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TEMPERATURE AND SALINITY INFLUENCE ON RHEOLOGICAL PROPERTIES OF AQUEOUS DIUTAN GUM SOLUTION

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Abstract. *Using biopolymers is getting more importance as a constituent part of drilling fluids in oil wells. These fluids must have specific characteristics, especially carrying the suspended solids generated by the drilling process. Water-based solutions are indispensable in this environment because, differently of oil-based solutions, they are not harmful to the environment. The present work analyzed the rheological behavior of diutan gum, one of the biopolymers used in the composition of the fluids due to its high viscosity and its emulsifying, and stabilizing characteristics.*
Diutan gum is a polymer of microbial origin, secreted by bacteria of the genus Sphingomonas, and it is used in other industrial sectors, especially in food industry. Stationary and dynamic tests were performed to observe the behavior of rheological parameters of the samples, such as Elastic, viscous and complex modulus, besides complex viscosity. The analysis of the influence of salt on the rheological properties of the material was also done.
The tests were carried out at temperatures of 20ºC, 40ºC and 60ºC, in the proportion of 4300 ppm of diutan gum and 40000 ppm of sea salt. Results were obtained through flow curves and frequency ramps.

Keywords: *biopolymers, diutan gum, rheological properties*

1. INTRODUCTION

The drilling fluids, usually called of "drilling mud", are complex mixtures of solids, liquids and even gases. It basically has the function of transport the gravel generated by the drilling bit to the surface, to keep these fragments in suspension in fluid flow stops in the well , to refresh and to lubricate the drill bit and to stabilize the well wall`s.

They are classified according to their main constituent, in water-based, oil-based and gas-based fluids. In the selection process of the fluid to be used, among other variables, environmental degradation is taken into account and, because of that, water-based fluids are the most used in almost all the drilling operations worldwide, because they are ecologically safe, biodegradable, it has low toxicity and low bioaccumulation. (Amorim, L. V. *et al*, 1999; Bonferoni, M. C. *et al.*,1993).

As the demand for oil and gas increases, so does the need for more economic ways to tap these resources. Drilling process comprises of eighty percent of the total well cost. Drilling has evolved from vertical, inclined, horizontal to sub-sea and deep-sea drilling. These specialized drilling processes require specialized drilling fluids to fulfill the objectives. Since reservoir type and the drilling process adopted to harness the reservoir fluid is unique, the drilling fluid has to be customized to suit the drilling process and reservoir conditions.

These consist of water/brine as the base fluid. As they are environment friendly, the drill cuttings can be disposed of easily. A conventional Water Based Muds (WBM) uses a polymer as a viscosifying agent. The polymers used can be linear polymers, crosslinked polymers, synthetic polymers, or biopolymers. A viscoelastic surfactant (VES) drilling mud is a WBM which uses a surfactant having both viscous and elastic characteristics and thus can reheal itself and restore the rheological properties. Although the VES based drilling mud is expensive compared to conventional WBM, the former does not require frequent mud conditioning and thus saves a significant amount of rig time.(Shah,S.N.*et al*,2010)

The main function of the water is to provide the average dispersion for colloidal materials such as clays and polymers. For the application of a specific type of polymer, it must present a high hydrolysis degree, high viscosity at low concentrations, pseudo plastic behavior and its rheological properties must be stable under the action of salinity, temperature and alkalinity (Shah, A. K.*et al*, 1999).

In this paper, it was investigated the temperature and salinity influence on rheological properties of aqueous diutan gum solution at the temperatures of 20ºC, 40ºC and 60°C. It was used a solution of diutan gum at the concentration of 4300 ppm in deionized water. The NaCl was added to the diutan gum solution at the proportion of 40000 ppm.

The use of sodium chloride in the solutions is justified because it is the salt of the highest percentage present in sea water and reservoirs, and the evaluation of the influence of the temperature becomes necessary since it varies according to the oil well to be explored.

2. RHEOLOGICAL CHARACTERIZATION

2.1 Ideal Fluids

The simplest constitutive equation for purely viscous liquids is that in which the tensor tension is proportional to the shear rate, that is show at Eq. (1): (Bretas and D´Ávila, 2005)

$$\tau_{ij} = \mu\dot{\gamma}_{ij} \tag{1}$$

The proportionality constant μ is called Newtonian viscosity or simply viscosity. This parameter represents the resistance to flow or flow of the material. The higher the viscosity of a material, the greater its resistance to flow. Fluids that during the flow obey the constitutive Eq. (1), that is, have constant viscosity, are called Newtonian fluids. These materials have the same flow resistance, regardless of applied stresses or deformations. (Bretas and D´Ávila, 2005)

Low molecular weight liquids like water and gases are fluids (SI), Newtonian. In the international system of units, the viscosity has units of Pa.s. (Bretas and D´Ávila, 2005)

2.2 Non Newtonian Fluids

Fluids that do not obey the Newtonian model are, by definition, Non – Newtonian. The majority of non – Newtonian fluids can be successfully described with the power law model, showed at Eq. (2): (Steffe and Daubert, 2006)

$$\sigma = K\dot{\gamma}^n \tag{2}$$

Where K is the consistency coefficient (units of Pas^n) and n is the dimensionless flow behavior index. The Newtonian model is a special case of the power law model: when n = 1.0, the equation collapses into the Newtonian model and K = μ. Values of 0 < n < 1 indicate shear thinning behavior (very common), and n > 1 indicate shear thickening behavior (uncommon). Synonyms for shear thinning and shear thickening are pseudoplastic and dilatent, respectively. (Steffe and Daubert, 2006)

Equation (3) show the power law model, that may be described in terms of the apparent viscosity (η) defined as shear stress divided by shear rate (Steffe and Daubert, 2006):

$$\eta = \frac{\sigma}{\dot{\gamma}} = \frac{K\dot{\gamma}^n}{\dot{\gamma}} = K\dot{\gamma}^{n-1} \tag{3}$$

Apparent viscosity varies with shear rate and depends on the numerical values of K and n. If a fluid is Newtonian, the apparent viscosity and the Newtonian viscosity are equal. (Steffe and Daubert, 2006)

2.3 Flow Curve Tests

Flow Curves are usually measured at a constant measuring temperature, i.e. at isothermal conditions. In principle, flow behavior is combined always with flow resistence, and therefore with an internal frictional process ocurring between the molecules and particles. (Mezger, 2014)

Using a cone and plate apparatus, the shear versus shear rate curve may be obtained directly so the calculations are quite simple. The instrument is a moderate shear rate device which is inappropriate for fluids with large particles because the cone angle (θ) is small, preferably less than 0.09 rad (5 degrees). In operating a cone and plate viscometer, the Apex of the cone almost touches the plate and fluid fills the gap. The cone is rotated at a known angular velocity (Ω) and the resulting torque (M) is measured on the fixed plate or through the cone. Some instruments are designed with rotating plates and fixed cones. (Steffe, 1996)

The Figure 1 illustrates the cone and plate geometry:

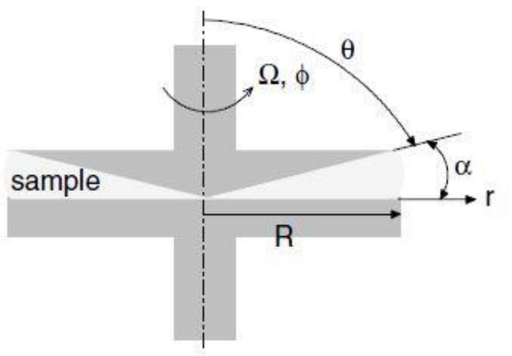

Figure 1. Geometria Cone-Placa. (Gunaserakam and Ak, 2003)

However, when using a small cone angle (less than 5 degrees), sufficiently low rotational speeds, and with no erros due to surface tension effects at the free fluid surface (surface should be spherical in shape with a raius of curvature equal to the cone radius), the shear rate at r may be calculated as the Eq. (4): (Steffe, 1996)

$$\gamma = \frac{r\Omega}{r\,tan\,\theta} = \frac{\Omega}{tan\,\theta} \tag{4}$$

Indicating that the shear rate is constant throughtout the gap. This is one of the main advantadges of a cone and plate geometry. With the small angles found in typical fixtures, $\tan\theta = \theta$ (Steffe, 1996)

To develop an expression for shear stress, consider the differential torque on an anular ring of thcikness dr, as illustrated at Eq. (5), Eq. (6), Eq. (7) and Eq. (8): (Steffe, 1996)

$$dM = (2\pi r dr)\sigma r \tag{5}$$

$$\int_0^M dM = \int_0^R (2\pi r^2 \sigma) dr \tag{6}$$

$$M = 2\pi\sigma \int_0^R r^2 dr \tag{7}$$

$$\sigma = \frac{3M}{2\pi R^3} \tag{8}$$

This result shows that, like $\dot{\gamma}$, is constant throughout the gap. Using Eq. 3.51 and 3.55, shear rate and shear stress can be easily calculated. By varying the angular velocity, cone angle and cone radius, a wide variety of conditions can be tested. If a specific model is selected, rheological properties can be calculated directly. (Steffe, 1996)

2.4 Oscillatory Tests

In oscillatory instruments, samples are subject to harmonically varying stress or stain. Results are very sensitive to chemical composition and physical structure so they are useful in a variety of applications incluiding gel strength evaluation, monitoring starch gelatinization, studying the glass transition phenomenon. (Steffe, 1996).

In oscillatory tests, materials are subjected to deformation (in controlled rate instruments) or stress (in controlled stress instruments) which varies harmonically with time. Sinusoidal, simple shear is typical. (Steffe, 1996).

The Maxwell fluid model is often used to interpret data from dynamic testing of polymeric liquids. If the strain input is harmonic $\gamma = \gamma_0 \sin \omega t$, then $\dot{\gamma} = \gamma_0 \omega \cos \omega t$. This relantionship can be substituted and the the resulting differential equation solved to produce a number of frequency dependent rheological functions for Maxwell fluids, as Eq. (9), Eq. (10), Eq. (11) and Eq. (12): (Steffe, 1996).

$$G' = \frac{G\omega^2\lambda_{rel}^{\ 2}}{1+\omega^2\lambda_{rel}^{\ 2}} \quad (9)$$

$$G'' = \frac{G\omega\lambda_{rel}}{1+\omega^2\lambda_{rel}^{\ 2}} \quad (10)$$

$$G^* = \sqrt{(G')^2 + (G'')^2} \quad (11)$$

$$\eta^* = \frac{G^*}{\omega} \quad (12)$$

Where λ_{rel}, the relaxation time of a Maxwell fluid, is equal do ${}^{\mu}/_{G}$ (Steffe, 1996).

G' is called shear storage modulus, [Pa]; G'' is the shear loss modulus, [Pa]; G^* is the shear complex modulus, [Pa]; η^* is the complex viscosity, [Pa.s].

3. METHODOLOGY

The tests were performed on a Haake RS50 rotational rheometer using cone-plate geometry (C35/2° Ti sensor, with a diameter of 35 millimeters and 2° of conicity). Dynamic and oscillatory tests were performed at temperatures of 20°C; 40°C and 60°C, yielding the following rheological properties, among others: viscosity; elastic modulus; viscous modulus; complex modulus and complex viscosity. The maximum allowable temperature deviation was ± 0.2K. Samples were kept resting for 12h before measurements to guarantee the absence of bubbles.

3.1 Sample Preparation

In the solutions production, the diutan gum (4300 ppm) was added as a powder in deionized water with 40000 ppm of NaCl. The solutions stayed under mechanical shaking at room temperature of 25 ° C, with the angular velocity of the mixer at 500 rpm for 1 hour and after that, they were left resting for 12 hours and, then, submitted to the deformation tests.

4. RESULTS AND DISCUSSION

Figure 2, Figure 3 and Figure 4 show the behavior of viscosity as a function of the shear rate of the aqueous solution of diutan gum (4300 ppm) with and without salt (40000 ppm) at 20°C, 40°C and 60 ° C. The diutan gum with and without salt showed a pseudoplastic behavior for all the temperatures.

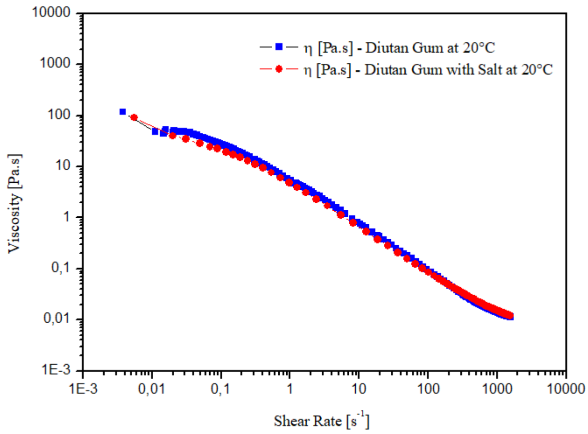

Figure 2. Flow Curve at 20°C (0.5-30 Pa) of Diutan Gum

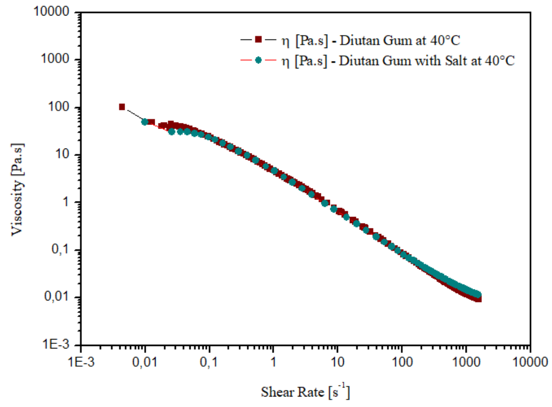

Figure 3. Flow Curve at 40°C (0.5 – 30 Pa) of Diutan Gum

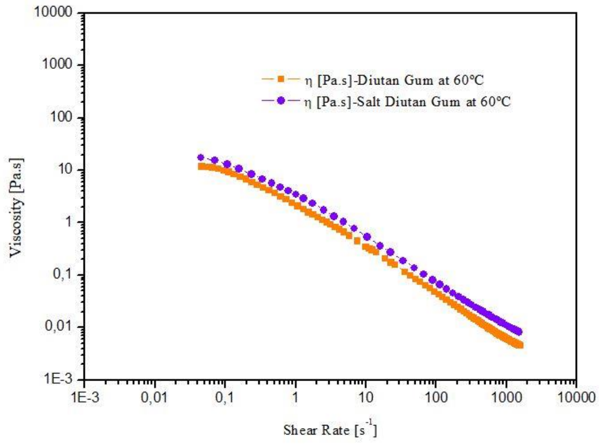

Figure 4.Flow Curve at 60ºC (0.5-30 Pa) of Diutan Gum

Figure 5 shows the result of the oscillation test (frequency ramp in the range of 0.01 to 10 Hz) with a constant stress of 1 Pa (within the linear viscoelasticity range) of the aqueous solution of diutan gum (4300 ppm) at 40 ° C. The elastic (G ') and complex (G *) modules increase with increasing frequency. The elastic modulus (G ') is greater than viscous modulus (G '') in the case of frequency higher than 1 rad/s, evidencing a predominance of elastic effects. The modulus of complex viscosity (η *) decreases with increasing frequency.

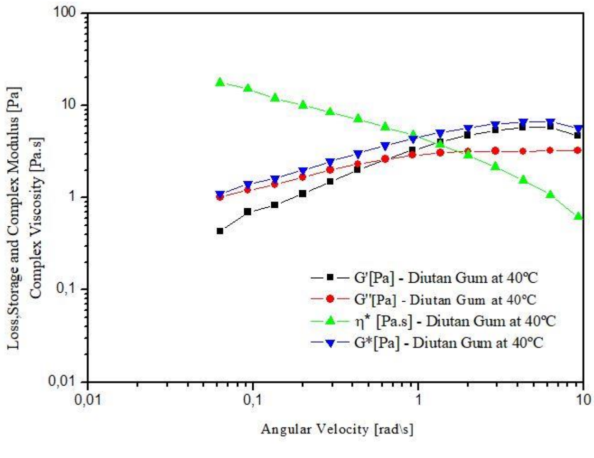

Figure 5.Frequency Ramp at 40ºC of Diutan Gum (0.01-10 Hz,1 Pa)

Figure 6 shows the result of the oscillation test (frequency ramp in the range of 0.01 to 10 Hz) with a constant stress of 1 Pa (within the linear viscoelasticity range) of the aqueous solution of salt diutan gum (4300 ppm) at 40 ° C. With the salt addition, the elastic modulus (G') and the viscous modulus (G") has, virtually, the same values in all the frequency range investigated. The modulus of complex viscosity (η*) decreases with increasing frequency, as expected.

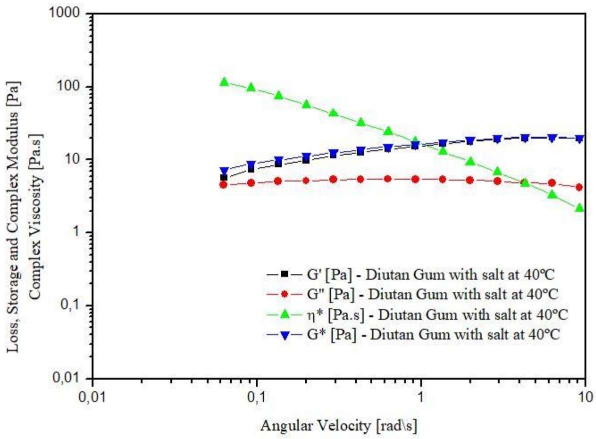

Figure 6.Frequency Ramp at 40ºC of Diutan Gum (0.01-10 Hz, 1 Pa)

Figure 7 shows the result of the oscillation test (frequency ramp in the range of 0.01 to 10 Hz) with a constant stress of 1 Pa (within the linear viscoelasticity range) of the aqueous solution of diutan gum (4300 ppm) at 60 ° C. The elastic (G ') and complex (G *) modules increase with increasing frequency. The elastic modulus (G ') is greater than viscous modulus (G ") in the case of frequency higher around 2 rad/s, evidencing a predominance of elastic effects. The modulus of complex viscosity (η *) decreases with increasing frequency.

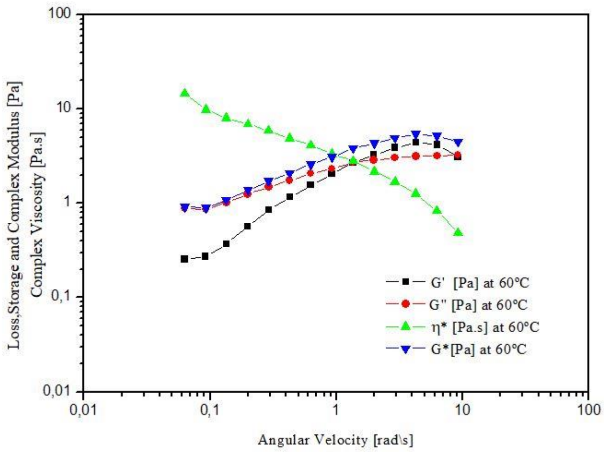

Figure 7.Frequency Ramp at 60ºC of Diutan Gum (0.01-10 Hz,1 Pa)

Figure 8 shows the result of the oscillation test (frequency ramp in the range of 0.01 to 10 Hz) with a constant stress of 1 Pa (within the linear viscoelasticity range) of the aqueous solution of salt diutan gum (4300 ppm) at 60 ° C. With the salt addition, the viscous modulus (G") starts lower than the elastic modulus (G') in the frequency range investigated, getting equal around 1 rad/s. The modulus of complex viscosity (η*) decreases with increasing frequency, as expected.

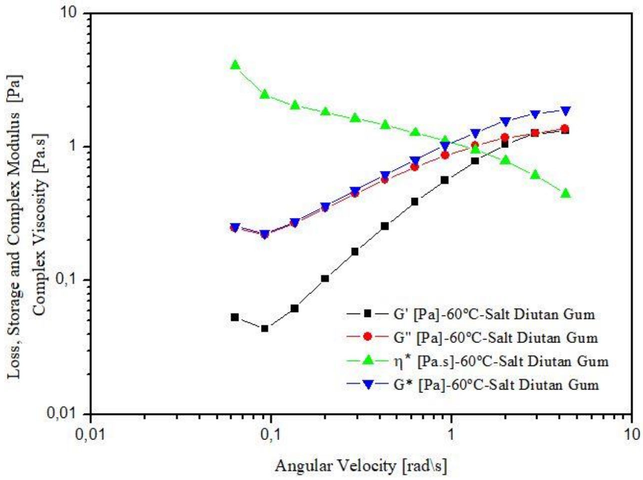

Figure 8.Frequency Ramp at 60ºC of Salt Diutan Gum (0.01-10 Hz,1 Pa)

5. CONCLUSION

Diutan gum showed a pseudoplastic and viscoelastic behavior, even with salt addition,for all the temperatures investigated. The viscosity increased in diutan gum,60°C, with salt, comparing with the gum without salt. For 20°C and 40°C, the viscosity didn´t change significantly with salt addition.

Withou the salt addition, the viscous modulus (G") keep higher than the elastic modulus (G') in the frequency range investigated.

On the other hand, with the salt addition, the elastic modulus (G') and the viscous modulus (G") showed approximated values in the frequency range investigated.

6. ACKNOWLEDGMENTS

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