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Research paper

Comparative study on the use of cationic–nonionic-organo-montmorillonite in oil-based drilling fluids

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A B S T R A C T

This work involves a comparative study of cationic–nonionic-organo-montmorillonite (CNOMt), cationic-organo-montmorillonite (COMt) and nonionic-organo-montmorillonite (NOMt), aiming their use in oil-based drilling fluids. Firstly, CNOMt, COMt and NOMt were prepared in aqueous solution. Secondly, organo-montmorillonites were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetric analysis (TG), contact angle test, and swell index. The results indicated that cationic and nonionic surfactants could solely or synergistically intercalate into the interlayer spaces of montmorillonite. The order of their thermal stabilities was CNOMt > NOMt > COMt. The order of surface lipophilicity (or hydrophobicity) and swelling indices in oils was the same, i.e., CNOMt > COMt > NOMt. Finally, organo-montmorillonites were added into emulsions with different ratios of oil to water and their apparent viscosities were characterized. The results exhibited that both CNOMt and COMt viscosified the oil-based fluids better than NOMt did. In addition, the apparent viscosity of CNOMt was a little higher than that of COMt in the emulsion with oil/water ratio of 95:5 while the result was inverted in the emulsion with oil/water ratio of 80:20. From the standpoint of characterization results, CNOMt presented a new kind of potential rheological control additive of oil-based drilling fluids, especially for high oil/water ratio fluids, and CNOMt would perform excellent thermal stability.

1. Introduction

Over the next 30 years, global energy is projected to rise almost 60%, a challenging trend that may be met only by revolutionary breakthroughs in energy science and technology (Esmaeili et al., 2011). Drilling fluids are compared as the "blood" in drilling processes. The oil industry is increasingly drilling more technically challenging and difficult wells. Drilling of deeper wells worldwide requires constant searching for adequate drilling fluids to overcome extreme conditions (Williams et al., 2011). Generally, drilling fluids are classified into two categories: (1) Water-based drilling fluids; (2) oil-based drilling fluids. The successful completion of an oil well and its cost depend to a considerable extent on the properties of the drilling fluids (Darley and Gray, 1988). Most of global drilling operations use water-based drilling fluids, because of their lower environmental impact and lower costs (Caenn and Chillingar, 1996; Meng et al., 2012). However, water-based drilling fluids are limited by their abilities of dissolving salts and interfering with the flow of oil and gas through porous rocks. Oil-based drilling fluids have been developed to overcome certain undesirable characteristics of water-based drilling fluids. Due to their continuous phase, oil-based drilling fluids are known to provide unequaled performance attributes with respect to the rate of penetration, shale inhibition, wellbore stability, high lubricity, and high thermal stability (Caenn and Chillingar, 1996; Khodja et al., 2010). Therefore, oil-based drilling fluids are quite qualified for offshore wells, geopressured formations, high temperature wells, and high angle holes.

Organo-montmorillonite (OMt) is an important rheological control additive of oil-based drilling fluids. Mostly, an oil-based drilling fluid can be viscosified by OMt. The viscous flow behavior of oil-based drilling fluids is strongly influenced by OMt nature and concentration (Hermoso et al., 2014). In addition, the thermal stability of OMt deeply influences the rheological properties of the oil-based drilling fluids under high temperature and high pressure. OMt is usually prepared from cationic surfactants (such as quaternary ammonium and quaternary phosphonium) using cation exchange (de Paiva et al., 2008) and it is called cationic-organo-montmorillonite (COMt). However, COMt has some disadvantages that nonionic surfactants do not present. Nonionic surfactants are less toxic and have a higher potential for biodegradation than ionic surfactants, and OMt produced with them can present higher thermal and chemical stability than those containing ionic surfactants (Shen, 2001; Ultracki, 2004). The use of nonionic-organo-montmorillonite (NOMt) in oil-based drilling fluids had been researched (Silva et al., 2014), but no comparative study with other OMt was done.

In recent years, the synergetic modification of montmorillonite with two kinds of organic surfactants, such as cationic–anionic-organo-

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montmorillonite (CAOMt) (Chen et al., 2008; Zhang et al., 2013; Sanqin et al., 2014), anionic–nonionic-organo-montmorillonite (ANOMt) (Zhuang et al., 2015) and cationic–nonionic-organo-montmorillonite (CNOMt) (Zhang et al., 2012) were reported. Theoretically, CNOMt may have both the advantages of COMt and NOMt. What's more, the properties of CNOMt may even precede the sum of COMt and NOMt. Nevertheless, there is no study on the use of CNOMt in oil-based drilling fluids compared with COMt and NOMt. The aim of this work is to make a comparative study about CNOMt, NOMt and COMt, especially research the use of CNOMt in oil-based drilling fluids.

2. Materials and methods

2.1. Materials

Na^+-treated montmorillonite (Na^+-Mt) was obtained from Kazuo Shuanglong Mining Co., Ltd., Liaoning Province, China. The cation exchange capacity (CEC) of Na^+-Mt was 76 mmol/100 g and the given purity was ≥95%. Both of nonionic surfactant OP-10 (purity of 99%) and cationic surfactant cetyl trimethyl ammonium bromide (CTAB) (purity of 99.9%) were bought from Shantou Xilong Chemical Co., Ltd., China. The structural formulas of organic surfactants were given in Fig. 1. The base oils (diesel oil and mineral oil) were bought from China National Petroleum Corporation. The anhydrous ethanol was bought from Beijing Chemical Work.

2.2. Preparation of organo-montmorillonites

All of OMt were prepared in aqueous solution. CNOMt was obtained as the following steps: 100 g Na^+-Mt was added into 3000 mL distilled water, stirring for 10 min; then a certain amount of OP-10 was added into the dispersion, stirring for 30 min; a certain amount of CTAB was added into the previous dispersion, stirring for another 30 min; and lastly, by centrifugation, drying at 60 °C for 24 h, milling and sieving with a 200-mesh sieve, CNOMt was prepared. For comparison, COMt and NOMt were also prepared using the same method, but only one kind of organic surfactant was used and the dispersion was stirred for 1 h after the addition of organic surfactants. A summary of preparation was presented in Table 1.

2.3. Characterization

The X-ray diffraction (XRD) analysis was conducted on a Rigaku D/max-rA (12 kW) X-ray powder diffractometer operating at Cu Kα radiation, 40 kV, 100 mA and a scan speed of 4.0°(2θ)/min. A Shimadzu DTG-60 simultaneous DTA-TG apparatus was used for thermal analysis (in air). A heating rate of 10 °C/min was applied until the temperature reached 900 °C. Contact angle tests were conducted on a contact angle measurement JC200D and the measurement was performed with distilled water. Swell index was tested according to ASTM D 5890-11 standard (2011) (using a dry temperature of 60 °C and organic media instead of water in the procedure). 2 g OMt sample was added into 100 mL organic media and swelled freely. Oil-based drilling fluids were prepared as follows: diesel oil, $CaCl_2$ aqueous solution (0.2 g/mL) and 16 g Span-80 (emulsifier) were placed in a Hamilton Beach N5000 blender and blended for 5 min, producing the base-fluid (an emulsion). 12 g (concentration of 30 kg/m^3) OMt sample was added into the emulsion and blended for 20 min. The resulting fluid was placed in a rotary oven heated to 66 °C, where it was aged for 16 h. The total volume of every fluid was 400 mL. The volume ratios of diesel oil to $CaCl_2$ aqueous solution were 80:20 and 95:5 respectively. The apparent viscosity (AV) was then determined at 66 °C according to the specification of API 13A (2010), using a FANN 35A viscometer.

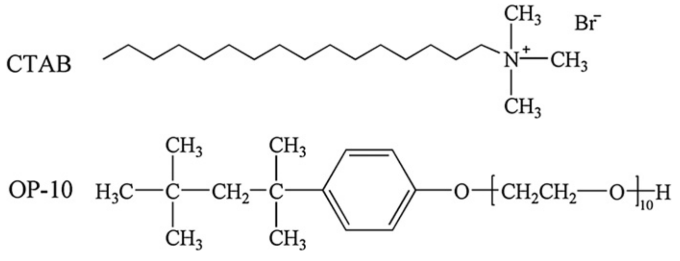

Fig. 1. The structural formulas of organic surfactants.

Table 1
A summary of preparation of OMt.

Samples	OP-10		CTAB		Na-Mt	Time
	CEC	g	CEC	g	g	h
CTAB(0.7)-Mt	0	0	0.7	20	100	1.0
CTAB(1.4)-Mt	0	0	1.4	40	100	1.0
CTAB(2.1)-Mt	0	0	2.1	60	100	1.0
CTAB(2.8)-Mt	0	0	2.8	80	100	1.0
OP-10(0.4)-Mt	0.4	20	0	0	100	1.0
OP-10(0.8)-Mt	0.8	40	0	0	100	1.0
OP-10(1.2)-Mt	1.2	60	0	0	100	1.0
OP-10(1.6)-Mt	1.6	80	0	0	100	1.0
OP-10(0.4)–CTAB(0.7)-Mt	0.4	20	0.7	20	100	0.5 + 0.5
OP-10(0.4)–CTAB(1.4)-Mt	0.4	20	1.4	40	100	0.5 + 0.5
OP-10(0.4)–CTAB(2.1)-Mt	0.4	20	2.1	60	100	0.5 + 0.5
OP-10(0.8)–CTAB(0.7)-Mt	0.8	40	0.7	20	100	0.5 + 0.5
OP-10(0.8)–CTAB(1.4)-Mt	0.8	40	1.4	40	100	0.5 + 0.5
OP-10(1.2)–CTAB(0.7)-Mt	1.2	60	0.7	20	100	0.5 + 0.5

3. Results and discussion

3.1. XRD

The XRD patterns of Na^+-Mt, surfactants and OMt were given in Fig. 2. The results of basal spacing of OMt were summarized in Table 2. The XRD reflection of Na^+-Mt related to the basal spacing appeared at $2\theta = 6.9°$ ($d_{001} = 1.28$ nm). With the increase of CTAB, the basal spacing of COMt increased gradually (see Fig. 2(A)). The addition of 0.7 CEC, 1.4 CEC, 2.1 CEC and 2.8 CEC CTAB caused the (001) basal reflection to shift to lower angles. The basal spacing (d_{001}) of CTAB(0.7)-Mt, CTAB(1.4)-Mt, CTAB(2.1)-Mt and CTAB(2.8)-Mt were 1.48 nm, 1.98 nm, 4.6 nm and 3.96 nm respectively. Although the basal spacing of CTAB(2.1)-Mt was ca. 4.6 nm, the basal reflection was wide and the intensity was low, indicating that the degree of order was not good enough. The basal spacing of CTAB(2.8)-Mt was 3.96 nm, but the intensity of the reflection was higher and the peak was sharper, demonstrating the high order degree of CTAB(2.8)-Mt. The similar phenomenon took place in the XRD patterns of NOMt. The basal spacing of NOMt increased along with the increase of OP-10. The addition of 0.4 CEC, 0.8 CEC, 1.2 CEC and 1.6 CEC OP-10 augmented the basal spacing to 1.6–4.47 nm (Fig. 2(B)). It can be concluded that the increase of surfactants' concentrations did not only expand the basal spacing of OMt, but also increased the degree of their order.

Note the XRD patterns of CNOMt (Fig. 2(C)). Synergistically modified with OP-10 and CTAB, the basal reflection of CNOMt shifted to lower angles ca. $2\theta = 2.5°$. With the increase of surfactants, the basal spacing increased. The basal spacing of CTAB(0.7)-Mt increased to 1.48 nm and that of OP-10(0.4)-Mt reached 1.60 nm. However, the basal spacing of OP-10(0.4)–CTAB(0.7)-Mt increased to 3.1 nm. This shift indicated that OP-10 and CTAB had synergistically intercalated into the interlayer spaces of Na^+-Mt. With the same addition of organic surfactants (except for CTAB(1.4)-Mt), the basal spacing of CNOMt was a little smaller than that of COMt and NOMt. However, it should be point out that the relative intensities (Na^+-Mt as a reference) of CNOMt were higher than those of COMt and NOMt, and the half-peak width of the basal reflection was also smaller, indicating more ordered lattices of CNOMt. In summary, XRD results demonstrated that both CTAB and