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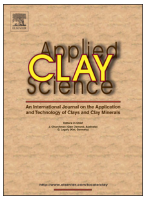

Research paper

Intercalation behavior of branched polyethyleneimine into sodium bentonite and its effect on rheological properties☆

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ABSTRACT

The inhibitive mechanism of low-molecular-weight branched polyethyleneimine (BPEI) with multiple primary amines and 1,6-hexamethylenediamine (HMDA) with two primary amines adsorbed on sodium bentonite (Na + Bent) has been investigated using isothermal adsorption, adsorption kinetics, scanning electron microscopy (SEM), X-ray diffraction (XRD) and elemental analysis (EA) techniques. The results indicate that as the number of primary amine groups in the inhibitor increases, the saturated adsorption amount decreases, and the adsorption rate increases. Low-molecular-weight BPEI molecules enter the interlayer space of Na + Bent and significantly reduce this space compared to that in hydrated Na + Bent. Moreover, there is no change in the clay interlayer space of Na + Bent with increasing BPEI concentration. A monolayer of BPEI intercalates into the clay interlayer and replaces the sodium ions in the interlayer. The BPEI molecules become firmly embedded in the Na + Bent interlayer between the primary amine groups and Si-O groups, resulting in the removal of water molecules. The inhibitive performance shows that BPEI inhibits clay hydration more effectively than HMDA and other inhibitors, and also indicates that as the number of primary amines increases, the inhibitive performance increases. When <1 wt% BPEI was added, the rheological properties improved significantly, and the American Petroleum Institute standard (API) fluid loss could be controlled well, indicating that BPEI can effectively create a balance between swelling inhibition and the rheological properties of water-based drilling fluids. Overall, the results indicate that BPEI is promising as a commercial shale inhibitor.

1. Introduction

The use of shale gas as a significant energy option has attracted much attention worldwide due to an increasing demand for energy. Drilling is a vital part of shale gas development (Yuan et al., 2015). Shale has a very low permeability and contains a high amount of water-sensitive clay minerals, causing several problems such as borehole instability and formation damage (Corrêa and Nascimento, 2005). Borehole instability in turn causes various problems such as hole collapse, tight hole, stuck pipe, bit balling, high torque and drag. This increases drilling time and costs, accounting for 75% of all the formations in the drilling process (Steiger and Leung, 1992; Dzialowski et al., 1993; Bol et al., 1994; Khodja et al., 2010). When a water-based drilling fluid is used to drill a shale, it hydrates the shale leading to borehole instability, which has been investigated by different methods (Cook et al., 1993; Mody and Hale, 1993; Van Oort, 2003; Guo et al., 2006). Oil-based drilling fluids provide excellent borehole stability. However, their use is limited by environmental-protection laws and relatively high costs (Morton et al., 2005; Chang et al., 2014). This has increased the demand for a high-performance water-based drilling fluid that prevents clay hydration, with an excellent inhibition performance similar to that of oil-based drilling fluid (Bruton and McLaurine, 1993; Rosa et al., 2005).

Many research papers have been devoted to the development of improved clay polymer nanocomposites (Liu et al., 2015; Mäkiniemi et al., 2015; Wang et al., 2015; Dedzo et al., 2016; England et al., 2016). In order to achieve the expected properties of the nanocomposites, a good dispersion of the clay particles is needed which helps to expand the interlayer space, allowing large polymer molecules to enter into the clay channels (De Paiva et al., 2008; Tan et al., 2008; Zhao et al., 2009; De la Orden et al., 2010). However, certain polymers are added as clay swelling inhibitors to maintain borehole stability during drilling operations, which insert into the interlayer of the clay sheet and decrease the interlayer space. This approach is contrary to that used in

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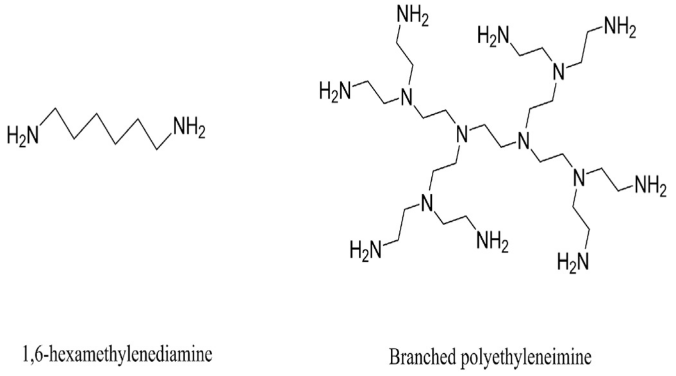

Fig. 1. Molecular structures of 1,6-hexamethylenediamine and branched polyethyleneimine.

the preparation of nanometer particles, where the clay layer spacing needs to be expanded.

Although common alkyldiamines can also reduce the clay interlayer space, it is difficult to balance the inhibitive performance and rheological properties of water-based drilling fluids. Moreover, most alkyldiamines are highly toxic, and thus are not environmentally safe. Polyethyleneimine (PEI) is a cationic polymer that is frequently used as a stabilizer for industrial suspensions. The adsorption of high-molecular-weight PEI on two types of bentonite clay suspensions as well as their rheological properties have been studied (Öztekin et al., 2002). High-molecular-weight PEI has also been studied as a shale inhibitor in drilling fluid (Guancheng et al., 2016). However, no study has been reported regarding the adsorption interaction between low-molecular-weight branched polyethyleneimine (BPEI) and homoionic sodium bentonite (Na + Bent), and the rheological properties of the resulting Na + Bent suspensions in BPEI solutions. BPEI is a type of water-soluble, hyperbranched polyamine containing a large number of primary amine groups on the ends of its molecular chains. These amine groups are capable of creating very strong hydrogen bonding interactions between BPEI and clays. Furthermore, because BPEI is a hyperbranched polymer, it offers several advantages, such as very low viscosity, high solubility, and multiple functional groups, which can help achieve a balance between the inhibitive performance and rheological properties of water-based drilling fluids.

A set of "rule-based" design criteria for cationic clay-swelling inhibitors has been reported (Suter et al., 2011). The cationic inhibitors should be able to exchange cations in the interlayer of bentonite and have no alcohol functional groups. The cationic inhibitor molecule should be water soluble with primary diamine groups and a sufficiently long hydrophobic carbon backbone, which can form a dense monolayer in the interlayer space (Suter et al., 2011). Oligomeric ether amines with PPG backbones have excellent clay swelling inhibition properties, and have 3 monomer units per charged amine group, which is the maximum backbone length before inhibition efficiency is diminished (Patel, 2009). The optimal backbone length is five or six carbon atoms. Amino inhibitors and their inhibition mechanism have been studied (Patel and Gomez, 2013). However, no report has been made on the influence of the number of primary amines on the inhibition of clay swelling.

In this paper, the saturated adsorption amount and adsorption rate of two inhibitors BPEI and hexamethylenediamine (HMDA), with different numbers of primary amine groups has been investigated by isotherm adsorption and dynamics analysis, in order to verify the hypothesis that a higher number of primary amine groups is beneficial for the inhibitive performance. We also investigated whether BPEI can cause significant reduction in the clay interlayer space through cation exchange and achieve a suitable balance between the rheology and filtration properties of water-based drilling fluids.

2. Experimental

2.1. Materials

Na + Bent was obtained from the Nanocor Company. The chemical composition of Na + Bent is 13.22% Al_2O_3, 71.30% SiO_2, 7.10% MgO, 4.79% Na_2O, and 3.59% Fe_2O_3. The samples were dried at 150 °C and then sifted through 200-mesh sieves. The cation exchange capacity (CEC) of Na + Bent is 145 meq/100 g. Branched polyethyleneimine (molecular mass Mn of 600) was acquired from Aladdin Co., Shanghai, China. 1,6-Hexamethylenediamine (HMDA), polyether amine, choline chloride (a quaternary ammonium salt with single amine group), and Na_2CO_3were purchased from Chengdu Changzheng Co., Ltd., China. The encapsulating agent (IND30) and fluid loss agent (SCH-I) were commercially available drilling fluid additives. The possible structure of the branched polyethyleneimine is shown in Fig. 1.

2.2. Structural characterization

The UV–Vis absorbance of alkylamine solution was measured by UV–Vis Spectrophotometer from Shanghai Onlab Instruments Co., Ltd., Shanghai, China. The changes in the clay interlayer space for alkylamine intercalated into Na + Bent were measured by X-ray diffraction (XRD). The XRD patterns were recorded on an X'Pert PRO MPD diffractometer from PANalytical B.V. equipped with a Cu Kα radiation source. The microstructures of hydrated Na + Bent and alkylamine - Na + Bent complexes were observed using scanning electron microscopy (SEM, FEI, Quanta 450). Elemental analysis (EA) for N element was performed using Var10EL-III from Elementar Analysensysteme GmbH.

2.3. Sample preparation

Na + Bent was dried at 150 °C for 24 h. Next, 1.0 g of Na + Bent was added into 25 mL distilled water to form a dispersion, which was stirred at 30 °C for 3 h. Then, 25 mL of the inhibitor solution was added into the Na + Bent dispersion. The concentration of the inhibitor solutions ranged from 1.4 CEC to 6.0 CEC; therefore, the final concentration of the inhibitor in the mixture ranged from 0.7 CEC to 3.0 CEC. The dispersion of the Na + Bent-inhibitor complex was stirred at 30 °C for 24 h. Then, the prepared dispersion was centrifuged at a speed of 5000 rpm for 20 min. The supernatant was collected in a volumetric flask. Then, 25 mL deionized water was added to the centrifugal sediment and stirred. The prepared dispersion was centrifuged and washed three times. The filtrate was combined with

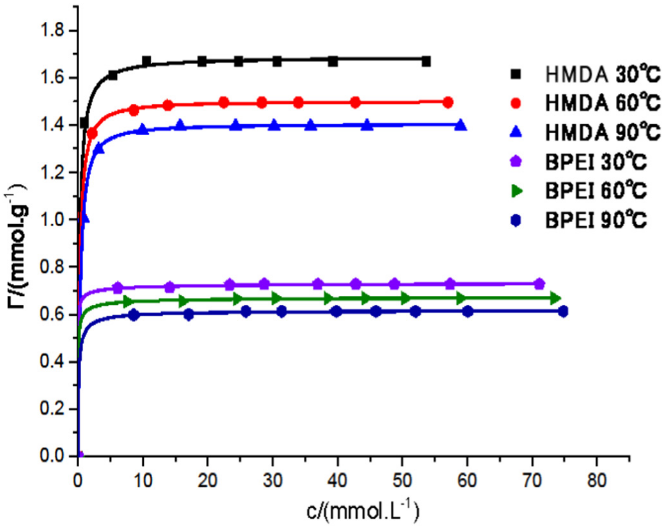

Fig. 2. Adsorption isotherm of HMDA and BPEI on Na + Bent.