



A strong inhibition of polyethyleneimine as shale inhibitor in drilling fluid

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ABSTRACT

In this paper, the inhibition property of polyethyleneimine (PEI) in montmorillonite solution was studied. The inhibition property was evaluated by linear swelling test and rolling recovery test. Compared with other inhibitors, the addition of PEI resulted in the lowest swelling height in drilling fluid. In rolling recovery rate study, the addition of PEI resulted in the highest recovery rate after rolled at 120 °C. More importantly, PEI was environmental friendly inhibitor. The inhibition mechanism was investigated by Fourier transform infrared spectroscopy, X-ray diffraction, Transmission electron microscope, Scanning electron microscopy, Atomic force microscope, Zeta potential and Particle-size analyzer. The spectrums and images showed that the negative charge in the surface of montmorillonite (MMT) was neutralized by the positive charge in amino group of PEI. PEI was adsorbed in the surface and intercalated into interlayer of MMT, which reduced the hydration repulsion of diffuse electric double layer and prevented the invasion of water. Hydrogen bonding between hydroxyl in the surface of clay and amino groups in the backbone and side chain of PEI can be formed in the process. The adsorption and intercalation of PEI in the surface and interlayer of MMT was the major factor to prevent water molecules from invading into the gallery of clay. There were a quantity of positive ions in solution because of the protonation of nitrogen in water. More positive ions resulted in the stronger force between inhibitor and clay.

1. Introduction

In oil and gas drilling operations, wellbore instability problem of shale is frustrating drilling engineers and exporters as these rocks make up over 75% of drilled formation (Rajnauth, 2012). The instability of shale formation results in serious operational problems, following major economic consequences for petroleum production and exploration (Al-Bazali, 2011; Akhtarmanesh et al., 2013; Karatela et al., 2016; Ma et al., 2015). More than 90% of wellbore instability problems are caused by problematic shale (Josh et al., 2012). It is one of the most significant technical problems in petroleum exploration and a major source of lost time and revenue. Cuttings from drilling shale and swelling of shale lead to various problems such as tight hole, stuck pipe, hole collapse and hole enlargement in drilling operation. These problems result in wellbore instability (Bybee, 2009; Rahman et al., 2000; Yu et al., 2003; Chen et al., 2003; Mohiuddin et al., 2007).

In drilling operations, one important function of drilling fluid is to prevent compacted clay minerals from taking up water continuous from drilling fluid (Suter et al., 2011). The invasion of water resulted in the swelling and hydration of clay minerals, which is considered as a major causal factor that leads to instability of shale (van Oort, 2003). The

degree of swelling of different clay minerals exhibited great difference. Smectite caused serious hydration when encountering water whereas kaolinite was unhydrated in water solution. Different composition of clay mineral exhibited different hydration capacity. In clay minerals, montmorillonite is considered as a major causal composition to cause the swelling of clay. Inhibiting the swelling of montmorillonite is an effective way to control wellbore instability (Díaz-Pérez et al., 2007; Paikaray et al., 2008; Bungler et al., 2014). The clay is unhydrated in oil based fluid. Oil based fluid is the preferred system in drilling these shale formations (Shivhare and Kuru, 2014). But fatal environment issues exist in the use of oil based fluid (Patel et al., 2007). Oil based fluid is not biodegradable and harmful for health and environment. Due to potential detrimental effects in the application of non-environment friendly oil based fluid, Environment Protection Agency and other regulatory bodies are imposing increasingly stringent regulations on the use and disposal of non-environment friendly oil based drilling fluid. It has been desirable to drill shale formations with water based fluid. Inhibitor is an available means to prevent clay from swelling in drilling shale formation with water based fluid. The drilling fluid industry has been searching for inhibitive water based fluid for years. Recently, the development of high-performance inhibitor has caused extensive research. Qiu group reported poly(oxypropylene)-amidoamine (POAA) was a potential inhibitor in water based fluid (Zhong et al., 2012). Qu group studied the inhibition of polyoxyalkyleneamine as shale inhibitor (Qu et al., 2009). Borges group evaluated the swelling ability of clay with different organic

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compounds and inorganic salt solutions (Balaban et al., 2015). Shadizadeh group reported a novel nonionic surfactant for inhibiting shale hydration (Shadizadeh et al., 2015). Our group evaluated the inhibition of chitosan quaternary ammonium salt (HTCC) (An et al., 2015). The commonly used inhibitors include KCl, CaCl₂, NH₄Cl, modified gilsonites and asphalts (Davis and Tooman, 1989; Gholizadeh-Doonechaly et al., 2009; Xiong et al., 2012). However, these approaches have some disadvantages such as short effectiveness, toxicity, low heat and salinity tolerance and pH sensitivity. Although some issues have been solved (Bonini et al., 2009), the hydration of water-sensitive shale is still not controlled completely, especially in drilling shale formation with water based fluid. Clay-particle is electronegative (Tang et al., 2014), then the effective shale inhibitor ought to be electropositive or nonionic. Coveney group recently reported the rule based design of clay swelling inhibitors (Suter et al., 2011). The rule showed that water soluble, hydrophobic backbone and primary di-amine or mono-quaternary amine functionality should be possessed by cationic inhibitors.

Polyethyleneimines (PEIs) are water soluble polymers with a quantity of cationic groups (Poghosyan et al., 2015; Foundas et al., 2015; Neville et al., 2013). Their solutions were alkaline (Rajagopalan et al., 2015). More importantly, it was environmental friendly. Polyethyleneimines have been widely applied in bioengineering (Wang et al., 2015a,b; Liu et al., 2015; Zhu et al., 2015), paper industry (Wang et al., 2015a,b), waste water treatment industry (Adewunmi et al., 2015), catalyst (Park and Kim, 2015; Zakharova and Syakaev, 2009) and sensor (Li et al., 2015). Polyethyleneimines are synthesized by ring opening polymerization of ethylene mine. There are a series of products which are classified by molecular weight and structure. In our previous work, our group evaluated the inhibition capacity of PEIs with montmorillonite. PEIs exhibited high performance of inhibiting montmorillonite to hydrate compared with other commonly used inhibitors. We studied the effect of molecular weight on inhibition property of PEIs. The results showed that the addition of PEI₁₀₀₀₀ resulted in the lowest swelling height. But the detailed interaction mechanism between PEI₁₀₀₀₀ and montmorillonite was not studied especially for the effect of temperature. In this paper, we evaluate the inhibiting property of PEI₁₀₀₀₀ at different temperatures and explore the inhibition mechanism with a variety of characterization methods. We wish to provide the guide of the application of polyethyleneimines in drilling shale formation with water based fluid. The swelling mechanism of MMT with PEI was showed in Fig. 1.

2. Materials and methods

2.1. Materials

Polyethyleneimine (PEI₁₀₀₀₀) was purchased from Gobekie Reagent Company. Chitosan quaternary ammonium salt (HTCC) (Mn 54 000 Da, Quaternary salt graft degree 60–80%, Purity ≥95%) was purchased from Jiaying Kerui Biological Technology Co., Ltd. Polyether amine was obtained from MI-SWACO. Montmorillonite (KSF) was purchased from Aladdin Inc.

Montmorillonite (MMT drilling fluid level) was supplied by Weifang Hua-wei Bentonite Group Co., Ltd. Shale was obtained from oil field. The other experimental chemicals were purchased from domestic reagent company. All the chemical materials were used without further purification.

2.2. Inhibitive properties

2.2.1. Linear swelling tests

The expansion height of montmorillonite solution with polyethyleneimine or other inhibitors is determined by CPZ-2 channel linear swellmeter (QingdaoTongchun,China). 5 g MMT or MMT(KSF) is poured into pressure tank, then be kept for 5 min at 10 MPa pressure by hydraulic press. A certain concentration inhibitor solution is prepared. Then the solution is poured into pressure tank and the value is recorded zero. The expansion height with time is recorded.

2.2.2. Rolling recovery tests

Shale was sieved and crushed between 6 meshes and 10 meshes. 20 g shale debris was prepared. The concentration of shale inhibitors solution is fixed on 2 wt%. 300 ml solution and 20 g shale debris was put into digestion tank. Then the digestion tanks were put into the BGRL-5 roller furnace (Qing dao, China) and rolled at 150°C for 16 h. The upper suspension was poured away after the solution is cooled to room temperature. Then adding 200 ml deionized water, and the procedure was repeated for three times. Precipitate is dried at 100 °C for 48 h. And then these precipitates were sieved to 40 meshes and weighted. Changing the rolled temperature to 80 °C, 100 °C, 120 °C, 130 °C and 140 °C. Hot rolled, cooled, washed suspension, dried and weighted, then the procedure was repeated. The rolling recovery rate is calculated by the following formula: Recovery = W₂/W₁. Shale debris denoted by W₁ and that after hot rolling denoted by W₂.

2.2.3. Preparation of MMT/PEI hybrids and the purification of PEI

300 ml aqueous solutions of PEI were prepared. The concentrations of PEI solution are fixed on 0, 0.5 wt%, 1 wt%, 2 wt% and 4 wt%. Then 6 g MMT was added into PEI solutions to make PEI/MMT suspension and the suspension was under vigorous stirring for 30 min at 8 000 rpm. Then the suspension bear rolling at 80 °C for 16 h to balance the adsorption and hydration between MMT and PEI. Centrifugal treatment was carried out at 10 000 rpm for 15 min. The precipitate was washed several times by deionized water until the upper liquid was clear. Finally the precipitate was dried at 100 °C for 24 h. Then be grinded into powder for FT-IR. and XRD.

2.3. Structure characterization techniques

2.3.1. Fourier transforms infrared spectroscopy (FT-IR) measurements

FT-IR spectral analyses of MMT/PEI hybrid were recorded by Magna-IR 560 spectrometer. 2 mg sample and 200 mg KBr was fully blend. The mixture was put into the mold and kept at 50 MPa pressure by hydraulic press.

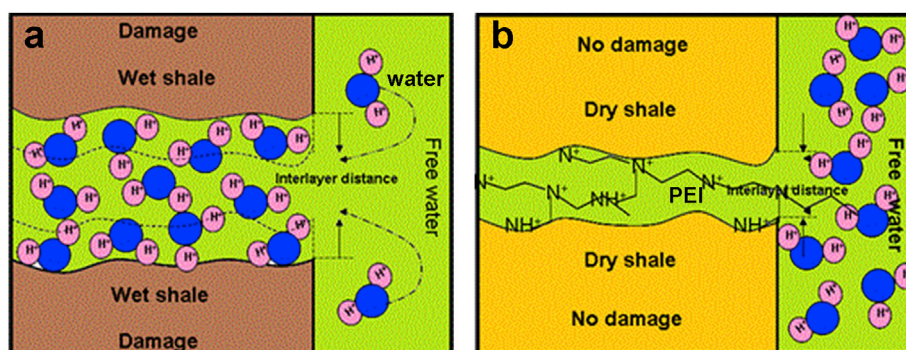


Fig. 1. Schematic representation of MMT swelling mechanism: (a) without PEI and (b) with PEI.

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