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Research paper

## Partially hydrophobized hyperbranched polyglycerols as non-ionic reactive shale inhibitors for water-based drilling fluids

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### ABSTRACT

The oil and gas industry demands drilling fluids that would be able to minimize the wellbore instability faced during the drilling of reactive shales. In this work we describe the synthesis of hydrophobized hyperbranched polyglycerols (HPG) with unique design and properties to be used as non-ionic reactive shale inhibitors. In association with KCl, HPG showed a superior performance in comparison with unmodified hyperbranched polyglycerol and with the commercial clay reactivity inhibitors PEG400 and PDADMAC. Intact cuttings recoveries were around 80%. The proposed inhibition mechanism suggests the formation of a complex between HPGs and K<sup>+</sup> ions and its penetration into the clay interlayer spacing to minimize the shale-water interactions and remove water molecules present in the clay galleries. In addition, these aggregates formed by the amphiphilic structures would cause obstruction of the clay minerals pore throats, thereby making it even more difficult for the penetration of water molecules.

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### 1. Introduction

The oil industry has been showing a large demand for new technologies to overcome the huge problems related to the drilling of wells. Nowadays, whenever possible, water-based drilling fluids (WBM) are employed, since oil based fluids face several environmental restrictions and involve much higher costs (He et al., 2014). However, when water-based fluids are used, several wellbore stability issues contribute to increase the challenges related to drilling, and these issues are, in large part, related to the water reactivity of some of the shales being drilled. Shales are clay rich sedimentary rocks that can present water sensitivity depending on their crystalline structure, composition, porosity and the existence of cracks and fractures on the rocks surface (Lal, 1999; Gomez and Patel, 2013; Al-Arfaj et al., 2014). Reactive shales, when in contact with WBM, can have their crystalline structure destroyed resulting in severe problems, such as trapping of column and/or well collapse. To deal with the possible damages caused by water, chemical inhibitors are added to the fluid formulation in order to minimize or even prevent the shale crystalline destruction. The literature reports the use of inorganic salts, such as KCl, and CaCl<sub>2</sub>, water soluble silicates (Gomez and Patel, 2013), cationic hydrophobized polysaccharides (Lopes et al., 2014), ionic liquids (Berry et al., 2009), poly(oxyalkyl)amines (Qu et al., 2009; Wang et al., 2011), poly(oxypropylene)amidoamine (Zhong et al., 2012), others amine

derivatives (Patel et al., 2007; Zhong et al., 2015a, 2015b) and non-ionic molecules/polymers (Shadizadeh et al., 2015), all of them presenting advantages and disadvantages. Regarding the environmental requirements for the drilling fluid formulation, amine derivatives such as quaternary alkyl ammonium salts or amine containing polymers are highly efficient shale inhibitors, but present elevated toxicity. Linear non-ionic polymers, such as polyglycols (PEGs) and polyols, although showing low toxicity, present limited field applications (Patel et al., 2007).

The hyperbranched polyglycerols are versatile structures which can be produced from glycidol (Sunder et al., 1999) or glycerol carbonate (Rokicki et al., 2005) a monomer obtained from glycerol. The glycerol is a co-product of the biodiesel industry. In Brazil, due to the increasing use of biodiesel, in partial replacement of the diesel obtained from petroleum, its annual production of about 500,000 m<sup>3</sup> demands for the development of new uses for the glycerol (ANP, 2016). The hyperbranched polyglycerol and its derivatives have been widely studied, e.g., as potential agents for the controlled release of drugs (Gupta et al., 2012), as sample pretreatment and immunosensors in analytical chemistry fields (Sun et al., 2015) and as additives for the encapsulation of pigments (Wan et al., 2014).

Reports from the literature suggest that the use of dendrimers and dendritic polymers can revolutionize fluids properties (Amanullah, 2013). Zhong et al. (2015c, 2016) proposed the use of polyamidoamine dendrimers and reached very good shale cuttings recovery. However, dendrimers demand laborious multistep synthetic procedures, in contrary, polyglycerols are usually produced in simple one-step procedures

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(Parzuchowski et al., 2008). Teixeira et al. (2014) applied hyperbranched polyglycerols obtained from glycerol carbonate, an eco-friendly precursor, in association with KCl, achieving high percentage cuttings recovery with a polymer concentration about 5 wt%. It has been demonstrated that the performance of these hyperbranched structures is superior to the ones obtained with linear PEGs. Also, the literature indicates that the performance of linear non-ionic inhibitors can be improved by increasing the degree of hydrophobicity of the polymers (Souza et al., 2010). In this work we are committed to the development and evaluation of new and unique hyperbranched polymeric structures, the hydrophobized hyperbranched polyglycerols, as reactive shales inhibition additives for water-based drilling fluids.

## 2. Experimental

### 2.1. Materials

Glycerol 99.5%, dimethyl carbonate – DMC  $\geq$  99%, potassium methoxide 95%, dodecyl tetradecyl glycidyl ether – DTGE technical grade, Poly(ethylene glycol) 400 Da – PEG400 and Poly(diallyldimethylammonium chloride) – PDADMAC solution 20 wt% in H<sub>2</sub>O ( $M_w$ : 200,000–350,000) medium molecular weight, were all supplied by Sigma-Aldrich.

### 2.2. Synthesis and characterization

Glycerol carbonate – GC and hyperbranched polyglycerol – PG were synthesized following procedures reported by Rokicki et al. (2005), with exception of the purification process, since PG was not purified. Several partially hydrophobized hyperbranched polyglycerols – HPG – were synthesized with different hydrophobization degrees, with molar ratios with respect to polyglycerol PG:DTGE of 1:1; 1:2 and 1:4 in order to obtain the products labeled HPG11, HPG12 and HPG14, respectively. The procedure employed was as follows: at the end of the polyglycerol synthesis, the temperature of the system was reduced to 125 °C, and dodecyl tetradecyl glycidyl ether – DTGE was added at a rate of 5.0 mL/h. The system was kept closed for 24 h under N<sub>2</sub> atmosphere. The characterization of the products was performed through Fourier transform infrared spectroscopy – FT-IR, and the measurements were carried out using a Nicolet 740 FT-IR spectrometer, in the range from 4000 to 400 cm<sup>-1</sup>. Nuclear magnetic resonance – NMR was also employed and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in d<sub>6</sub>-DMSO with a Bruker Advance DPX-300 spectrometer, operating at 300 and 75.4 MHz, respectively. Thermogravimetric analysis (TGA and DTGA) was conducted in a Shimadzu TGA-51 analyzer, at a ramp of 20 °C/min, from room temperature to 800 °C in a high-purity flowing nitrogen atmosphere (20 mL/min). Particle size was measured by Dynamic Light Scattering – DLS in a Malvern zeta sizer nano series Nano-ZS instrument, with water and tetrahydrofuran (THF) as solvent, in glass cells at 25 °C.

### 2.3. Clays characterization

Clay mineral samples (A1, A2 and A3) and the bentonite B1 were obtained from Bentonorte Company (Paraíba, Brazil). All clays were characterized by scanning electron microscopy Hitachi TM3000 with energy dispersive spectroscopy (X-ray microprobe SwiftED) – SEM-EDS. The chemical composition were determined in X-ray Fluorescence Spectrometer WDS-2, model AXIOS (Panalytical). The samples were placed at 1000 °C for 16 h, in muffle furnace, and weighed after cooling to verify the loss on ignition-LOI, which is related to the volatile components. Cation exchange capacity- CEC was quantified through the methylene blue test and textural analysis was performed with an ASAP 2010 Micrometrics analyzer, from nitrogen adsorption and desorption at – 196 °C. The specific areas and porous diameters were calculated by the BET method and the porous volumes were calculated

using the BJH method. The semi-quantitative mineral compositions were determined by X-ray Diffraction (XRD), using fluorite as internal standard.

### 2.4. Inhibitive ability evaluation methods

#### 2.4.1. Hot-rolling cuttings dispersion tests

This test provides a simulation of the long exposure that the shale cuttings face when in contact with the fluid under average drilling conditions, when cuttings are brought up and removed from the borehole (Patel et al., 2007). In this test, 50.0 g of sized sample A1 were classified employing 4 and 8 mesh sieves, 4.76 and 2.38 mm, respectively. After that, the sample was transferred to a Baroid cell along with 350.0 mL of the formulated drilling fluid. The cell was kept in a rolling oven Fann Instrument Company LW2000 at 66 °C for 16 h. Finally, the cuttings were removed from the cell, washed and transferred to an oven for drying at 80 °C for 24 h. After drying the cuttings, the total amount and the recovered clay percentage were determined according to Eqs. (1) and (2), where  $R_{total}$  is the total of cuttings recovered,  $W_f$ ,  $W_i$  and  $W_{\#8}$  are the weight of dry clay after and before the rolling process, and the weight recovered in the 8 mesh sieve, respectively, while  $R_{intact}$  is the percentage of recovered intact cuttings.

$$R_{total} = \frac{W_f}{W_i} \times 100\% \quad (1)$$

$$R_{intact} = \frac{W_{\#8}}{W_i} \times 100\% \quad (2)$$

High recovery percentages,  $R_{total}$  and  $R_{intact}$ , indicate that the inhibitor is a good dispersion suppressant and shale inhibitor. Polymer (PG, HPG11, HPG12 and HPG14) aqueous solutions were tested in a concentration range from 0.1 to 3.0 wt% either pure or associated with KCl 1.0 wt%. The HPGs (5.0 wt% combined with 3.0 wt% KCl) were tested using the clay samples A1, A2 and A3 and their performance compared with the ones from solutions of PDADMAC 3.0 wt% and KCl 3.0 wt%. The highly reactive shales A2 and A3 were tested by a modified procedure using 14.3 g of cuttings in 100.0 mL of polymer solution at 66 °C for 4 h.

#### 2.4.2. Bentonite inhibition test

The bentonite inhibition test is usually employed as a screening method that helps to evaluate the ability of a chemical compound to prevent bentonite swelling and maintain low rheological profile (Patel et al., 2007). Aqueous dispersions of the polymeric shale inhibitors being developed in this work were used in 8.0 lb/bbl (2.3 wt%), either pure or combined with KCl 1.0 and 3.0 wt%. The polymeric systems performance was compared with the one from water, and from KCl 1.0 and 3.0 wt% solutions. In Baroid cells 350.0 mL of the solutions were treated with 10.0 lb/bbl (2.8 wt%) of bentonite B1 stirred for 10 min. After aging at 66 °C for 16 h, rheological properties were measured in a viscometer Fann Instrument Company 35 A and another amount of bentonite B1 was added to the cell and the procedure repeated until the rheological parameters exceeded the measuring limits.

### 2.5. Drilling fluids formulation tests

The drilling fluids formulation tests were performed according to recommended standard procedures from the American Petroleum Institute- API (Recommended Practice, 2009). The Lubricity test was conducted in a Lubricity Tester 21200 Fann Instrument Company, and the fluid loss was evaluated in a HTHP Filter Press Series 387, Fann Instrument Company, at 25 °C, 100 psi for 30 min.

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