Rheological characterisation of xanthan gum in brine solutions at high temperature

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Abstract

Xanthan gum solutions are used in the oil industry for flooding, drilling and completion operations. The stabilization of the structure of xanthan gum solutions in presence of salts increases the value of both the order-disorder transition temperature and the gel strength. This effect is very important in order to design drilling and completion fluids since not only density and viscosity of the fluid can be improved by increasing the concentration of salts but also the range of temperature where the solution shows viscoelastic behaviour can be extended.

This paper presents results from a study on the rheological behaviour of xanthan gum solutions in different saturated brines. Chloride and formate potassium brines not only increase the viscosity of the solution but also extend the shear thinning behaviour to temperatures near 200ºC, maintaining a simple relaxation mechanism over the whole range of temperature where the ordered conformation dominates the rheological behaviour.

INTRODUCTION

Xanthan gum is a polysaccharide produced by “Xanthomonas campestris“ that is widely used in various industries due to the rheological characteristics of water solutions. In the oilfield, xanthan has been used from the 60’s as a viscosifier for flooding and drilling operations due to its high viscosity and pseudoplastic behaviour, at low concentrations and moderate temperature, and its high resistance to shear degradation (Ghoumrassi-Barr & Aliouche, 2016; Jang, Zhang, Chon, & Choi, 2015; Wei, Romero-Zerón, & Rodrigue, 2014). Nowadays, with the aims of protect the environment, the use of biopolymers in the oil industry has become an interesting alternative mainly due to their biodegradability and harmlessness characteristics. Furthermore, in hydraulic fracturing xanthan gum also has shown excellent abilities as proppant transport agent due to its gelling properties (Fink, 2013).

Xanthan gum has been studied extensively over the last past years from dilute to semi dilute concentrations. The rheological behaviour of xanthan solutions depends on many factors including concentration of biopolymer, salt concentration, pH and temperature. (Garcia-Ochoa, Santos, Casas, & Gomez, 2000). The structure of xanthan in distilled water, at low temperature, is a partially ordered broken helix, showing the rheological behaviour of a weakly structured material. In the presence of salt, xanthan gum undergoes a disorder-order transition. The ordered conformation improves the gel-like behaviour with a significant increasing of both the low shear viscosity and shear moduli, depending on the saline strength of the solution (Fitzpatrick, Meadows, Ratcliffe, & Williams, 2013). At high temperatures, an ordered (helix) to disordered (coil) conformational transition takes place that turns the gel-like behaviour to terminal Newtonian flow.

The effects of electrolyte nature, temperature, and shear history on the structure and rheological properties of xanthan gum solutions have been extensively studied over a wide range of xanthan concentrations. Whitcomb and Macosko (1978) studied the rheology of xanthan dilute solutions indicating the existence of a zero-shear-limiting viscosity at low shear and pseudoplastic behaviour at higher shear-rates. The shear rate for the transition from Newtonian to pseudoplastic behaviour seems to be independent of the concentration. Marcotte et al. (2001) studied the effect of concentration and temperature on the flow characteristic of xanthan solutions, at temperatures below the thermal transition, concluding that the pseudoplastic behaviour con be modelled by the model of Hershel-Bulkley model.

Dário et al. (2011) studied the effect of calcium ions from different salts on xanthan gum solutions at relatively high concentration. The flow behaviour was represented by a power law, observing that the effect of calcium salts at low concentrations decrease the consistency index values. These finding were explained assuming that low concentration induces a disordered state whereas the ordered state is recovered for higher concentrations, around 1 % w/v.

Rochefort and Middleman (1987) stated that not only the transition temperature increases with the salt content but also both steady-state and complex viscosity. Both oscillatory shear and steady-state viscous flow data could be generalized by the application of the Time Temperature Superposition Principle (TTSP) but the complex viscosity at a given frequency was greater than the steady-state viscosity at equivalent shear rate. Pelletier et al. (2001) reported that the TTSP holds partially in oscillatory shear but does not hold in steady-state flow. Choppe et al. (2010) concluded that xanthan solutions hold the TTSP, showing a unique characteristic relaxation time that increases exponentially with both concentration and ionic strength.

It is well-known that the stabilization of the structure of xanthan gum solutions due to the presence of salts increases both the value of the order-disorder transition temperature and the gel strength of the solution. This effect is very important in order to design drilling and completion fluids since both density and pseudoplasticity can be improved by controlling the type of salt and its concentration. Higher concentration of salts is necessary to adjust the density of completion fluids based on polysaccharide solutions. In this sense Howard et al. (2015) studied the effect of different brines on both the viscosity and the transition temperature of xanthan gum solution, concluding that formate brines increases significantly the transition temperature of xanthan gum solutions.

In spite of the large number of studies devoted to the rheological behaviour of xanthan gum in aqueous solutions, there is a lack of studies about the rheological behaviour at temperatures above the boiling point of water and very high salt concentrations, mainly due to the difficulty of accomplish rheological test which need to be performed under pressure to avoid the volatilization of the solvent.

This paper presents results from a study on the rheological behaviour of xanthan gum solutions in different saturated brines, at high temperature and pressure, with the aim of developing sustainable environmental friendly fluids for drilling and completion of oil wells.

EXPERIMENTAL

Materials

Commercial food-grade Xanthan gum (lot 0066563) from Guinama S.L. (Spain) was used without further purification.

Sample Preparation

Native xanthan solution 1.0 wt%, were prepared by adding xanthan powder without purification to distilled water, 0.01 wt% sodium azide was added to the solution as a preservative. In order to accomplish the full hydration of the polymer, firstly the polymer was slowly added to distilled water. The samples were maintained at rest to fully hydrate 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 dissolving small quantities of potassium formate, potassium chloride and calcium chloride salts at 25ºC, using a low shear flour-blade mixer at 500 rpm, in native xanthan solution 1.0 wt% previously prepared until saturation. The density of the xanthan saturated brine solutions were measured at 20ºC with an Anton Paar DMA5000 densimeter, resulting 1.5004 g/mL, 1.1728 g/mL and 1.4115 g/mL respectively.

Rheological measurements

The rheological characterization was carried out using controlled stress rheometers. A Physica MCR-301 rheometer (Anton Paar, Austria), equipped with a pressure cell and coaxial cylinder geometry CC33/PR/XL (33.204 mm inner diameter, 36.01 mm outer diameter, and 43.038 mm length) and double gap geometry DG35.12/PR (32.826 mm inner diameter 1, 35.126 mm inner diameter 2, 36.01 mm outer diameter and 59.97 mm length) was used for all measurements. A Haake Mars II Rheometer (ThemoHaake, Germany), equipped with conventional coaxial cylinder geometry DINZ20 (19.994 mm inner diameter, 21.71 mm outer diameter, and 30.038 mm length), cone-plate CP35-1 (35.002 mm of diameter and 1.002º angle) and serrated plate-plate PP35R (34.997 mm of diameter) was used as reference rheometer to investigate the effect of gas pressurization on the samples, at temperatures below 80ºC.

Steady-state viscosity curves were collected in the range of temperature of 20 to 190ºC. Samples were loaded into the Anton Paar pressure cell at room temperature and pressurized with an inert gas (N_2) to avoid evaporation of water at temperatures above 100ºC. The pressure cell was heated to achieve the measuring temperature and the pressure was regulated to 50 bar. The viscosity data 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, using the continuous shear rate mode option of the rheometer. The two sets of data were very similar (within 5% of each other) so only the downward flow curves behaviour are presented here. The effect of the pressurizing inert gas was studied comparing flow curves at 80ºC for each sample, with and without pressurization with measurements from conventional geometries.

Linear viscoelastic measurements were carried out in the range of 20 to 190ºC using the Anton Paar pressure cell and conventional geometries (CP35-1 and PP35R). Frequency sweeps, from 0.01 to 10 rad/s, were carried out at a shear stress inside the linear viscoelasticity region, previously determined by shear stress sweeps at the frequency of 1 rad/s. At least two replicates of each test were undertaken. The standard deviation among replicates was within ±5%.

Results and discussion

It is well known that xanthan gum solutions behave as non-Newtonian fluids at temperatures below the order-disorder transition. Figure 1A shows the evolution with temperature for native xanthan gum solution, 1 wt% in distilled water. At temperature below 60ºC, a highly degree of pseudoplasticity (shear thinning) can be observed. In this region of temperature xanthan gum in water solution adopts a partial self-associated conformation due to polymer entanglements and hydrogen bonds (Rochefort & Middleman, 1987; Ross-Murphy, 1995) that shows high viscosity at low shear-rates.

This weak structure partially disrupts and the polymer chains are oriented under shear in the direction of flow showing a shear-thinning behaviour as the shear rate increases. As the temperature increases above 60ºC, a transition from a partially ordered random broken helix conformation to disordered random coil conformation progressively takes place (Pelletier, Viebke, Meadows, & Williams, 2001). As a result, the xanthan becomes less viscous and less pseudoplastic. In addition, a tendency to reach the Newtonian plateau at lower shear rate is clearly noticed. At temperatures above 120ºC, the random coil conformation dominates the rheological behaviour and the solution behaves almost as a Newtonian liquid with a significant loss in viscosity. No significant effect on the flow behaviour is observed due to the presence of the pressurizing gas (50 bar of N_2) comparing the flow curves in Figure 1A measured at 80ºC, at atmospheric pressure (open symbols), and at 50 bar (solid symbols).

The flow behaviour of xanthan gums solutions has been satisfactorily modelled by different equations such as the power law (Song, Kim, & Chang, 2006) or more general models such as the Hershel-Bulkley model (Marcotte, Taherian Hoshahili, & Ramaswamy, 2001), the Carreau model (Jang et al., 2015) and the Cross model (Giboreau, Cuvelier, & Launay, 1994; Rodd, Dunstan, & Boger, 2000; Wyatt & Liberatore, 2009) depending temperature, concentration and presence of salts. In this work, the Cross' model has been used (Cross, 1965):

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

Where η_∞ is the infinite viscosity at high shear rate, η_o is the at zero-shear limiting viscosity at low shear rate, k is a constant related with the rupture of the physical linkages and m is the power index (Cross, 1965). The parameters for the model are shown in Table 1.

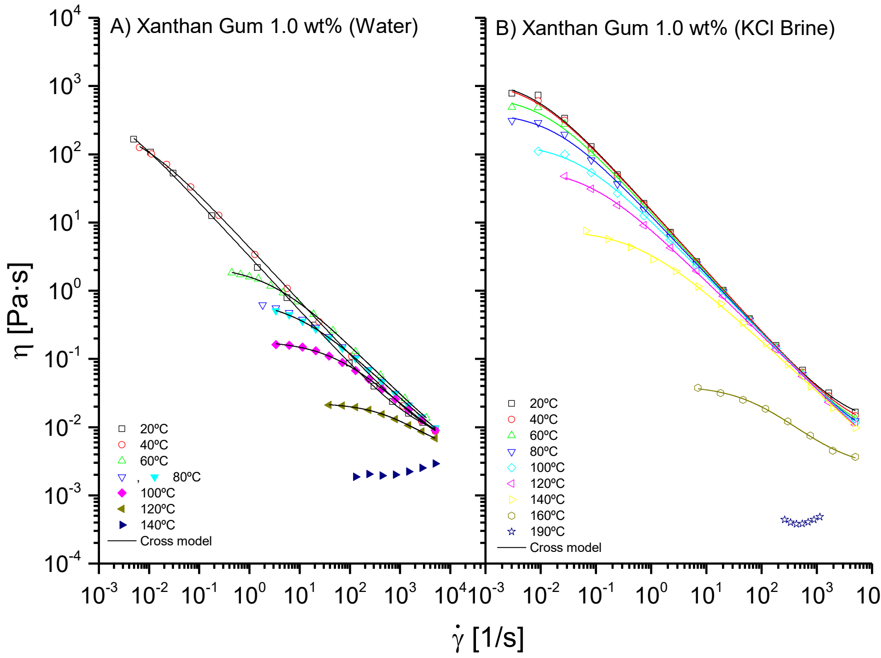

Figure 1. Viscosities versus shear rate. A) Native xanthan gum 1.0 wt% solution in distilled water, at ambient pressure (open symbols) and 50 bar of Nitrogen (filled symbols). B) Xanthan gum 1.0 wt% solution in saturated KCl brine.

The Cross' model takes into account the shear-thinning region and both trends to reach limiting values of the viscosity, zero-shear- viscosity and the infinite viscosity, at low and high shear rate respectively.

Table 1. Parameters of the Cross' model for the samples studied.

		Native xanthan 1.0 wt%		
T (ºC)	η_0 (Pa·s)	η_∞ (Pa·s)	K (s^{-1})	m
20	7,85E+02	5,83E-03	1,00E+03	0,797
40	2,84E+02	3,81E-03	1,93E+02	0,794
60	2,32E+00	1,89E-03	3,55E-01	0,746
80	7,46E-01	1,77E-03	1,01E-01	0,727
100	1,85E-01	2,75E-03	1,62E-02	0,757
120	2,26E-02	3,68E-03	1,25E-03	0,872
		Xanthan 1.0 wt% KCl brine		
20	1,26E+03	1,01E-02	1,34E+02	0,899
40	1,20E+03	7,74E-03	1,34E+02	0,893
60	7,20E+02	6,23E-03	8,55E+01	0,886
80	4,14E+02	4,38E-03	5,61E+01	0,865
100	1,45E+02	2,38E-03	2,18E+01	0,835

120	6,44E+01	5,92E-04	1,25E+01	0,795
140	7,96E+00	0,00E+00	1,61E+00	0,741
160	4,07E-02	2,46E-03	1,25E-02	0,855
Xanthan 1.0 wt% $CaCl_2$ brine				
20	1,57E+01	1,53E-02	5,44E+01	0,716
40	1,31E+01	1,00E-02	1,57E+01	0,816
60	1,58E+01	1,13E-02	1,44E+01	0,699
80	1,03E+01	9,34E-03	1,72E+01	0,671
100	8,00E+00	5,37E-03	1,05E+01	0,648
120	1,64E+00	3,61E-03	5,68E-01	0,707
Xanthan 1.0 wt% KFo brine				
20	1,81E+03	3,04E-02	2,01E+03	0,753
40	2,01E+02	1,92E-02	1,10E+02	0,770
60	4,01E+02	1,66E-02	1,11E+02	0,818
80	2,99E+02	1,08E-02	5,86E+01	0,818
100	1,58E+02	7,89E-03	3,07E+01	0,807
120	8,55E+01	5,38E-03	1,71E+01	0,792
140	3,20E+01	4,47E-03	5,25E+00	0,798
160	2,28E+01	2,65E-03	5,18E+00	0,763
190	4,83E+00	2,58E-03	6,68E-01	0,784

The pseudoplastic behaviour of xanthan solutions is required in drilling operations where a high viscosity is necessary to maintain cut solids in suspension when the flow is stopped and a low viscosity is necessary to ensure the drill bit can rotate without any excess energy being required. Consequently, native xanthan gum solutions have a limited temperature range of application or a “temperature ceiling” due to its thermal transition about 70-120ºC. In addition, for completion operation the density of the fluids need to be regulated using suspension of an insoluble compound, such as barite (barium sulphate) or soluble salts. However, brines not only increase the density of the solution but Howard has also shown that brines can modify both the viscosity and the thermal resistance of xanthan gum (Howard, Kaminski, & Downs, 2015).

To test this further, Figure 1B presents the flow curves for xanthan gum, 1.0 wt%, in saturated KCl brine, over the range of temperatures of 20-190ºC. In this case, the expected pseudoplastic behaviour is observed for temperatures below 160ºC. In the low shear rate region, the viscosity decreases as the temperature increases up to 160^{o}C, but above a shear rate of 10 s^{-1}, the viscosity is approximately independent of temperature. The degree of pseudoplasticity changes with temperature and can be quantified by the parameters of the Cross' model, as will be discussed later. In addition, a clear tendency to reach a zero-shear limiting viscosity in the low shear rate region is noticed over the whole range of temperature studied.

As temperature increases, xanthan 1.0 wt% in KCl brine seems to exhibit the typical sensitivity of xanthan solutions to temperature, retaining the shear thinning properties. This fact, could be explained assuming that the charge screening effect of the negatively charged xanthan (Muller, Anrhourrache, Lecourtier, & Chauveteau, 1986) produced by KCl leads to a conformational change from a partially ordered/disordered state to an ordered (helix) conformation more stable to temperature (Rochefort & Middleman, 1987). Consequently, the transition is displaced to higher temperatures (140ºC -160ºC region).

Figure 2A shows the flow curves for xanthan 1.0 wt% in in saturated $CaCl_2$ brine. As expected the pseudoplastic behaviour is observed for temperature below 120ºC. Over this temperature range, as the temperature increases, the viscosity, at a given shear rate, increases indicating a higher degree of structuring in the system, and consequently, the tendency to reach a zero-shear viscosity value in the low shear-rate region is displaced beyond of the experimental shear rate window. The experimental low shear-rate region is limited by the friction torque of the bearings (<50 μN·m) in the pressure cell requiring the minimum shear stress to be greater than around 0.1Pa. Nevertheless, the tendency to reach a high-shear limiting viscosity is evident in the high shear region. However, at temperatures above 120ºC a significant loss in both viscosity and pseudoplastic behaviour is notice.

The flow behaviour of xanthan gum 1.0 wt% in formate brine as function of temperature is depicted in Figure 2B. As in the above-mentioned samples, xanthan gum in formate brine behaves as a pseudoplastic liquid, showing the trend for reach both the zero-shear viscosity, at lower shear rates, and the infinite-shear viscosity value at higher shear rates.

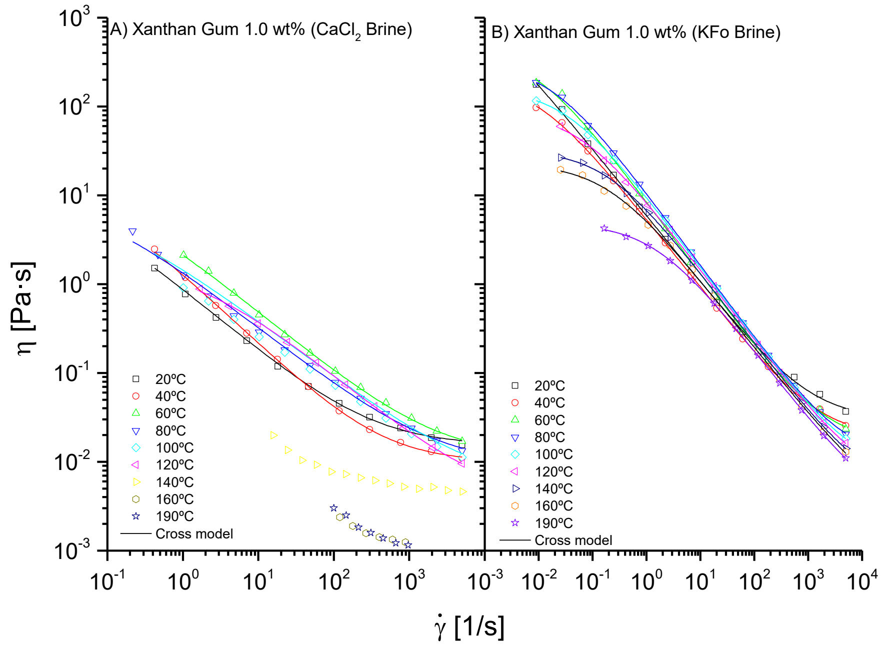

Figure 2. Viscosities versus shear rate for xanthan gum 1.0 wt% solution. A) in saturated $CaCl_2$ brine. B) in saturated KFo brine.

It can be seen that the pseudoplastic drop is almost unaffected until 140ºC. At temperatures above 140ºC, the solution becomes somewhat more sensitive to temperature. The Newtonian region appears at low shear rates, the pseudoplastic region is shortened and a progressive decrease in the values of the low shear viscosities is observed, as the temperature rises from 160ºC to 190ºC. Nevertheless, at 190ºC, the non-Newtonian behaviour is still retained over three orders of magnitude of shear rate. The thermal resistance of xanthan 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. In the presence of formate brine the transition temperature is displaced to temperatures above 200ºC, the original pseudoplastic behaviour is recovered to a large extent after cooling from 190ºC to 80ºC, nevertheless a slight degradation of the structure or thermal aging takes place when the brine is submitted to temperatures near 200ºC for long time (Howard et al., 2015).

In order to compare the effect of the different salts on the flow behaviour of the xanthan solutions, Figure 3 shows the flow curves, at selected temperatures, and Figure 4 depicts the evolution of the parameters k and m of the Cross' model with temperature for the xanthan brines solutions studied.

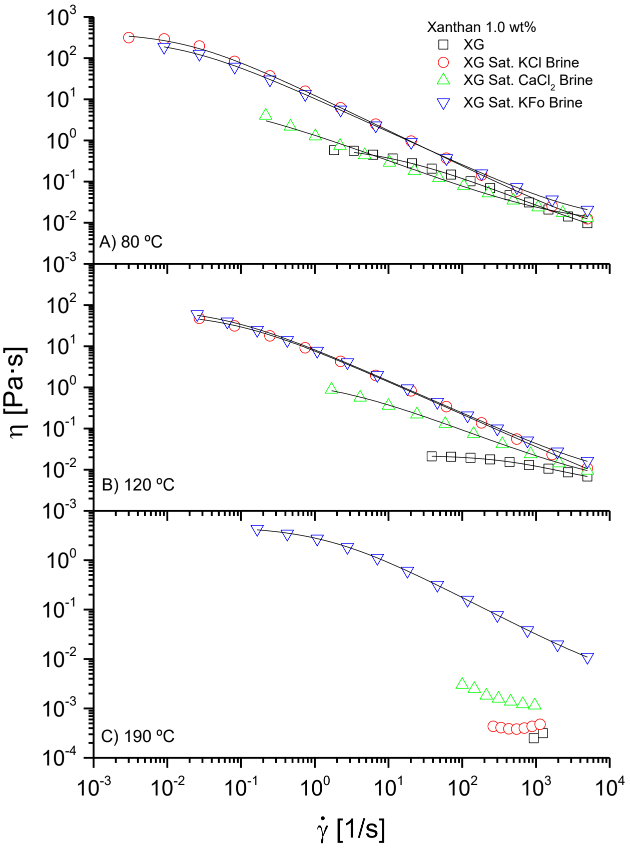

Figure 3. Comparison of flow curves for xanthan gum solution at 1.0 wt% in different brines.

At 80ºC, a temperature near the thermal transition of native xanthan in water solution (Choppe, Puaud, Nicolai, & Benyahia, 2010), both potassium chloride and formate brines significantly enhance the viscosity of the system, exhibiting higher viscosity in the low shear-rate region while in the high shear-rate region the flow curves converge to a very similar tendency to the limiting viscosity for all the solutions tested. At this concentration, calcium chloride brine does not enhance the viscosity over the native xanthan solution. Similar conclusions have been obtained in previous works for less concentrated calcium chloride solutions studied by (Dario, Hortencio, Sierakowski, Queiroz Neto, & Petri, 2011; Xie & Lecourtier, 1992). Nevertheless, the time constant k for calcium brine shows higher values than that for the native solution and slightly lower ones than those for potassium brine. Higher time constants would indicate more sensitivity to shear (Muller et al., 1986). This is in agreement with the development of weak structures in the solution as consequence of the presence of salt that has been pointed out for several authors (Mohammed, Haque, Richardson, & Morris, 2007; Ross-Murphy, 1995).

At the temperature of 120ºC, both potassium formate and chloride brines show a slight decrease of the values of their rheological properties. Calcium chloride brine presents the tendency to reach the zero-shear limiting viscosity, with a decrease in the time constant. At this temperature, the calcium brine is near to the transition temperature (Muller et al., 1986). On the other hand, the native xanthan solution in distilled water behaves as Newtonian, losing its shear thinning properties which is a consequence of a conformational change of the xanthan from a helix to a disordered structure. Finally, at the temperature of 190ºC, calcium and potassium chloride brine solutions fail showing artefacts due to flow instabilities at higher shear rates. Nevertheless, the formate brine solution still shows a high degree of shear thinning, with time constant and power index values similar to those for potassium chloride at 120ºC. The resistance to order-disorder thermal transition of xanthan solutions in formate salts has been attributed to the capacity of the formate anion to enhance the hydrogen bonding and self-association of xanthan molecules in water which is the origin of the salting-in effect seen initially in proteins(Clarke-Sturman & Sturla, 1988; Clarke-Sturman, Pedley, & Sturla, 1986; Howard et al., 2015).

As can be seen in Figure 4A, the time constant of the Cross' model is less sensitive to temperature for brine solutions than for the native xanthan solutions, indicating a higher degree of structuring of the biopolymer in brine solutions that may lead to an improvement of the resistance to temperature breakdown of the structure. The effect of temperature on the shear thinning behaviour of xanthan is less significant in the presence of salt due to the stabilization effect of the ionic strength, as can be deduced from the slope of the evolution of the Cross' time constant with temperature in Figure 4A.

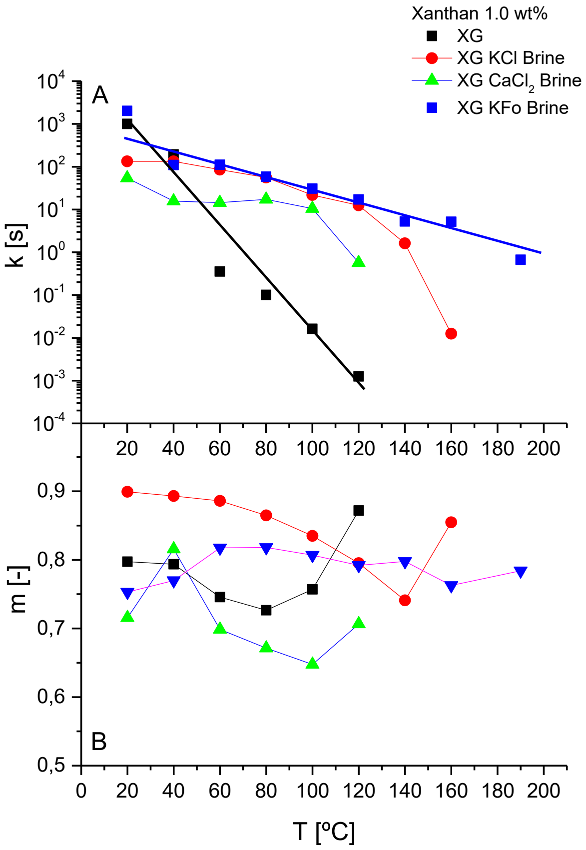

Figure 4. Evolution with temperature of both consistency and flow indexes for xanthan gum solution at 1.0 wt% in different brines.

On the other hand, the values of the power indices (Figure 4B) slightly decrease with temperature in the region of temperatures below the transition, except for the formate brine that remains approximately constant. A suddenly increase of the power index near the transition temperature is observed, independently of the value at which the transition takes place. Thus, on the basis of the parameters of the Cross' model, the thermal transition may be characterised by both the fall of the time constant values and the rise in the power index.

Figures 5 to 7 display both storage and loss moduli versus frequency, in the range of temperature from 20 to 190ºC, for the xanthan solution in potassium chloride, calcium chloride and formate brine respectively. As can be observed, at low temperatures, below

80ºC, the storage modulus is always higher than the loss modulus, indicating that a typical weak-gel structure is developed in xanthan solutions in the brines. In addition, both storage and loss moduli show only a weak dependence on frequency and temperature in this region. This fact is more apparent for both potassium chloride and calcium chloride brines than for formate brine that shows higher slope in the evolution of moduli with frequency.

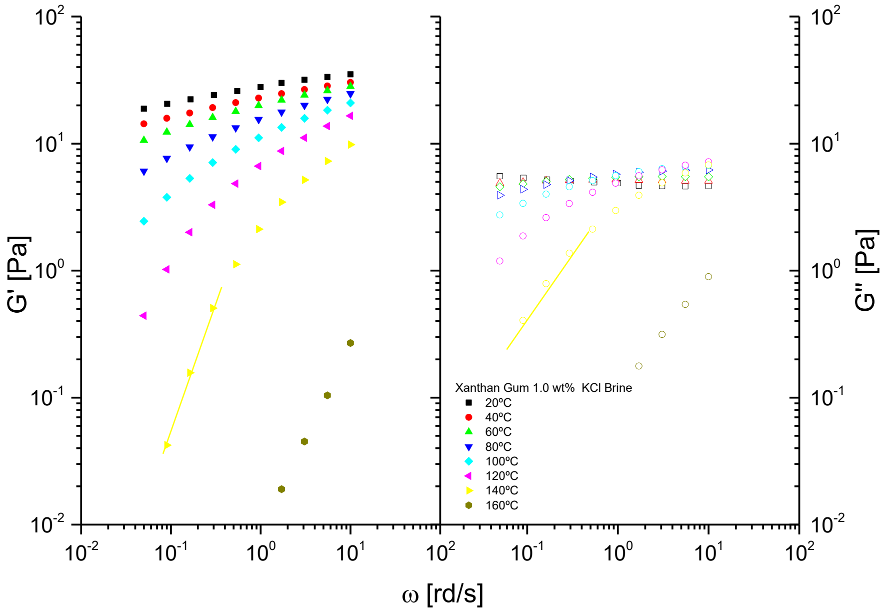

Figure 5. Storage and loss moduli versus frequency for xanthan gum 1.0 wt% solution in saturated KCl brine

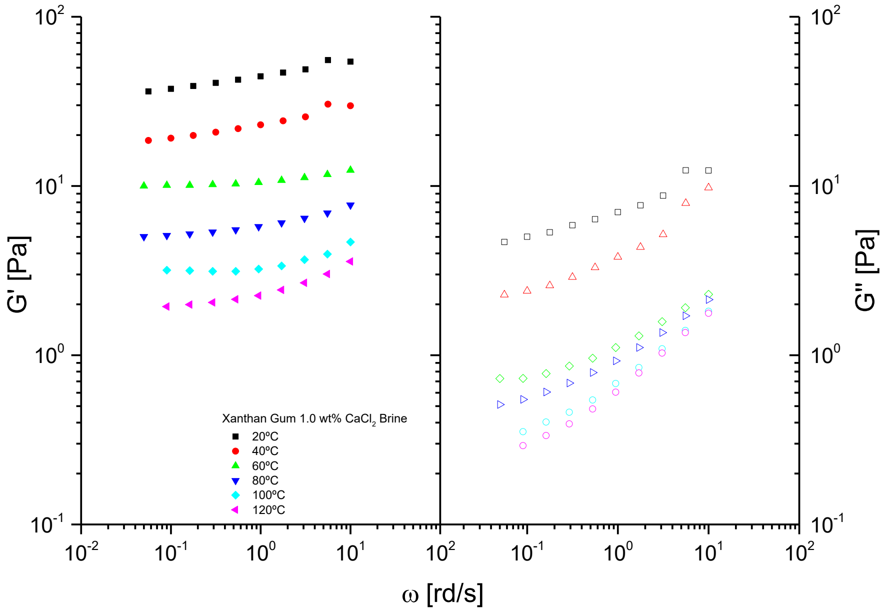

Figure 6. Storage and loss moduli versus frequency for xanthan gum 1.0 wt% solution in saturated $CaCl_2$ brine.

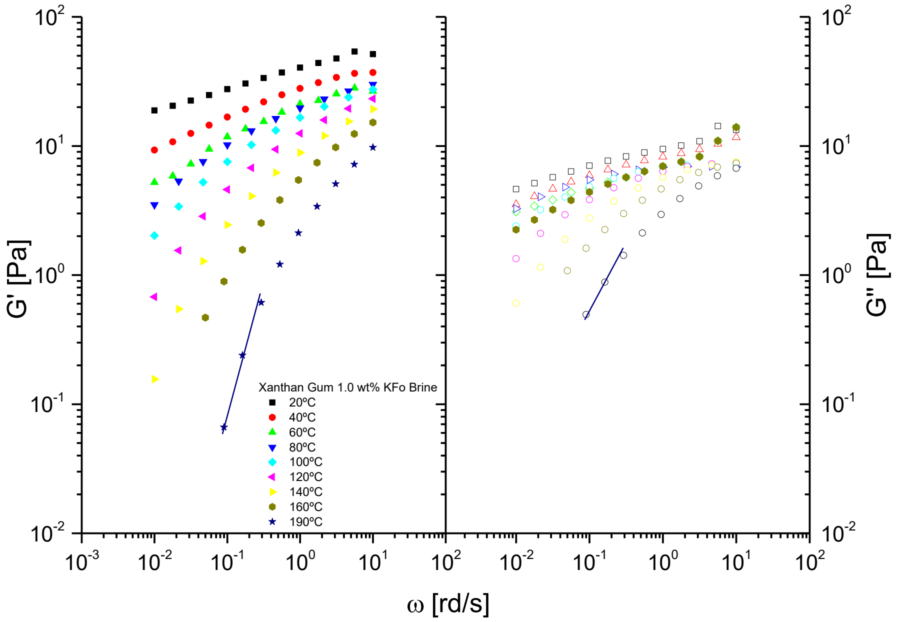

Figure 7. Storage and loss moduli versus frequency for xanthan gum 1.0 wt% solution in saturated KFo brine.

As the temperature increases above 80ºC, the values of both moduli and the slope of the evolution of the moduli with frequency increase. In the high temperature region, the disordered conformation dominates the rheological behaviour, the slope in log scale of the storage and loss moduli becomes very close to 2 and 1 respectively at low frequencies, indicating that the flow terminal region of the mechanical spectrum has been reached at 140ºC for KCl brine and at 190ºC for formate brine. In addition, the crossover point, at which the loss tangent becomes 1, appears and it is displaced to higher frequencies as the temperature rises. This fact indicates that the weak-gel structure of xanthan in the brine is disappearing as the temperature increases (Rochefort & Middleman, 1987), becoming more a viscoelastic or viscous liquid.

Xanthan solution in calcium chloride brine shows predominant elastic behaviour over the whole range of temperature measured up to 120ºC. In this range the moduli decrease progressively with temperature. At temperature above 120ºC this sample experiences a rapid decrease in the strength of the rheological properties (see Figures 2A and 8) probably due to the order-disorder thermal transition that takes place in this region (Seright & Henrici, 1990) and the linear viscoelastic moduli cannot be accurately measured.

Potassium samples show two regions in the evolution of the moduli with the temperature, one below 80-100ºC where the elastic properties predominates over the viscous ones in the whole range of frequency studied, and the region above 100ºC where the thermal disruption of the structure is important and changes both the strength and elasticity of the system. Nevertheless, potassium chloride brine shows the crossover point at higher frequency than the formate brine, a fact that could be related to the effect of the anion on the oxidation processes that takes places near the transition temperature as has been point out by Howard et al. (2015).

The dynamic properties of xanthan solution of similar concentration, 1% w/w, with low content in NaCl (0.008M), have been studied by Pelletier et al. (2001). TTSP was found to hold in the range of temperature 25-80ºC. These authors took 25ºC as temperature of reference, using only horizontal shift factors, a_T, on the frequency axis to superpose the moduli data on a master curve. The evolution of the shift factors, a_T, with temperature was modelled by a William-Landel-Ferry (WLF) equation. It is well-known that if a material shows thermo-rheological simplicity, time and temperature are interchangeable for all linear viscoelastic functions. Thus, a master curve can be constructed at a reference temperature, shifting over the frequency axis the curves of the same linear viscoelastic function measured at other temperatures (Ferry, 1980). Figure 8 shows the master curves, at the reference temperature of 100ºC. For the xanthan 1.0 wt% in saturated KCl solution, a single master curve is obtained over the whole range of temperature studied, no significant changes in the viscoelastic properties due to temperature and/or pressure are observed. From an engineering point of view, TTSP holds with some scattering, mainly in the loss modulus at high frequency, which could be considered within the experimental error. The thermo-rheological simplicity would indicate that the one phase dominates the rheological behaviour in the range of 20-160ºC even through the structural changes induced by the thermal transition in aqueous solution. This result is in agreement with previous studies for concentrated xanthan solutions with and without salt added (up to 10 g/L of xanthan and 0.1M KCl) at temperatures below the thermal transition, which hold the TTSP using both vertical and horizontal shift factors (Choppe et al. 2010). Nevertheless, as can be seen in the inset of Figure 8A, the shift factor, a_T, deviates from the WLF equation, this is a consequence of structural changes at the thermal transition.

In the case of $CaCl_2$ saturated solution, the set of curves of the viscoelasticity moduli do not superimpose even with the help of vertical shift factors. Consequently, the thermo-rheological complexity of this solution seems to be clear. In the case of the formate brine solution a slight deviations from the master curve in the low temperature region at low frequencies is observed in Figure 8, mainly in the loss modulus. Nevertheless, a unique master curve can be obtained in the range of temperature 80-190ºC indicating the thermo-rheological simplicity of the brine in this region, in spite of the conformational changes. In this case, the WLF equation seems to be valid for the entire range of temperature tested.

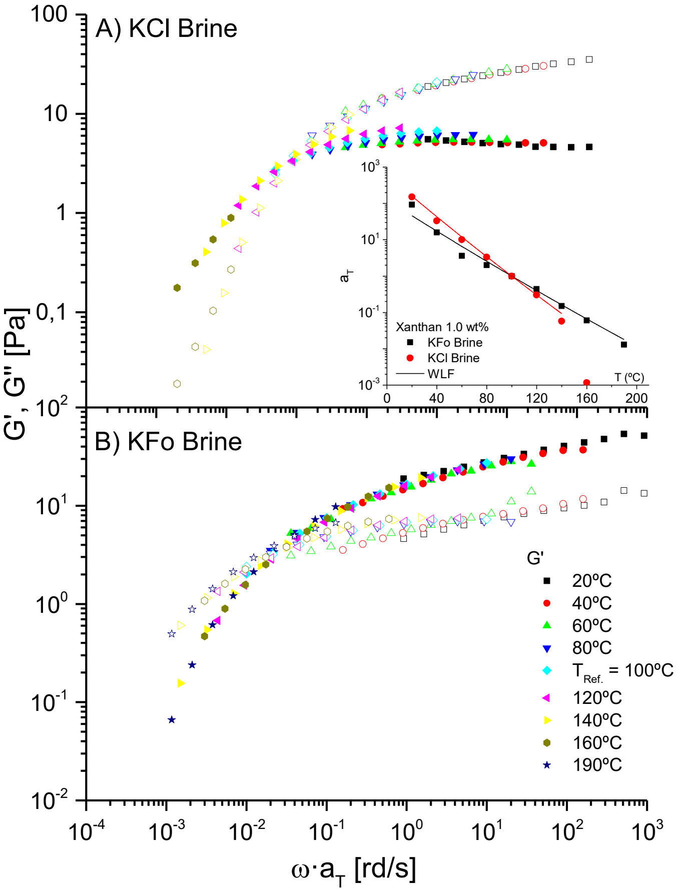

Figure 8. Master curves at the reference temperature of 100ºC Storage Modulus filled symbols, Loss Modulus open symbols. A) Xanthan1.0 wt% in KCl brine. B) Xanthan 1.0 wt% in KFo brine. The inset represents the

evolution of the horizontal shift factors with temperature. Parameters of the WLF equation C_1^0 and C_2^0 49.4 and 1873.5 for KCl; 50.0 and 2487.5 for KFo.

Figure 9 compares the evolution of both complex viscosity and steady shear viscosity versus frequency and shear rate respectively at selected temperatures of 60ºC and 160ºC. As can be observed, the steady shear viscosity values are higher than the complex viscosity ones for all samples at all temperature tested. Positive deviations of the Cox-Merz rule (Cox & Merz, 1958) have been observed in the literature for xanthan solutions of similar concentration but lower ionic strength (Choppe et al., 2010; Gibereau et al., 1994; Pelletier et al., 2001).

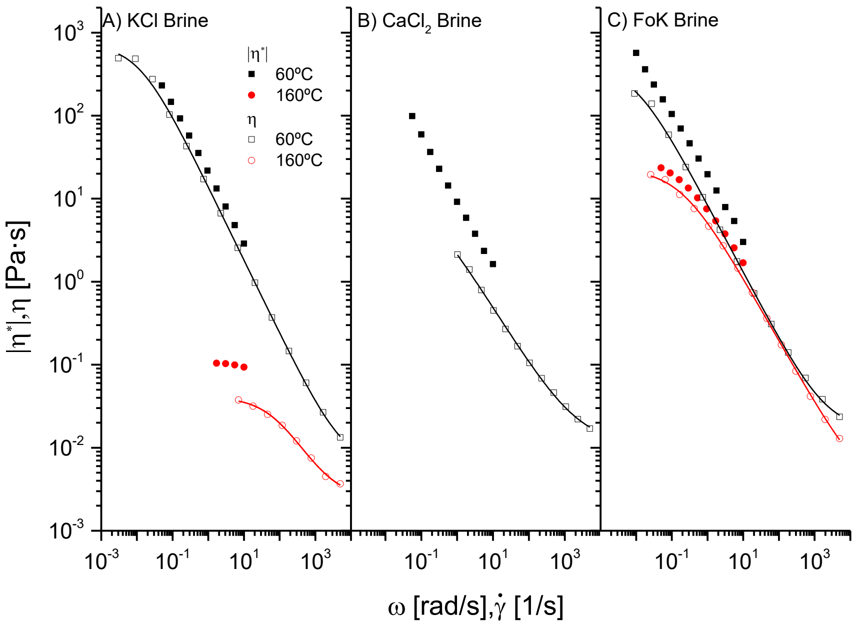

Figure 9. Steady-state viscosity and oscillatory complex viscosity (Cox-Merz plots) for Xanthan gum brines, at selected temperatures.

Conclusions

The relatively concentrated solution of xanthan gum (1.0 wt%) in potassium and calcium saturated brines behave as non-Newtonian fluids, showing shear thinning behaviour that can be modelled by the Cross' model in a wide range of temperature.

Saturated calcium chloride brine increases both the strength and elastic behaviour compared with native xanthan solution but does not extend the range of temperature over which the solution shows shear-thinning behaviour. Nevertheless, chloride and formate potassium brines improve the strength of the solution and shifts the order – disorder conformational thermal transition to higher temperatures, particularly in the case of formate brine, where the transition temperature increases up to around 160°C.

The rheological behaviour near the thermal transition seems to be simple and similar to that of the lower temperature region for potassium brines. Apart from calcium brines, the TTSP holds in the whole range of temperature tested. Thus, the relaxation mechanism for the xanthan solutions in the range of brines studied does not change at least over the range of temperature and pressure studied, although the temperature at which there is an order-disorder transition is much higher for the potassium formate brines, suggesting that formate stabilised brines would be suitable in oil field applications at higher temperatures than the xanthan in chloride brines.

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