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RHEOLOGICAL BEHAVIOUR OF DIUTAN GUM AND ITS EFFECTS AS A DRAG REDUCING AGENT

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Abstract. *The drag reduction phenomenon by addition of small amounts of polymer has been known for more than 70 years. The synthetic polymers Polyethylene Oxide (PEO) and Polyacrylamide (PAM) and the biological polymer Xanthan Gum (XG) are some of the most used drag reducing agents. Researches on a recent biopolymer, called Diutan Gum (DG), show promising results concerning its drag reduction ability. However, its rheological characteristics lack further information. With this objective, Diutan Gum is analyzed in terms of viscosity and its effects as a drag reducing agent. It is verified that Diutan Gum presents high pseudoplastic behaviour, even for concentrations as low as 25 ppm. Diutan Gum has a lower overlap concentration in relation to Xanthan Gum, which suggests that it has a higher molecular weight. The elastic modulus is more prominent than the viscous modulus for a wide frequency range and concentrations above 750 ppm. Therefore, Diutan Gum is expected to show greater drag reduction than Xanthan Gum.*

Keywords: biopolymer, diutan gum, drag reduction.

1. INTRODUCTION

The drag reduction phenomenon has been investigated for more than 70 years and Toms (1948) was one of the pioneers to observe the flow increase due to addition of polymers. Among the drag reducing polymers, the most used are Polyethylene Oxide (PEO), Polyacrylamide (PAM) and Xanthan Gum (XG). PEO and PAM are synthetic, flexible and water-soluble polymers with linear chain. XG is a bacterial polysaccharide, that is, it has a natural origin. It originates from fermentations by bacteria of the species Xanthomonas campestris. It also has a linear chain and is soluble in water, but it is considered a rigid polymer (Bewersdorff and Singh, 1988).

Another gum that has been studied is Diutan Gum (DG). Like Xanthan Gum, DG is also a bacterial exopolysaccharide. Diutan Gum is a biopolymer originated by the aerobic fermentation of the bacterium Sphingomonas sp. ATCC 53159. This organism was isolated from an algae collected from a swamp near the city of Eureka, California (Peik et al., 1992). The first known works with Diutan Gum are from the mid-1980s to the early 1990s. Since then, its good rheological properties have been presented and has become a promising drag-reducing agent, as shown by Navarrete and Shah (2001) and Ferreira et al. (2005). The polymer's chemical structure consists of a tetrasaccharide backbone [→3)-β-D-Glcp-(1→4)-β-D-GlcpA-(1→4)-β-D-Glcp-(1→4)-α-L-Rhap-(1→] and a disaccharide side chain with L-rhamnose units (Chowdhury et al., 1987). Lee and Chandrasekaran (1991) have shown that the chemical structure of Diutan Gum adopts a double helix conformation. In it, the side chains of the polymer are turned towards the main chain glucuronic acid units. The authors state that the side chains provide greater stability to the double helix due to the hydrogen bonds with the main chain. Further evidence of good stability of Diutan Gum was presented by scanning electron microscopy images, in which the structure of the Diutan Gum appears to be more compact and complex than other polymers (Li et al., 2017). In a direct application of drag reduction in petroleum drilling services, Sarber et al. (2010) showed results of the substitution of Xanthan Gum by Diutan Gum as the base biopolymer. The new system showed a 20% reduction in pump pressure.

Researchers have been studying the interaction of Diutan Gum with other substances, such as surfactants (Mukherjee et al., 2010). Its effects as a concrete additive were also presented by Sakata et al. (2003), Khatami and O'Kelly (2018), Pei et al. (2015) and Schmidt et al. (2017). In this area, the effects of Diutan Gum in oil wells cementing were presented by Sonebi (2006), Zhang et al. (2010) and Ma et al. (2018). It is noted that the search for new exopolysaccharides has resulted in many recent advances, especially in those that provide improvements in drag reduction. The recent discovery

of Diutan Gum has raised questions about its rheological behaviour and its role as a reducing agent provokes interest in its real potential.

2. MATERIALS AND METHODS

Diutan Gum was provided by CP Kelco and Braschemical in powder form. Xanthan Gum was acquired from Sigma-Aldrich. The polymer were carefully deposited on the surface of deionized water. Instead of mechanically mixing, the dilution occurred by Brownian motion of the particles, in order to prevent possible early disaggregation (see Soares et al., 2015). The solutions were stored for 48 hours. The tests were carried out using HAAKE MARS III rheometer, manufactured by Thermo Scientific, using a double gap device (Fig. 1), the same as used by Pereira and Soares (2012).
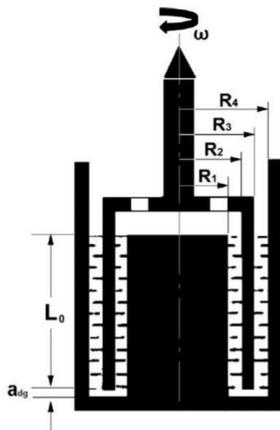

Figure 1. The axial symmetric double gap geometry.

The Reynolds number and the Fanning friction factor are given by Eq. (1) and (2):

$$Re = \rho \bar{h} u / \eta = \rho \bar{h} \omega \bar{R} / \eta, \tag{1}$$

$$f = 2\tau \rho u^2 = 2\tau \rho \omega \bar{R}^2, \tag{2}$$

where ρ is the specific mass, $\bar{h}$ is the average gap given by $((R_2 - R_1) + (R_4 - R_3))/2$, u is the characteristic velocity, ω is the rotor angular speed, $\bar{R} = (R_2 + R_3)/2$ is the mean radius, η is the solution's viscosity and τ is the shear stress.

Another portion of the rheological characterization was performed using Cannon-Fenske capillary viscometer, employed for measuring specific viscosity of polymer solutions. Specific viscosity, η_{esp}, represents the increase in viscosity given by the polymer (Flory, 1953, p. 309-311). It is given by Eq. (3), where t is the solution flow time and t_0 is the solvent flow time.

$$\eta_{esp} = (t - t_0)/t_0. \tag{3}$$

3. RESULTS AND DISCUSSION

3.1 Specific viscosity

The specific viscosity, η_{esp}, represents the increase in viscosity given by the polymer. High molecular weight polymers are capable of intensely increasing the viscosity of solutions in which they are diluted, even at low concentrations (Flory, 1953, p. 309-311). Thus, the higher the molecular weight, the greater the increase in viscosity or higher the specific viscosity. Specific viscosity measurements of Diutan Gum and Xanthan Gum solutions are shown in Fig. 2.
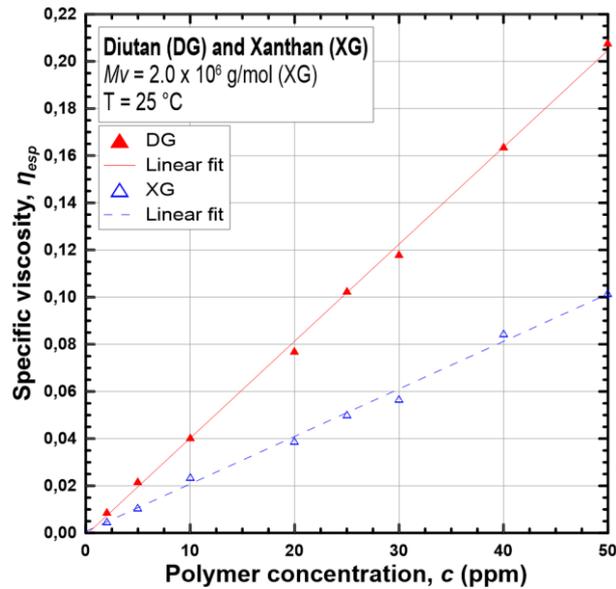
Figure 2. Specific viscosities of DG and XG solutions.

It is noticed that the slope of the line of specific viscosity of Diutan Gum is steeper than that of Xanthan Gum. Consequently, increasing Diutan Gum concentration leads to greater variation in solution viscosity. Therefore, apparently, Diutan Gum has a higher molecular weight than Xanthan Gum. Moreover, as presented by Virk (1967), Paterson and Abernathy (1970), Choi et al. (2000) and Pereira and Soares (2012), higher molecular weight polymers have greater drag reduction capacity. Thus, Diutan Gum is expected to exhibit greater drag reduction. Further information about the influence of molecular weight will be discussed in the overlap concentration subsection.

3.2 Flow curves and rheological model

Figure 3 presents the relationship between the viscosity and the shear rate for Diutan Gum solutions at concentration ranging from 25 ppm to 10000 ppm.
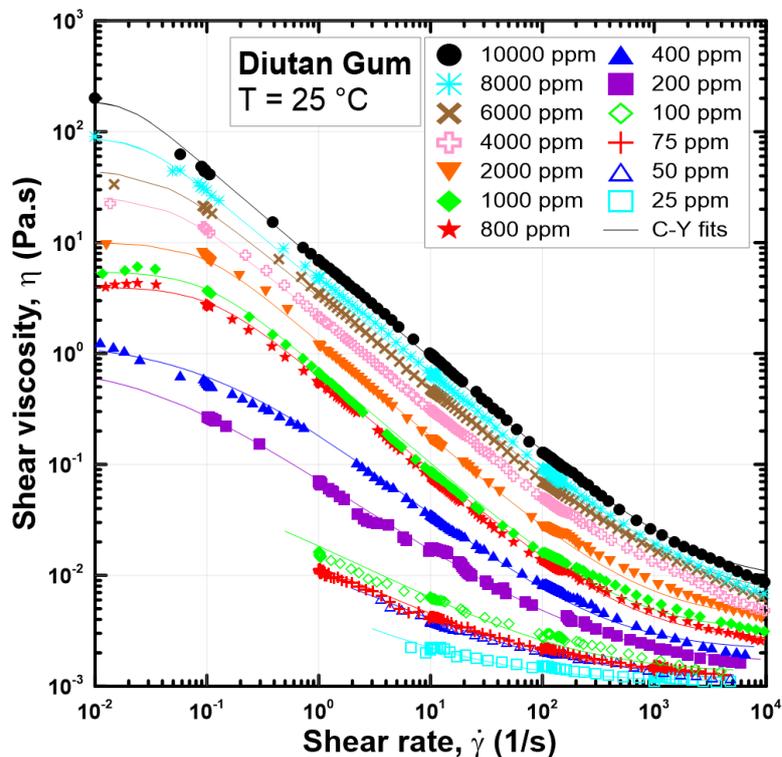

Figure 3. Flow curves of Diutan Gum solutions.

The pseudoplastic behaviour of the material can be perceived at concentrations as low as 25 ppm. This behaviour becomes more prominent as the concentration increases. The curve fits were based on the Carreau-Yasuda equation, Eq. 4.

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{[1 + (\lambda_{CY}\dot{\gamma})^a]^{n/a}}.$$

(4)

In the above equation, the parameters η_0, η_∞, $\dot{\gamma}$, λ_{CY}, n and a represent, respectively, the viscosity at the zero-shear rate, viscosity at the infinite-shear rate, the shear rate, the time constant, the power law exponent and a parameter describing the transition between the flat regions of the beginning and end of the curves (Yasuda et al., 1981). The values of the parameters of each adjustment performed are shown in Tab. 1.

Table 1. Carreau-Yasuda parameters of Diutan Gum.

c (ppm)	η_0 (Pa.s)	η_{inf} (Pa.s)	λ_{CY} (s)	n	a
25	0,3300	0,0011	25,00	0,22	0,18
50	0,4000	0,0012	25,00	0,29	0,20
75	0,4500	0,0012	28,00	0,29	0,21
100	0,5000	0,0013	30,00	0,30	0,25
200	0,8000	0,0016	33,00	0,32	0,80
400	1,3000	0,0021	9,00	0,20	0,70
500	1,5000	0,0021	9,00	0,21	1,10
750	4,0000	0,0025	9,00	0,15	1,60
1000	5,5000	0,0031	10,00	0,13	1,60
2000	10,0000	0,0039	11,00	0,14	1,80
4000	26,0000	0,0054	21,00	0,18	1,70
6000	45,0000	0,0061	26,00	0,19	1,80
8000	90,0000	0,0067	38,00	0,16	2,30
10000	190,0000	0,0086	50,00	0,14	3,00

Other researchers (Sakata et al., 2003; Li et al., 2017) have already analyzed the viscoelastic behaviour of Diutan Gum. Navarrete and Shah (2001) showed that Diutan Gum exhibits more shear thinning behaviour than Xanthan Gum. Xu et al. (2015) attribute this characteristic to a perfect double helix conformation of the Diutan Gum, which manages to adhere more water molecules in its interior. Xanthan Gum has an irregular structure with weaker bonds (Wyatt et al., 2011). Therefore, the stronger molecular structure and the higher water retention (Sonebi, 2006) lead to greater viscoelasticity of Diutan Gum in relation to Xanthan Gum.

3.3 Overlap concentration

Overlap concentration is considered to be the one that separates dilute solutions from concentrates. That is, below this concentration, the solution is considered diluted. This means that there are no considerable interactions between polymeric molecules. However, above the overlap concentration, molecules begin to interact and influence each other movement (Launay et al., 1997). As noted in the previous subsection, the zero-shear rate viscosity, η_0, increases with increasing polymer concentration. This dependence is a method of determining overlap concentration (Rodd et al., 2000) and can be analyzed by looking at Fig. 4.
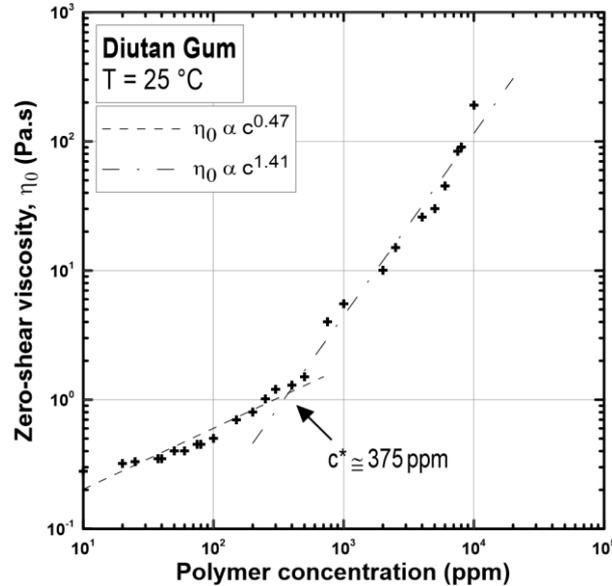
Figure 4. Overlap concentration, c*.

In more dilute solutions, the increase in concentration leads to a lower increase in viscosity. Therefore, the amount of polymeric molecules is not yet sufficient to produce greater intermolecular interactions. That is represented by the small slope of the linear curve. However, after a given concentration, the average distance between molecules decreases, generating greater interactions. Then, the increase in concentration has a greater impact and this effect is represented by the steeper slope of the linear curve in the most concentrated solutions. The concentration at which the change occurs between the two situations discussed is called the overlap concentration, c*. The overlap concentration found for Diutan Gum was 375 ppm. Xu et al. (2015) obtained a value of 120 ppm for Diutan Gum 410 ppm for Xanthan Gum. Pereira, Andrade and Soares (2013) and Wyatt and collaborators (2011), using the same techniques, found different values for Xanthan Gum: 940 ppm and 70 ppm, respectively. These discrepant values may be a result of the difficulty in obtaining the overlap concentration, as slight changes in straight line inclinations cause large changes in the c* value. Nevertheless, it is a fact that the overlap concentration is related to the molecular weight of the polymer. The higher the molecular weight, the greater and more frequent the intermolecular interactions will be, thus reducing the overlap concentration. Therefore, according to the values found by Xu et al. (2015), Diutan Gum has higher molecular weight than XG, a fact corroborated by Navarrete, Seheult and Coffey (2000). Thus, the higher molecular weight of DG suggests that its solutions will show greater drag reduction than XG solutions.

3.4 Storage and loss moduli (G' and G")

One way to know the degree of elasticity and viscosity of a material is by measuring the storage modulus (or elastic, G') and loss modulus (or viscous, G") with frequency sweep, as seen in Fig. 5. The storage modulus represents the energy stored by the elastic structure of the material. The loss modulus represents the viscous part, or the amount of energy dissipated by the material (Chhabra and Richardson, 2008, p. 97-101). In fact, G' and G" inform about the microstructure, that is, they indicate the ordering level of intermolecular bonds (Roscoe, 1980).
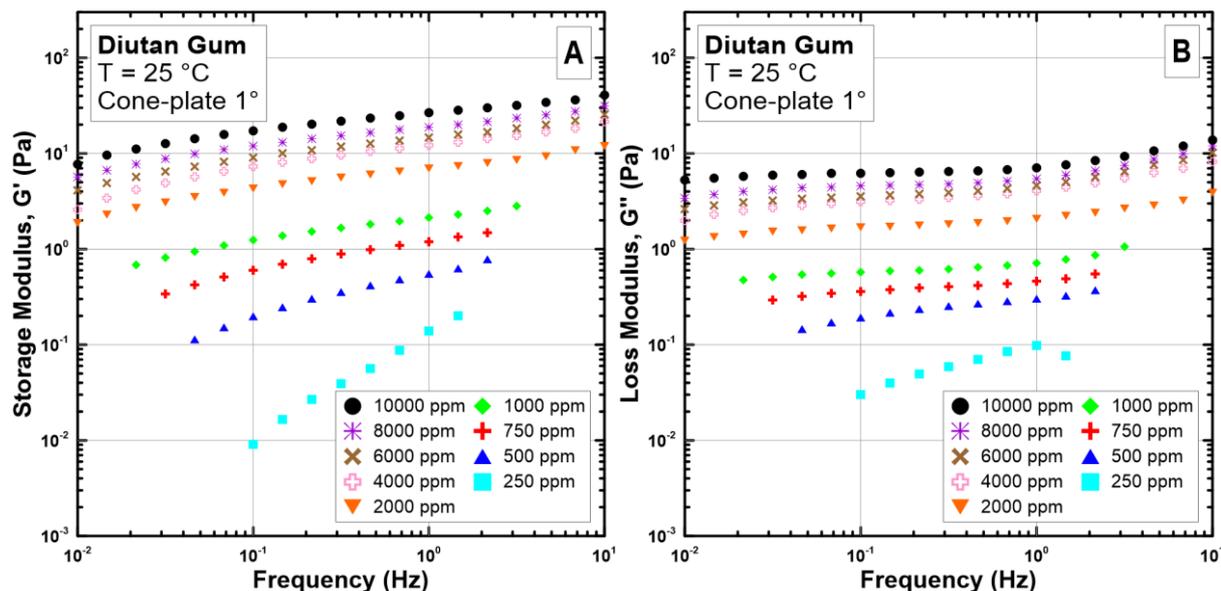
Figure 5. Frequency sweep of storage modulus (A) and loss modulus (B).

It can be seen that the increase in concentration raises the values of G' and G". This means that as the polymer concentration increases, the material's structure increases its energy storage and dissipation capacity. In order to better understand the relationship between storage and loss moduli, the ratio between G' and G" is shown in Fig. 6.
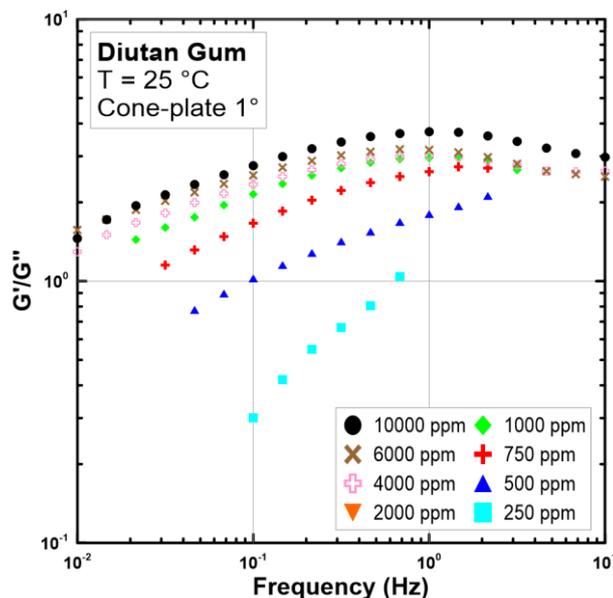

Figure 6. Storage and loss moduli ratio.

An important point to note is the moment when the elastic modulus becomes greater than the viscous modulus, i.e. the frequency related to G'/ G" = 1, or crossover frequency. It represents the beginning of elastic dominance and generally tends to higher values as the solution becomes more diluted and the molecular structure disappears (Rochefort and Middleman, 1987). For example, the crossover frequencies of the 500 ppm and 250 ppm solutions are approximately 0.1 Hz and 7 Hz, respectively. It can be seen that for the tested frequency range, G' is greater than G" at concentrations above 750 ppm. This means that there is a predominance of elastic behaviour in the microstructure of the material for the entire frequency range. On the other hand, when G" is higher, energy dissipation is prevails. This result is consistent with that found by Carmen García et al. (2018), Li et al. (2017) and Xu et al. (2015) for Diutan Gum solutions. The authors compared the storage and loss moduli of DG and XG and they found that those of Diutan Gum are larger, which indicates its higher viscoelasticity.

3.1 Friction factor

In order to know the drag reduction capacity of Diutan Gum solutions, the Fanning friction factor can be represented in Prandtl-von Kármán coordinates, as in Fig. 7.
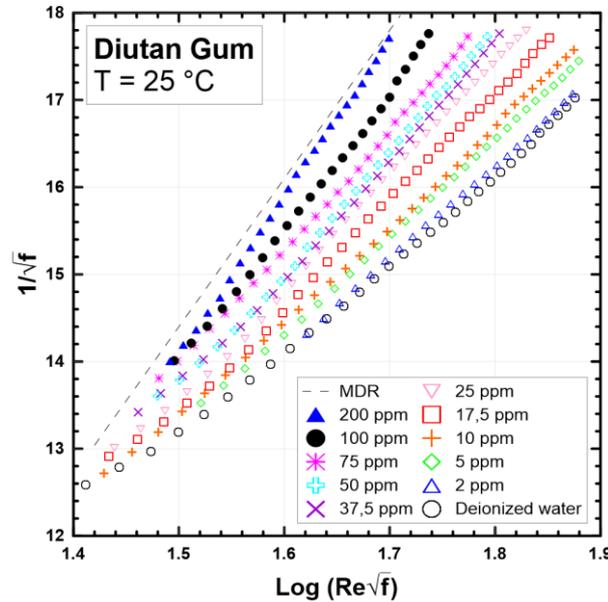

Figure 7. Fanning friction factor, *f*, as a function of Reynolds number, *Re*, for Diutan Gum solutions.

The curves are in a region limited by deionized water (solvent) and by the maximum drag reduction asymptote (MDR), given by Eq. 5, as proposed by Pereira, Andrade and Soares (2013) as an alternative to the MDR equation in double gap geometry.

$$1/\sqrt{f} = 17{,}00 \log(Re\sqrt{f}) - 11{,}55 \tag{5}$$

Figure 7 shows that the increase of polymer concentration leads to curves closer to MDR. This fact indicates the drag reduction capacity of Diutan Gum. As shown by Virk (1975), rigid polymers have a Type B drag reduction, in which the onset is independent of the Reynolds number and the drag reduction occurs even for low Re. Similar results were found by Pereira, Andrade and Soares (2013) using Xanthan Gum in the same geometry.

4. CONCLUDING REMARKS

The rheological characterization tests were performed in rheometer and capillary viscometer. The results showed that Diutan Gum has high capacity to increase the viscosity of the solution and presents high pseudoplastic behaviour. In relation to Xanthan Gum, Diutan Gum has a lower overlap concentration, which suggests that it has a higher molecular weight. Since molecular weight is an important factor in drag reduction, Diutan Gum is expected to show greater drag reduction than Xanthan Gum. In addition, Diutan Gum has a predominance of the storage module, which indicates a more elastic internal structure even in poorly concentrated solutions.

5. ACKNOWLEDGEMENTS

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