shear-rate region, and a pseudoplastic fall, characterized by an exponential decrease of the viscosity in the intermediate shear-rate region. In the disordered state, XT solutions lose their pseudoplasticity and behave as a low viscosity liquid (Choppe et al., 2010). Variables such as the chemical composition and concentration, side-chain substituents, presence of ions, pH, and temperature may influence the structure, and consequently, the rheological behavior of the solution and its engineering properties (Garcia-Ochoa et al., 2000; Sutherland, 1994).

The presence of salt heavily influences the order-disorder state of XT in solution and its engineering properties. At low concentration, the polymer chains contract by the screening effect of cations, decreasing the viscosity of the solution. For higher concentrations, the ordered conformation improves the gel-like behavior by associations with hydrogen bonds, altering the shear viscosity, depending on the saline strength and pyruvate content of the polymer (Fitzpatrick et al., 2013). When the temperature increases, the order-disorder conformational transition takes place, depending on concentration of both salt and polymer and the type of anions present in the solution, the rheology of the solution changes from gel-like behavior to the Newtonian flow (Wyatt and Liberatore, 2009).

The influence of salts on both the rheological and thermal properties of xanthan solutions is very important to design solid-free drilling and completion fluids. Suitable rheological behavior, preselected density and thermal resistance can be combined by controlling the type of salt and its concentration (Hermoso et al., 2017). In these solutions, salts can act not only as weighting agents for adjusting density but also as thermal stabilizers, extending the range of temperature where the solution retains its pseudoplastic behavior (Bradshaw et al., 2006). In this sense, formate salts improve significantly both the density and the resistance to thermal degradation of XT in brine solutions (Howard et al., 2015), being extensively used in many HP/HT challenged fields with success (Gao, 2019). Nevertheless, the formulations of formate drilling fluids with biopolymers such as XT have limited thermal resistance to degradation at high temperature, being a challenge to increase both the time of exposure at high temperature and the temperature ceiling for application in HP/HT environments.

However, there are in the open literature few papers devoted to the study of the flow behavior of XT in formate brines at high temperatures and the influence of the thermal degradation on the pseudoplastic properties of these solutions.

To bridge this knowledge gap, in a previous study (Reinoso et al., 2019) we discussed the rheological behavior of the solution of xanthan gum at 1 wt% in concentrate chloride and formate brines, concluding that potassium formate shifts the thermal transition of the biopolymer to higher temperatures, enlarging the range of temperature at which the solution behaves as a weak gel. In this paper, we focus on the study of the flow behavior of low concentration solutions in calcium and potassium brines, evaluating the effect that potassium formate exerts on both the flow properties and the resistance to thermal degradation of xanthan solutions as a function of the biopolymer concentration. Potassium formate brine enhances the resistance of xanthan solutions to thermal degradation, improving the conservation of the pseudoplasticity proportionally to XT concentration and suggests that XT in potassium formate brines would extend the operational temperature range of any drilling fluid where it is present.

2. Materials and methods

Native XT solutions were prepared by adding xanthan powder (Mw ~10^6 g/mol; lot 0066563; Guinama S.L., Spain) without purification to distilled water, 0.01 wt% sodium azide (Sigma–Aldrich Co., Germany) was added to the solution as a preservative. The polymer was slowly added to water using a magnetic stirrer, maintaining the solution at rest to fully hydration for 24h, after which, the solutions were stirred in a Silverson mixer at 25ºC, at 600 and 2000 rpm for 15 minutes respectively.

Brine solutions were prepared by dissolving potassium formate, potassium chloride or calcium chloride salts (all from Sigma–Aldrich Co., Germany), in the native XT solutions previously prepared until saturation, at room temperature (~20ºC), using a low shear mixer at 500 rpm (235 g KFo/100 ml; 34.4 g KCl/100 ml; 98.2 $CaCl_2 \cdot 2H_2O$/100 ml). The density of the XT saturated brine solutions was measured at 20ºC with an Anton Paar DMA5000 densimeter, resulting 1.5004±0.0005 g/mL, 1.1728±0.0002 g/mL and 1.4115±0.0003 g/mL respectively.

The rheological characterization was carried out using a controlled stress rheometer Physica MCR-301 (Anton Paar, Austria), equipped with a pressure cell and coaxial cylinder geometries CC33/PR/XL and DG35.12/PR. A conventional coaxial cylinder CC28 was used as reference geometry at standard pressure.

Steady-state flow curves were conducted in the range of temperature of 20 to 190ºC. Samples were loaded into the pressure cell at room temperature and pressurized with an inert gas (N_2) to avoid vaporization of water at temperatures above 100ºC. The pressure cell was heated to achieve the measuring temperature and the pressure was maintained at 50 bar throughout an automatic Isco pump model 260D (Isco Teledyne, USA). The flow curves were obtained by increasing the shear rate (upward curve) and then decreasing the shear rate, with the data collected over a period of 60 seconds at each shear rate, in the controlled shear rate mode of the rheometer. The effect of the pressurizing inert gas and thermal degradation were studied comparing flow curves at 80ºC. At least two replicates of each test were undertaken, with a standard deviation among replicates within ±5%.

3. Results and discussion

Figure 1 shows the flow curves for low concentrate XT solutions (0.25 wt%) in potassium and calcium brines, at selected temperatures. As can be seen on Figure 1A, at 20ºC, both native and brine XT solutions behave as non-Newtonian shear-thinning fluids, showing a high degree of sensitivity to shear-rate, that can be measured by the slope of the viscosity versus shear rate. At this temperature, the XT solution at 0.25 wt% would adopt a partial self-associated structure (Rochefort and Middleman, 1987; Ross-Murphy, 1995; Pelletier et al., 2001) that partially disrupts under shear, showing a shear-thinning behavior due to the orientation of the polymer chains in the direction of flow as the shear rate increases. This shear-thinning or pseudoplasticity can be quantified by means of characteristic parameters from different models such as the power law (Song et al., 2006), Hershel-Bulkley (Choppe et al., 2010), Carreau model (Jang et al., 2015) and Cross model (Fitzpatrick et al., 2013). For this study, several engineering parameters such as the limiting viscosity at both high shear-rate, η_{∞}, and low shear-rate, η_o, the flow index m and the consistency index k, have been quantified with the help of the Cross' model (Cross, 1965):

$$\eta = \eta_\infty + \frac{\eta_o - \eta_\infty}{1+(k\cdot\dot{\gamma}\,)^m} \qquad (1)$$

The presence of cations increases the pseudoplasticity of XT at 0.25 wt% in concentrated brines. The index m decreases in the order potassium chloride, calcium chloride and potassium formate brine, from 0.665 for native xanthan up to 0,554 for formate brine, at 20ºC. In the low shear rate region, the native XT solution at 0.25 wt%, shows a tendency to reach the Newtonian plateau. The value of the zero-shear-limiting viscosity predicted by the Cross' model for the native XT solution is lower than that for the brine solutions as has been previously reported by Wyatt and Liberatore (2009) and Wyatt et al. (2011). Nevertheless, at intermediate shear rates, the viscosity of native XT solution is higher than those for brine solutions. The decrease of viscosity at low concentrations of XT in solution in the presence of salt has been attributed to the screening effect of charge that shrinks the polymer chains in the brine solutions, decreasing the interaction among them (Bergmann et al., 2008; Nieto et al., 2018). In the high shear rate region, XT in calcium chloride and potassium formate achieve higher values of the limiting viscosity than those for the native and the potassium chloride brine solutions, at low and intermediate temperature (Figure 1A and 1B). This fact indicates lower orientation of the entangled polymer chains in the direction of the flow for higher concentrated brines (due to the higher solubility in water of calcium chloride and potassium formate compared to potassium chloride brine). It is likely that, the polymer chains in high ionic strength solution develops robust entangled rod-like structures that increases the hydrodynamic volume under flow, increasing the values of the infinite-shear-limiting viscosity (Mezger, 2014).

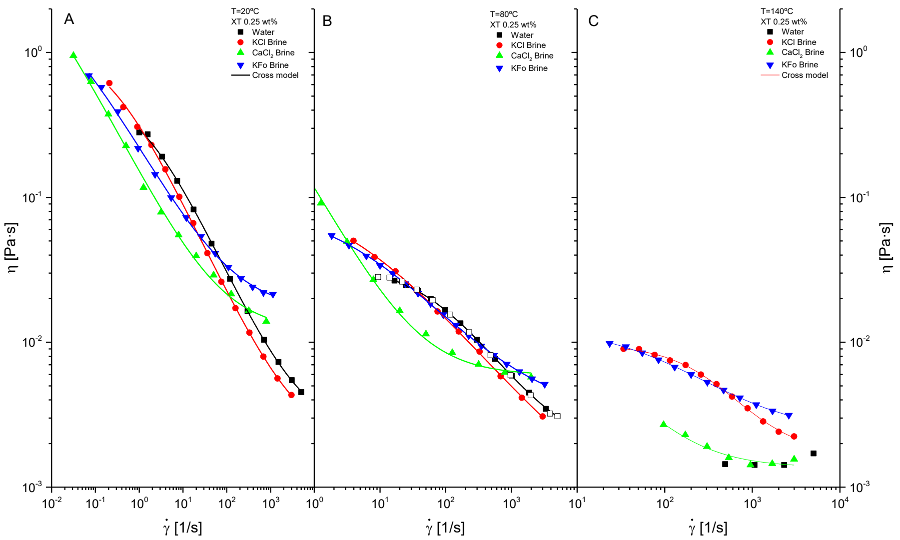

Figure 1. Evolution of the viscosity versus shear rate as a function of both temperature and type of brine for xanthan gum 0.25wt%. A) 20ºC. B) 80ºC. C)140ºC.

At 80ºC, the degree of shear-thinning for both the native XT solution and potassium brines decreases (values of the index m increase up to 0.755 for native XT and 0.705 and 0.630 for chloride and formate brines respectively), being nearly insensitive to temperature for calcium brine (Figure 1B). At this temperature, the viscosity values for XT in brine are higher than those for the native solution at low shear rates, being very similar when the shear rate increases. Native XT solution progressively undergoes the order/disorder transition from a partially ordered random broken helix to a disordered random coil conformation at this temperature. XT solution becomes less viscous and less sensitive to shear as have been previously reported by Pelletier et al. (2001). In brine solutions, the self-association by hydrogen bonds, which may increase the shear-thinning region and shifts the transition temperature to higher values, competes with the shielding effect of divalent cations that may decrease the viscosity values. The former phenomenon would be predominant in the case of potassium brines and the later in the case of calcium brine. In the high shear rate region, the rod-like entangled chains hinder the orientation into the flow direction, which could explain the increase in viscosity (Mezger, 2014). As can be seen in Figure 1B, the presence of the pressurizing gas (50 bar of N_2) does not influence significantly the flow behavior of xanthan solutions since both curves at atmospheric pressure and pressurized with 50 bar of N_2 were inside of the variability among replicates.

At higher temperatures, native XT solution behaves almost as a Newtonian liquid of low viscosity. Brine solutions shift the XT structural transition to higher temperatures, retaining the non-Newtonian properties over a large range of temperatures (Howard et al., 2015; Reinoso et al., 2019). As can be seen in Figure 1C, at 140ºC, XT 0.25 wt% in potassium brines show shear-thinning behavior with indices m of 0.923 and 0.756 for chloride and formate brines respectively. XT in calcium brine shows significantly lower viscosity at the same shear rate and an index m near the unity (0.998). Nevertheless, the increase of the viscosity; at higher shear rate, for both the native and the calcium chloride solutions maybe artefact due to the contribution of the turbulent flow. The degradation of the viscous properties for XT solution of similar concentration in calcium brines has been previously reported by Xie and Lecourtier (1992) and it has been attributed to the thermal transition that the biopolymer undergoes at lower temperatures in calcium than in potassium brines (Seright and Henrici, 1990).

The properties of formate salts (mainly high solubility in water and the antioxidant properties of the formate anion) make these compounds better than other salts (chloride and bromide) for the formulation of solid-free drilling and completion fluids (Howard et al., 2015; Reinoso et al., 2019). Formate salts provide a large range of fluid density, while at the same time increase both the range of pseudoplastic behavior of the solution and its thermal resistance. In this sense the evolution of the flow properties of XT in concentrate formate brine as function of biopolymer concentration has been studied.

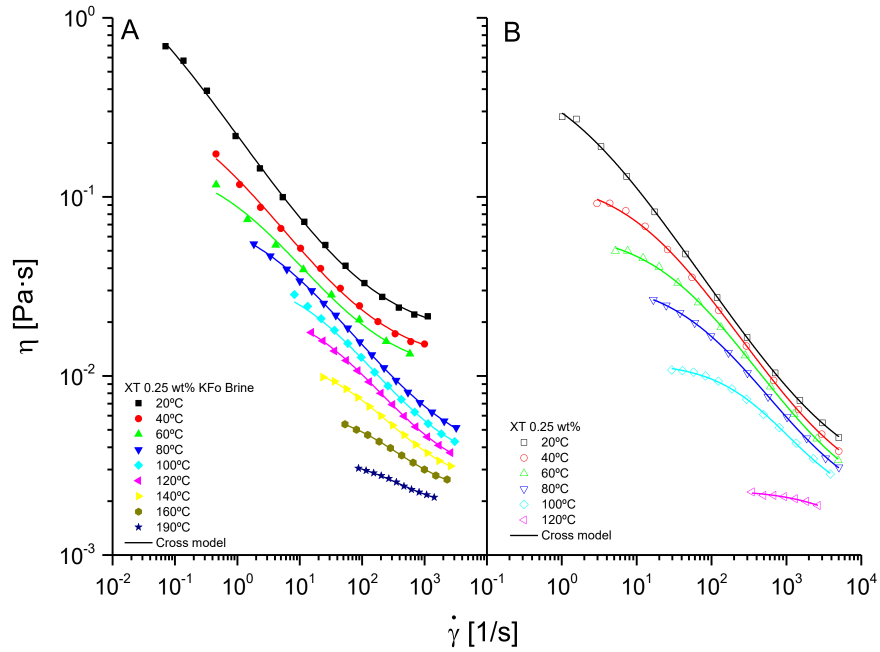

Figure 2. Evolution of the viscosity versus shear rate as a function of the temperature. A) Xanthan gum solution at 0.25wt% in potassium formate (KFo) brine. B) Xanthan gum solution at 0.25wt% in distilled water.

Figures 2A to 4A depict the flow curves of XT in formate brine, at selected concentrations of XT, 0.25, 0.50 and 0.75 wt% respectively, in the range of temperature from 20ºC to 190ºC. In Figures 2B to 4B the flow curves of the native XT solutions have been included as reference.

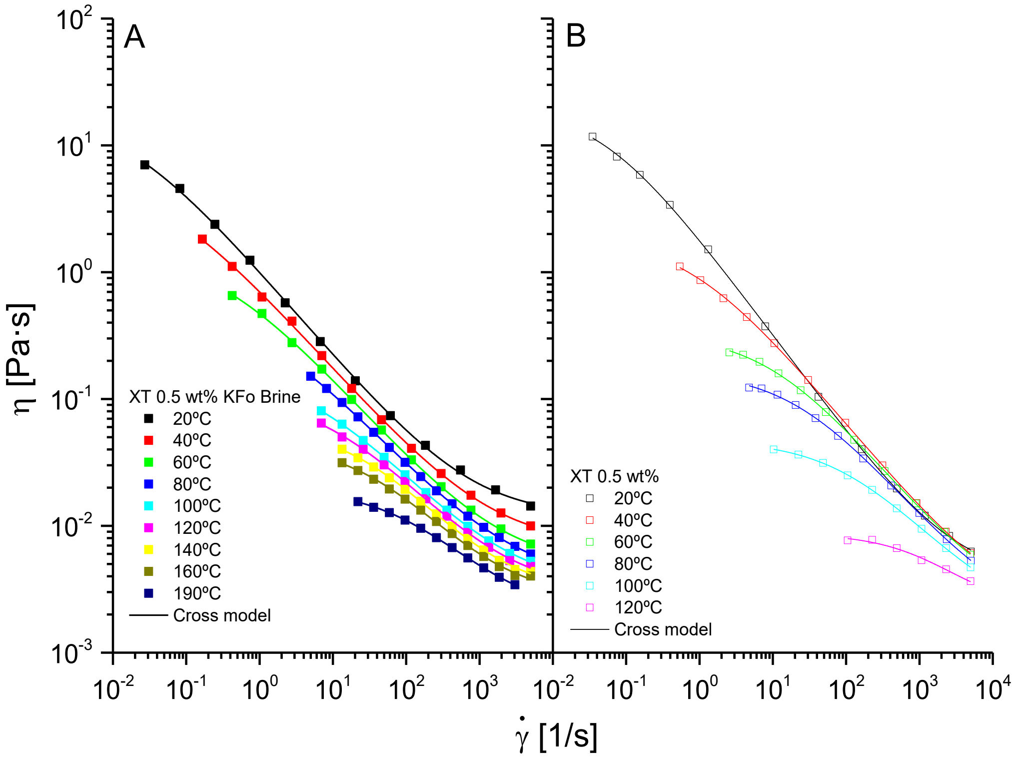

Figure 3. Evolution of the viscosity versus shear rate as a function of the temperature. A) Xanthan gum solution at 0.5wt% in potassium formate (KFo) brine. B) Xanthan gum solution at 0.5wt% in distilled water.

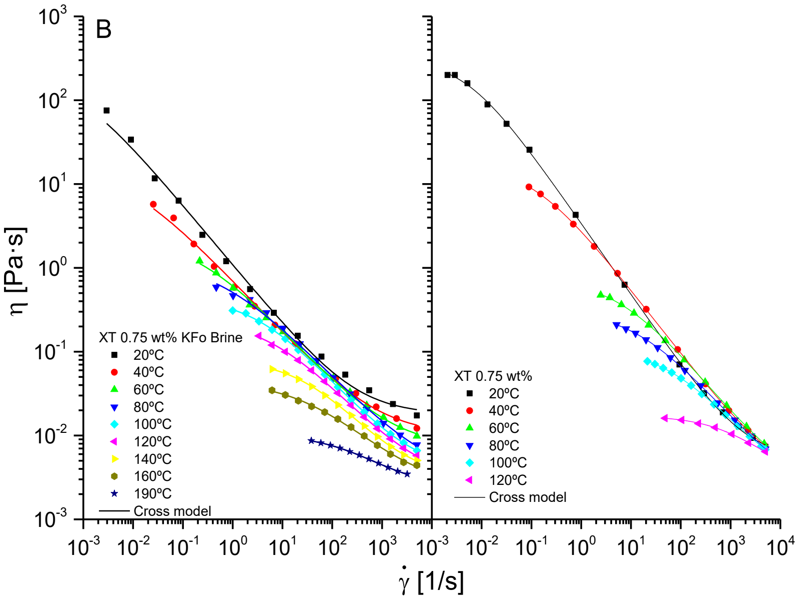

Figure 4. Evolution of the viscosity versus shear rate as a function of the temperature. A) Xanthan gum solution at 0.75wt% in potassium formate (KFo) brine. B) Xanthan gum solution at 0.75wt% in distilled water.

Native XT solutions reveal their typical shear-thinning behavior, showing a trend for reach a zero-shear viscosity at lower shear rates, a pseudoplastic fall at intermediate shear-rate, and a slight tendency to reach an infinite shear viscosity in the high shear-rate region, beyond the experimental shear-rate window. As expected, the shear-thinning behavior of native XT solutions progressively vanishes as temperature increases approaching to the order-disorder transition. The side chains progressively lose their associations and the polymer is randomly dispersed in the solution, being less sensitive to shear (Pelletier et al., 2001). At temperatures above 120ºC, the flow behavior is mainly Newtonian, independently of the XT concentration due to the thermal degradation of the ordered conformation of the biopolymer (Lambert and Rinaudo, 1985).

XT in formate brine retains the shear–thinning behavior over a wide range of temperature compared with the native solution. As can be seen in Figures 2A, 3A and 4A, the pseudoplastic drop for XT in formate brine is slightly affected by the temperature until 140ºC. Above this temperature, the solution becomes more sensitive to temperature, being more evident for solutions of lower XT content. The pseudoplastic region is shortened and a progressive decrease in the values of the shear viscosity, at a given shear rate, is observed as the temperature rises to 190ºC.

To gain insight on the effect of temperature on the flow behavior of XT in formate brine solutions, Figure 5 shows the evolution of the zero-shear limiting viscosity and the infinite viscosity for XT in formate brine, estimated by the Cross' model as a function of temperature. The tendency on evolution of the zero-shear limiting viscosity for the native XT solutions has been also included for comparison.

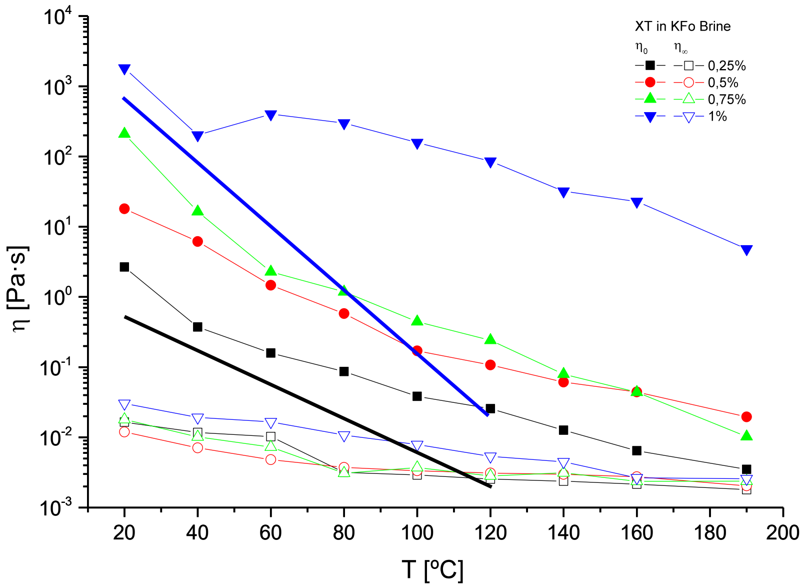

Figure 5. Evolution of the Cross´s model, zero-shear-viscosity (η_0) and infinite shear viscosity (η_∞) parameters, with the temperature for different concentrations of xanthan in KFo brine (lines and symbols). (Evolution of η_0 for the native XT solutions, black line 0.25wt% and blue line 1.0wt%, included for comparison).

For native XT solutions at constant temperature, the zero-shear-limiting viscosity increases exponentially with the concentration of XT, being 9.81C(wt%) at 20ºC decreasing for higher temperatures to 3.64C(wt%) at 100ºC (results not shown in Figure 5). These results agree with those previously reported by other authors for XT solutions without salt at similar concentration and temperature (Choppe et al., 2010; Wyatt et al., 2009). At constant concentration, a higher negative slope in the evolution of the zero-shear limiting viscosity with temperature is observed for the most concentrate native XT solution (1 wt%, continuous line in Figure 5). The increase in thermal susceptibility with XT concentration, in the range 20-120ºC, would indicate the development of a higher degree of weak association among polymer chains as the biopolymer content increases (Choppe et al., 2010; Wyatt et al., 2009; Xie and Lecourtier, 1992).

XT solutions in formate brine exhibit a slightly lower exponential increasing of zero-shear-limiting viscosity with concentration, nearly constant in the whole range of temperature tested, around 8.5C(wt.%) (results not shown in Figure 6). The evolution of zero-shear limiting viscosity with temperature is flattened and seems to be independent of XT concentration. Previous studies indicate that the evolution of the viscosity with temperature below the thermal transition can be modelled with both the Arrhenius model (Marcotte et al., 2001) and the WLF model (Pelletier et al., 2001), using shift factors based on the Time-Temperature Superposition Principle (TTSP). In this case, covering a larger temperature range, the decrease of the zero-shear limiting viscosity is less marked than those reported for less concentrated solutions (Choppe et al., 2010). This evolution can be modelled by empirical equations such as the Vogel model (result not shown). Consequently, formate brines, on the one hand, significantly decreases the thermal susceptibility of the XT solutions and, on the other hand, shifts the thermal transition to higher temperatures, as has been previously reported (Howard et al., 2015; Reinoso et al., 2019).

Figure 6 depicts the evolution of the parameters k and m of the Cross' model with temperature for the xanthan brine solutions studied. As expected, the time constant k (Figure 6A) of the Cross' model is less sensitive to temperature for XT solutions in formate brine than for the native XT solutions, indicating the higher degree of structuring of the biopolymer. In addition, the power index (Figure 6B) remains approximately constant for XT concentration higher than 0.5 wt%. For the solution of 0.25 wt%, a sharp increase of the power index is observed, indicating the sensitivity of this solution to thermal effects.

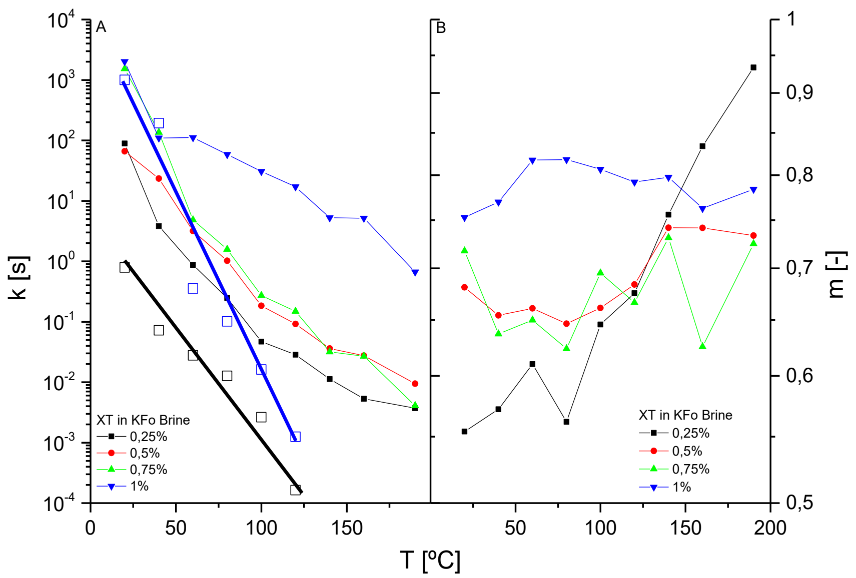

Figure 6. Evolution of the Cross´s model time constant k, and the index m, with the temperature for different concentrations of xanthan in KFo brine (line and symbols). (Evolution of parameter k for the native XT solutions, black line and open symbols 0.25wt% and blue line and open symbols 1.0wt%, included for comparison).

Figure 7 compares the flow curves, at selected temperatures, for XT solutions in formate brine as function of XT concentration. It may be observed that both the shear-thinning behavior and the viscosity values increase with XT concentration, being practically non-susceptible to temperature. The enhancement of the thermal resistance of XT in formate salts has been related to the capacity of the formate anion to reinforce the structure of the biopolymer in solution by promoting hydrogen bonding and self-association (Clarke-Sturman et al. 1986).

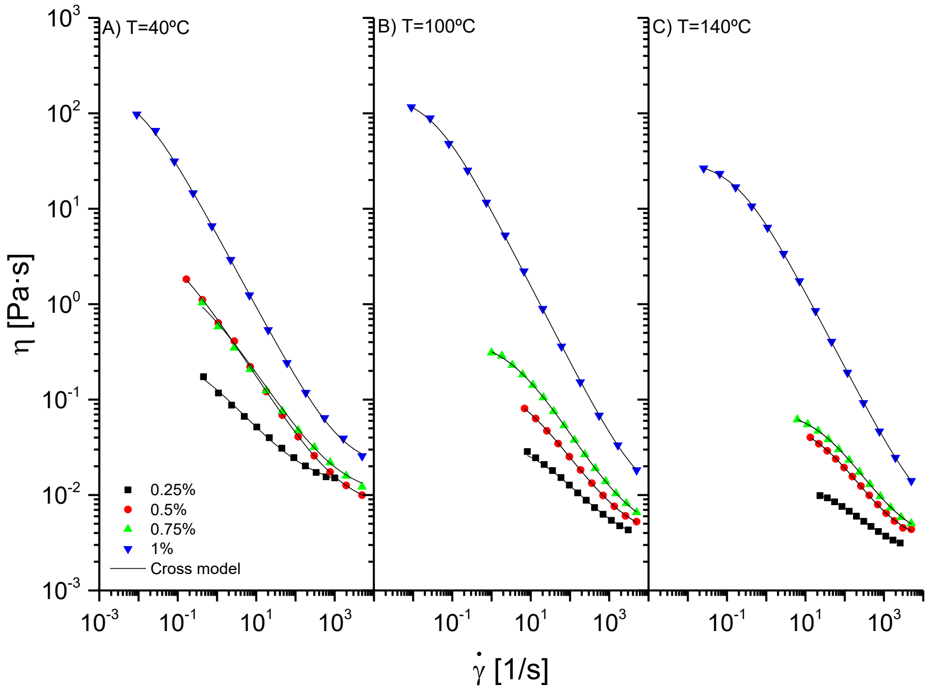

Figure 7. Evolution of the viscosity versus shear rate as a function of xanthan concentration in potassium formate brine (KFo). A) 40ºC. B) 100ºC. C) 140ºC.

Nevertheless, XT in solution experiences a slow degradation at high temperature as has been reported in the literature (Howard et al., 2015; Lambert and Rinaudo, 1985). The thermal degradation may decrease the recovery of the pseudoplasticity after exposing the XT solutions to high temperature. In this sense, Figure 8 compares the flow curves for selected XT concentrations in formate brine, measured at 80ºC, before and after submitting the sample to the stepwise program of temperatures for the flow characterization from 80 to 190ºC (steps at 80ºC, 100ºC, 120ºC, 140ºC, 160 ºC, 190ºC and return to 80ºC, 1.5 hours interval). In addition, the parameters of the Cross model are presented in Table 1. As can be seen on Figure 8A, for low XT concentration (0.25 wt%) an important decrease in viscosity is observed over the whole region of shear rate tested, more significantly in the low shear region. In contrast, the more concentrated XT solutions recover the original pseudoplastic characteristic to a large extent after cooling from 190ºC to 80ºC (see Fig. 8B and 8C for 0.5 and 1.0 wt%, respectively). These results indicate that the effect of short-term thermal degradation on the pseudoplasticity of XT solutions depends on XT concentration, being more significant for the low concentrate solutions, where a lower degree of interactions between polymer chains leads to a weaker gel structure, which exhibits a rheological behavior very sensitive to polymer degradation. For the more concentrated XT solutions, a stronger structure would be developed due to a higher degree of interactions between polymer chains (higher density of chains), that damps the effect of thermal degradation on the bulk viscosity of the solution. Nevertheless, high temperature destroys part of the structure, as is indicated by the decrease in the values of zero-shear limiting viscosity, at 80ºC, displayed in Table 1 after submitting the solution to 190ºC (62%, 53% and 45% of decrease respectively). However, the power index m increases significantly only for brine with low XT content (0.25 wt%), being practically the same for higher XT concentration.

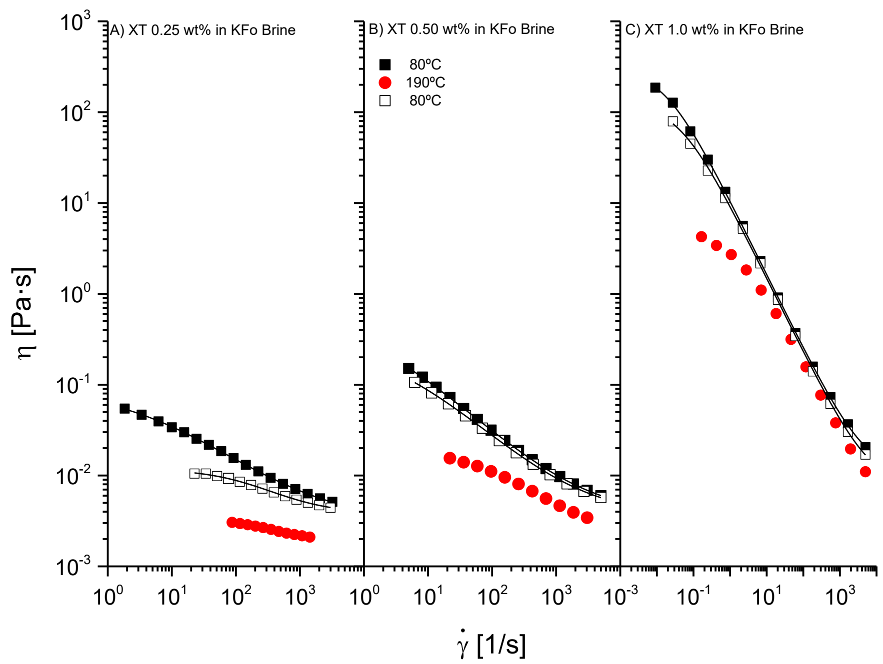

Figure 8- Recovery of the pseudoplasticity, at 80ºC, after submitting the sample at the temperature of 190ºC.

These results suggest that XT, at concentrations below 0.5 wt%, might have limited effectiveness as a component for rheology control in HP/HT environments where the drilling fluid is submitted at temperatures near 190ºC due to the negative effect of the short-term degradation on the pseudoplasticity. An increase in XT concentration would mitigate these negative effects on the rheology, enlarging the time interval in which the fluid retains acceptable rheological properties for HP/HT applications.

The thermal degradation of pure XT starts around 232ºC as has been reported by Srisvastava et al. from TGA results of pure polymer (Srivastava et al., 2012). In solution, the thermal stability of XT increases in the presence of salts (Lambert et al., 1985; Xie and Lecourtier, 1992) where the ionic strength would protect the helical structure from the chemical attack. Several mechanisms of degradation of the structure and properties of XT in solution such as mechanical degradation, free-radicals, hydrolysis and enzymatic degradation have been proposed in the literature (Ash et al., 1983; Wellington, 1983).

The XT solutions in formate brine studied in this work show high resistance to mechanical degradation when they were submitted to shear loops in the range 10^3-$5\cdot10^{-3}$ s^{-1} even at the highest temperature of 190ºC, in agreement with the good mechanical resistance reported previously for XT solutions of similar concentration submitted to the shear conditions typical in oilfield (Seright et al., 2011).

Free-radicals oxidation of the hydroxyl groups has been proposed as a degradation mechanism for XT solutions in the presence of oxygen. Oxidation can be minimized reducing the oxygen concentration in solution via oxygen scavengers and increasing the brine concertation (Wellington, 1983). In this sense, the thermal resistance of XT solution in formate brines has been related to a slowdown of the degradation of the structure due to the antioxidant properties of the formate anion in combination with the salting out of the presence of the cations (Howard et al., 2015). For these XT solutions, a minimal concentration of oxygen could remain in the pressure cell even thought it was pressurized with 50 bar of Nitrogen, thus some degree of oxidative degradation would be possible.

Table 1. Parameters of the Cross' model for different concentration of XT in formate brine, samples were submitted to temperatures of 80ºC-190ºC-80ºC at 50 bar of pressure.

XT 0.25 wt% in KFo brine			
	80ºC	190ºC	80ºC
η_o (Pa·s)	0.0864	0,0035	0,0122
η_∞ (Pa·s)	0,0031	0,0018	0,0038
k (s)	0,247	0,0034	0,0055
m (-)	0,562	0,933	0,871
XT 0.5 wt% in KFo brine			
	80ºC	190ºC	80ºC
η_o (Pa·s)	0,5789	0,0196	0,2726
η_∞ (Pa·s)	0,0037	0,0020	0,0037
k (s)	1,020	0,0094	0,342
m (-)	0,646	0,734	0,658
XT 1.0 wt% in KFo brine			
	80ºC	190ºC	80ºC
η_o (Pa·s)	299,2	4,825	124,813
η_∞ (Pa·s)	0,0107	0,0025	0,0076
k (s)	58,64	0,667	22,62
m (-)	0,818	0,784	0,818

Other mechanisms such as the hydrolysis of acetyl groups have also been suggested as responsible of short-term XT degradation at high temperature (Seright and Henrici, 1990; Wellington, 1983). For these solutions, the initial pH measured in the solution, at 80ºC, before pressurizing was around 8.1 and the final value, after submitting the sample to 190ºC, returning to 80ºC, and depressurizing was around 7.5. In this range of pH, XT solutions in brines show maximum thermal stability against hydrolysis as has been reported by Seright and Henrici (1990), therefore, degradation by hydrolysis seems to be unlikely. Further systematic studies would be necessary to understand the nature and kinetic of XT degradation at high temperature in concentrated formate brines, this would then provide a basis to improve the development of fluids for HP/HT applications.

4. Conclusions

Xanthan solutions at moderate concentration in potassium and calcium concentrated brines show non-Newtonian pseudoplastic behavior that can be modelled by the Cross' model in the range of temperature of 20-190ºC. Potassium brines shift the reversible thermal conformational transition of XT to higher temperatures, retaining the non-Newtonian properties over a wide range of temperatures, mainly formate brine.

XT in formate brine experiences a slow thermal degradation process at high temperature that decreases the recovery of the pseudoplasticity after exposing the solutions to high temperature. The detrimental effect of short-term thermal degradation is characterized by a decrease in the values of both the zero-shear limiting viscosity, the time constant k, and an increase in the value of the index, m, being more significant for low polymer concentration. An increase in XT concentration, would mitigate these negative effects on the rheology, enlarging the time interval in which the fluid retains acceptable rheological properties for HP/HT applications.

From the structural point of view, the low density of chains in low concentrate XT solutions would lead to the development of weaker gel structures, with rheological behavior very sensitive to thermal degradation of the side chains, probably due to irreversible free-radical oxidations at high temperature. The increase of XT concentration enhances the strength of the structure, softening the effect of the thermal degradation on the pseudoplastic behavior.

Acknowledgements

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