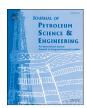
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Rheological properties of bentonite-free water-based drilling fluids with novel polymer viscosifier



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ABSTRACT

Water-based drilling fluids with no bentonite content was particularly advantageous in oil and natural gas exploration due to the excellent characteristics including faster rates of penetration, enhanced hole cleaning, less formation damage, etc. However, how to keep the excellent rheological regulation of bentonite-free drilling fluids was still one of the most serious issues for the mud designers. In this study, novel polymer viscosifier (SDKP) was prepared under optimal synthesis conditions through the copolymerization of N-vinylcaprolactam and sodium 2acrylamido-2-methylpropane sulfonate. The effect of SDKP on rheological behavior of bentonite-free fluids was studied according to American Petroleum Institute standard. Results showed that SDKP could improve the rheological properties of bentonite-free fluids. In addition, the good thermal stability and salt stability in improving rheological behavior of fluids made SDKP more attractive. Rheological behavior of SDKP based bentonite-free fluids at different temperatures was also evaluated. Results showed that SDKP based bentonite-free fluids showed certain thermo-viscosifying behavior in the temperature range of 80-140 °C even in high salinity, which was benefit for carrying cuttings. Shear test showed that the magnitude of the thermo-thickening viscosity was very sensitive to shear rate, and SDKP containing fluids became better shear-thinning upon heating, which could be more easily pumped into the well. In addition, the mechanism of SDKP in improving rheological behavior of bentonite-free fluids was revealed based on the investigation of morphology of SDKP through Environmental Scanning Electron Microscopy experiment.

1. Introduction

Extensive application of bentonite in water-based drilling fluid was long known in oil and natural gas exploration due to its important functions. The functions of bentonite in oil or gas well drilling included improving the hole cleaning properties and hole stability, forming low permeable filter cake, reducing the loss of fluids into permeable formation, etc. (Njobuenwu and Wobo, 2007; Vipulanandan and Mohammed, 2015). However, high bentonite content of drilling fluid could give rise to serious adverse effects, for example, excessive torque and drag, increasing chances of differential sticking, reducing the rate of penetration, serve formation damage, etc. (Vipulanandan and Mohammed, 2015; Azouz et al., 2016; Song et al., 2016). Furthermore, bentonite had the limitations of flocculation, degradation, and instability at high temperature, which could become more serious in ultra-deep wells (Mahto and Sharma, 2004; Jilani et al., 2002). These problems could increase the

fluid filtration into formation, decrease the effective carrying capacity of drilling cuttings and finally make the fluid ineffective for HTHP drilling applications. Thus, less or no bentonite should be contained to maintain the desired rheological and filtration properties. Nevertheless, bentonite was the most widely used fluid loss agent and viscosifiers, and water-based drilling fluid with low or no bentonite could not provide required rheological and filtration properties for oil and gas drilling operations. Therefore, one or more polymers must be used to substitute bentonite and achieve the satisfactory performance. A wide range of water-soluble polymers, for example, biopolymers [including xanthan gum (Hamed and Belhadri, 2009), starches (Dias et al., 2015), and chemically modified cellulose (Song et al., 2016a, 2016b; Li et al., 2016; Li et al., 2015)] and synthetic polymers [including polyacrylamides and related derivatives (Kuang and Xia, 2014; Yan et al., 2013; Jain and Mahto, 2017)], could be used to substitute bentonite and achieve the desired rheological and filtration properties. And the bentonite-free

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drilling fluids, which showed great advantage in increasing drilling rate, reducing formation damage, etc., were successfully developed by using these water-soluble polymers (Jilani et al., 2002; Zhang et al., 2017; Galindo et al., 2015).

Water-soluble polymers played a key role in low-bentonite or bentonite-free drilling fluids (Yan et al., 2013). Because rheological and filtration performance of these fluids were mainly controlled through the thickening effect of water-soluble polymers rather than bentonite. However, as temperature increased, these polymer viscosifiers would degrade, which could result in major accident during drilling operation (Stefano et al., 2013; Tehrani et al., 2009). Although considerable research had been made to increase the temperature limitation of polymers (Salami and Plank, 2016; Liu and Urban, 2010; Volpert et al., 1998), it could not fundamentally solve the problem. Moreover, according to the Arrhenius law, increasing temperature could decrease the viscosity and structure of drilling fluids due to thermal expansion. Therefore, the network structure in bentonite-free drilling fluids, especially at high temperatures, could not be made up by the common polymers, which was not conducive to carrying drilling cuttings and weighting material (Xie et al., 2016). So it was very crucial and necessary to develop new polymer viscosifiers to meet the performance of bentonite-free fluids. One possible way was the use of thermo-thickening polymers, which generally thermo-responsive chains characterized by a Lower Critical Solution Temperature (LCST) (Bokias et al., 2001). These functional blocks or grafts chains were normally poly(ethylene oxide) (Karakasyan et al., 2010), poly(N-isopropylacrylamide) (Durand and Hourdet., 1999), etc. The functional blocks or grafts chains gradually became hydrophobic with increasing temperature above LCST and the resulting hydrophobic character could induce hydrophobic association, which could result in increase in network structure and viscosity. Therefore, thermo-thickening polymers were beneficial to build up the network of drilling fluids and could be potentially used to provide satisfactory rheological properties of fluids, especially for bentonite-free water-based drilling fluids at high temperatures. Nevertheless, few papers on thermo-thickening polymers in water-based drilling fluid were reported, which was mainly due to the following reasons, firstly, most thermo-thickening polymers had poor thermal resistance, especially after long-term interaction (Zhong et al., 2006). Secondly, thermo-thickening polymer was not exactly the same as the thermo-sensitive polymer, despite the existence of various thermo-responsive polymers, most of them showed thermo-thinning behavior or phase separation with increasing temperature rather than expected thermo-thickening property (Durand and Hourdet, 1999; Guptaa et al., 2015; Karakasyan et al., 2008).

In our previous work (Xie et al., 2016), we have prepared a novel viscosifier (SDKP) by micellar radical polymerization, which showed good thermal resistance and certain thermo-thickening property in drilling fluid. However, the performance of SDKP in bentonite-free drilling fluids was not systematically investigated. The problems of high temperature rheological instability for bentonite-free drilling fluids were more prominent due to no bentonite content. Theoretically, thermo-thickening polymers could make up viscosity and structure of drilling fluids upon heating and can be a good potential candidate for formulating bentonite-free drilling fluids. So it was highly desirable to carry out a comprehensive performance evaluation of SDKP in bentonite-free drilling fluids. In this paper, the copolymer viscosifier (SDKP) under the optimum synthesis conditions (Xie et al., 2016), was prepared. The ability of copolymer in adjusting rheological performance of bentonite-free fluids was investigated systematically. And the temperature resistance and salt tolerance of copolymer containing fluids was also discussed. Thermo-thickening behavior of copolymer containing fluids upon heating was evaluated by the rheometer. And the influence of various factors, such as, copolymer concentrations, salinity and shear rate, on thermo-thickening behavior was evaluated systematically. The HE300, which was the high performance rheology modifier of Chevron Phillips Drilling Specialties Company, was used for comparison. In relation with macroscopic viscosity properties, a distinctive mechanism of

Table 1Feed molar ratio, elemental content and polymer molar ratio.

Sample	Feed molar ratio	Elemental content (w %)			Polymer molar ratio
	M _{NaAMPS} : M _{NVCL} : M _{DVB}	С	N	S	M _{NaAMPS} : M _{NVCL} : M _{DVB}
SDKP	39.00:60.00:1.00	40.86	6.39	8.03	54.92:44.98:0.10

SDKP in improving the rheological behavior of bentonite-free fluids was revealed based on the investigation of morphology of copolymer through Environmental Scanning Electron Microscope.

2. Experimental section

2.1. Materials

Based on the previous study (Xie et al., 2016), the copolymer viscosifier (SDKP) was prepared under optimal synthesis conditions. The molar ratio of polymerized monomer was shown in detail in Table 1. The monomers used for the polymerization were as follows, N-vinyl-caprolactam (NVCL, 98%), industrial products, was purified under vacuum distillation; 2-acrylamido-2-methylpropanesulphonic acid (AMPS, 99%), industrial products, was recrystallized before use; sodium dodecyl sulfate (SDS), sodium hydroxide (NaOH), divinyl benzene (DVB) and acetone, analysis of pure, were used as received. Specifically, the reaction product must be washed several times with 9:1 (v/v) mixture of acetone and water in order to remove SDS. The molecular structure of copolymer viscosifier was illustrated in Fig. 1. Viscosifier HE300 from Chevron Phillips Chemical Company was used as a comparison.

2.2. Characterization

CARLO ESRA-1106 elemental analyzer was used to carry out the elemental analysis of SDKP. Result from elemental analysis shown in

$$\begin{array}{c|c}
& SO_{3}^{-} \\
& CH_{2} \\
& O = C \\
& - CH_{2} - CH \\
& - CH_{3} \\
& - CH_{2} \\
& - CH_{2} - CH \\
& - CH_{3} \\
& - CH_{2} - CH \\
& - CH_{3} \\
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& - CH_{3} - CH_{3} \\
& - CH_{2} - CH_{3} \\
& - CH_{3} - CH_$$

Fig. 1. Chemical structure of SDKP.

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