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Research paper

Applied properties of oil-based drilling fluids with montmorillonites modified by cationic and anionic surfactants

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ABSTRACT

Montmorillonites modified by cationic surfactants have been used in oil-based drilling fluids for a period of time, while few studies focused on the use of montmorillonites modified by both cationic and anionic surfactants in oil-based drilling fluids. Compared with cationic surfactants, anionic surfactants have an advantage in thermal stability. Here, two parts of work were described. First, montmorillonites were modified by cationic and anionic surfactants through mechanochemistry. The structure and properties of organomontmorillonites were studied by X-ray diffraction, thermal analysis, contact angles and dispersion. Second, the applet properties including thixotropy, viscosity properties, gel properties and filtration loss resistance of oil-based drilling fluids with organomontmorillonites as additives were further studied at both room temperature (25 °C) and higher temperatures (200–220 °C). Characterizations indicated that cationic and anionic surfactants had intercalated into the interlayer spaces of montmorillonites, and the cationic–anionic organomontmorillonites had high surface polarity, better thermal stability and dispersion in high polar solvent than cationic organomontmorillonites. The properties of oil-based drilling fluids under both room and high temperatures showed that cationic and anionic organomontmorillonites performed better thixotropy, and had better rheological properties and less filtration loss than cationic organomontmorillonites in different oil–water ratio oil-based drilling fluids. The novel cationic and anionic organomontmorillonites have the potential to be widely applied in oil-based drilling fluids.

1. Introduction

Drilling fluids can be divided mainly into two types, water-based drilling fluids and oil-based drilling fluids (Huang et al., 2009; Wang, 2011; Yang, 2012). As a common use in the drilling industry, water-based drilling fluids have advantages in easy-preparation and low cost. Water-based drilling fluids have been widely researched and developed for a relatively long period of time (Abdo et al., 2015; Darley and Gray, 1988; Ebeltoft et al., 1997; Lummus and Azar, 1986). However, due to water-based drilling fluids' unstable performances and poor ability in anti-calcium/salt, water-based drilling fluids have several application limitations in complex drilling, horizontal drilling and shale drilling processes (Darley and Gray, 1988; Lummus and Azar, 1986). Oil-based drilling fluids, due to their salt resistance and high temperature resistance, good lubrication and little damage to reservoir, have been widely used in deepwater and complex oil/gas and shale gas drilling fields compared to water-based drilling fluids (Caenn and Chillingar, 1996; Ghalambor et al., 2008).

The ideal oil-based drilling fluids should have the proper thickness, viscosity and the ability to suspend or transport solid particles when drilling is interrupted (Abdo and Haneef, 2013). The functions are dependent on the rheological properties of oil-based drilling fluids, including viscosity, gel strength and thixotropy (Bergaya and Lagaly, 2013). Thus, organomontmorillonites (OMts) that can maintain and enhance the rheological properties of oil-based drilling fluids should possess favorable rheological properties and thermal stability.

The weaknesses of existing OMt compositions for non-aqueous systems are that most commercial oil-based drilling fluid systems have limitations as reduced rheology and filtration control when the fluids are exposed to temperatures higher than 149 °C for prolonged periods of time (Portnoy et al., 1986). In recent years, in order to enhance rheological properties of oil-based drilling fluids under high temperature, most OMts used in oil-based drilling fluids were prepared from montmorillonite (Mt) that was modified by cationic surfactants with different functional groups or chain length (including benzyl methyl ammonium, alkoxylated organic cation and polyalkoxylated quaternary ammonium salt) (Dino and Thompson, 2002; Finlayson, 1984; Nae et al., 1995). Lewis and Szymanski (2010) prepared OMts with myristyl amine oxide, and the oil-based drilling fluids containing the OMt showed stability reading of about 120 V after standing for 2 h

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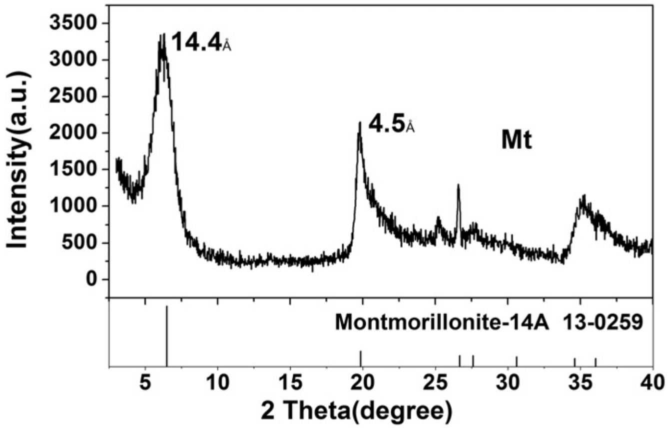

Fig. 1. XRD patterns of Mt and JPDF of montmorillonite-14A.

and showed no significant signs of settling over 12 h. Dino and Thompson (2013) prepared OMts with an organic cation provided by an alkoxylated quaternary ammonium salt, and an organic cation that was not provided by an alkoxylated quaternary ammonium salt, which demonstrated an improved temperature stability by exhibiting a higher rheology after dynamic heat aging at 204 °C. Hermoso et al. (2014) studied two organobentonites prepared from Mt with benzyl methyl ammonium as a viscosity modifier in oil-based drilling fluids. In most of research, OMts and corresponding oil-based drilling fluids show favorable rheological and viscosity properties below 150 °C, while often totally failing at temperatures over 180 °C (Dino and Thompson, 2002). Silva et al. (2014) studied oil-based drilling fluids with Mt modified by nonionic surfactants. Results showed that nonionic OMts can disperse well and exhibit good rheological properties in the oil-based drilling fluids at room temperature, while the thermal stability and applied properties of oil-based drilling fluids were not reported at high temperatures. Zhuang et al. (2015) studied cationic–nonionic organomontmorillonites in oil-based drilling fluids. The development of novel OMts that exhibit good rheological properties in oil-based drilling fluids at high temperatures has drawn attention. Compared with wide research on the Mt that was modified by cationic surfactants used in oil-based drilling fluids, research on Mt that was modified with both cationic and anionic surfactants in oil-based drilling fluids have not been reported.

In this study, cationic–anionic OMts (CA-OMts) were prepared from Mt modified by cationic and anionic surfactants in the process of mechanochemistry. The structure, surface properties, thermal stability and dispersion of CA-OMts and DG-OMts were compared. The performances of oil-based drilling fluids containing CA-OMts and DG-OMts separately at both room (25 °C) and high temperatures (200–220 °C) were further compared to study the effect of different OMts on the applied properties of oil-based drilling fluids.

2. Experiment

2.1. Materials

Mt was purchased from Ningcheng, Inner Mongolia, China, with a purity of 96%. The Mt is ground by mortar for 10 min and passed through a 200-mesh sieve. The cation exchangeable capacity (CEC) of Mt is 78 mmol/100 g. The XRD result in Fig. 1 showed that the basal spacing of the Mt is 14.4 Å. The results of chemical composition are shown in Table 1.

DG-OMt, modified by cationic surfactants and already used as a lipophilic colloid in oil-based drilling fluids, was purchased from the Hualian organic clay factory in Tianjin, China, which was being set as the control group in this series of experiments. The XRD pattern of DG-OMt is shown in Fig. 2.

The liquid organic dispersion media used in the experiment is commercial 0# diesel oil from Sinopec with a density of 0.853 g/cm^3 at 25 °C. The cationic surfactant cetyltrimethyl ammonium bromide (CTAB), butanol, xylene and $CaCl_2$ were analytical reagents, purchased from Beijing Chemical Works, China. Anionic surfactant sodium dodecyl sulfate (SDS), sorbitan oleate (SPAN-80), t-octylphenoxypolyethoxyethanol (OP-10) and odecyl trimethyl ammonium bromide (DTAB) were chemically pure and purchased from Shantou Xilong Co., Ltd., China. Barite was technical grade, which was also purchased from Shantou Xilong Co., Ltd., China.

2.2. Preparation of OMt and oil-based drilling fluids

2.2.1. Preparation of cationic organomontmorillonite

Cationic organomontmorillonite (C-OMt) was prepared through mechanochemistry (Xie et al., 2014). 10 g Mt, CTAB equivalent to 2.2 CEC of Mt were mixed and milled by a planetary ball mill at 500 rpm. Samples were dried at 60 °C for 24 h and finally milled to pass through a 200-mesh sieve.

2.2.2. Preparation of CA-OMt

CA-OMt was prepared through mechanochemistry. 10 g Mt, CTAB equivalent to 1.5 CEC of Mt and SDS equivalent to 0.9 CEC of Mt were mixed and milled by a planetary ball mill at 500 rpm. Samples were dried at 60 °C for 24 h and finally milled to pass through a 200-mesh sieve. Mt modified with CTAB equivalent to 1.5 CEC and SDS equivalent to 0.9 CEC was named as CA-OMt-1, Mt modified with CTAB equivalent to 1.0 CEC and SDS equivalent to 0.5 CEC was named as CA-OMt-2, and Mt modified with CTAB equivalent to 0.6 CEC and SDS equivalent to 0.5 CEC was named as CA-OMt-3. Samples were dried at 60 °C for 24 h and finally milled to pass through a 200-mesh sieve.

2.2.3. Preparation of oil-based drilling fluids

The 80:20 and 90:10 oil–water ratio oil-based drilling fluids were prepared according to Mu (2007): 256 ml 0# diesel and 64 ml 3% $CaCl_2$ solution/288 ml 0# diesel and 32 ml 3% $CaCl_2$ solution (according to different oil–water ratios) were placed in a blender and blended for 5 min at 4000 rpm, producing the base-fluid (an emulsion). Then 3.0 g SPAN-80, 3.0 g OP-10, 2.0 g DTAB, 1.6 g SDS and 6 g of different OMts were added to 320 ml of base-fluid emulsion and the mixtures were blended for 20 min at the speed of 4000 rpm. At last, 268 g barite was added as the weighting agent into the emulsion and the emulsion was blended for another 30 min. The resulting fluids were tested first and then placed in a rotary oven heated to 150 °C, 180 °C, 200 °C and 220 °C where they were aged for 16 h. After cooling, the fluids were tested again. In this process, SPAN-80, OP-10, DTAB and SDS were used as emulsifiers and stabilizers in oil-based drilling fluids.

2.3. Characterization methods

2.3.1. XRD

XRD analysis was performed on a D/max-rA 2000 diffraction (Rigaku, Japan) at 40 kV and 100 mA, using a Cu tube (Cu-Kα radiation, $\lambda = 0.154$ nm). Scans were recorded between 1° and 25° (2θ) with a step size of 0.02°, at a scanning rate of 4°/min; 1/6° was chosen for the

Table 1
Elementary composition of Mt.

Composition	C	Na	Mg	Al	Si	Ca	Ti	Fe	P	O	Others
Wt.%	4.50	0.15	2.4	7.78	22.4	2.45	1.06	6.237	0.38	50.14	2.50