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Modification of bentonites with nonionic surfactants for use in organic-based drilling fluids



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ABSTRACT

The use of organophilic bentonites as additives in organic-based drilling fluids has long been a subject of study, but few studies have focused on the modification of these clays with nonionic surfactants. The advantage of nonionic surfactants over ionic ones is that they improve the thermal and chemical properties of organoclays (OC), and are also more readily biodegradable. The work described here involves a study of bentonites modified by nonionic surfactants, aiming at their use as dispersants in the composition of organic-based drilling fluids. The organophilization process was analyzed by X-ray diffraction and thermogravimetry, and the interaction of organoclays with the solvent medium was assessed based on the swell index and the determination of the apparent viscosity of clay-containing dispersions. The results indicate an effective intercalation of the nonionic surfactants in organoclays, and the content of incorporated surfactants was also quantified. The swelling results demonstrate chemical compatibility between diesel and kerosene organic media and the organoclays produced. From the rheological standpoint, some of the organophilic clay samples present a potential for use as raw materials for additives in organic-based drilling fluids, despite being considered of poor quality when analyzed for water-based drilling fluids.

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1. Introduction

Bentonites are rocks whose predominant component is a smectite mineral originating from the alteration of glassy materials of igneous origin (Bergaya et al., 2006; Grim and Güven, 1978; Murray, 2007). Their wide versatility, natural abundance, low cost, wide range of industrial uses, and their propensity to be chemically and physically modified, are the reasons bentonites are used in numerous areas, meeting a wide range of technological needs (Abdou et al., 2013; Menezes et al., 2010; Tiwari et al., 2008).

Bentonites have high specific surface areas, in theory ranging from 700 to 850 m²/g (Bergaya et al., 2006), and from 20 to 130 m²/g by the N₂-BET method (Kaufhold et al., 2010). Thus, bentonites can react with various organic compounds, such as ionic, amphoteric and nonionic surfactants, through a series of specific mechanisms (Bergaya et al., 2006; Ultracki, 2004), forming a special group of materials called organophilic clays. These are clays in which organic molecules have been incorporated, thereby changing their surface properties from

hydrophilic to hydrophobic or organophilic (Bergaya et al., 2006; Groisman et al., 2004).

Today, a wide range of technology sectors use clays modified with organic compounds, ranging from environmental applications to the development of advanced materials with specific properties (tailor-made) (Anirudhan and Ramachandran, 2007; Lee and Kim, 2002; Sora et al., 2005; Yue et al., 2007; Zampori et al., 2008, 2009, 2010). The rheological control of organic-based drilling fluids stands out among these applications. Researches in recent years (Akkal et al., 2013; Fjelde, 2009; Hermoso et al., 2014; Rodrigues et al., 2010; Zhang et al., 2013) have focused on the study of oil-based drilling fluids (water/oil emulsions) containing organophilic clays. However, the number of studies is small in view of the particularities of this technology and of the demand for new technologies in the oil and gas extraction sector.

Oil-based drilling fluids were initially obtained using organophilic clays modified with quaternary ammonium salts, which are ionic surfactants. However, these salts have some limitations that nonionic surfactants do not present, such as low thermal stability and high resistance to degradation when discarded in the environment. To solve these problems, nonionic surfactants were introduced in drilling fluid formulations (Cardoso et al., 2012). Nonionic surfactants are less toxic and have a higher potential for biodegradation than ionic surfactants, and organophilic clays produced with them can present

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higher thermal and chemical stability than those containing ionic surfactants (Shen, 2001; Ultracki, 2004). Moreover, larger basal spacings and higher amounts of organic carbon can be obtained in organophilic bentonites by using nonionic surfactants.

On the other hand, the organic dispersion media most commonly used in oil-based fluids are the ones with high aromatic content, such as conventional marine diesel and mineral oils, but these materials are highly polluting, which has led to the search for alternatives with lower levels of aromatics and polluting power (Bernier et al., 2003). Thus, this work is aimed at developing organophilic clays using nonionic surfactants for use in organic-based drilling fluids.

2. Materials and methods

Four bentonite samples were used in this study, referred to as samples Bent1, Bent2, Bent3 and Bent4. These clays, which were donated by the company Bentonita União Nordeste, Paraíba, Brazil, are known commercially as Pedra Lavrada clays. Samples Bent1, Bent2, Bent3 and Bent4 are classified here as Grey Clay, Light Clay, Dark Green Clay and Bentonite, respectively. The bentonites under study have been characterized mineralogically in previous studies (Silva et al., 2013), in which they were found to be naturally polycationic, containing Mg and Ca as exchangeable cations consisting of nontronite, kaolinite and quartz, with chemical analysis indicating Fe₂O₃ contents of less than 8%. In terms of particle size distribution, the clays presented an average diameter varying from 3.3 μm to 12.2 μm. The cation exchange capacity (CEC) of the clays, measured by the methylene blue method, varied from 56 to 64 meq/100 g and the specific surface area (SA) from 477 to 499 m²/g.

The nonionic surfactants used here were Ultramine 20 (TA20), 100% active ethoxylated amine TA20®, and Ultramine 50 (TA50), 100% active ethoxylated amine TA50®, supplied by Oxiteno S/A, Brazil. The chemical formulas of the compounds used are presented in Fig. 1.

The liquid organic dispersion media used here were commercial diesel oil with a density of 0.853 g/cm³ at 25 °C; commercial kerosene with a density of 0.80 g/cm³ at 25 °C; Varsol (C₈–C₁₀ aliphatics) with a density of 0.76 g/cm³ at 25 °C (ExxonMobil Chemical); commercial edible soybean oil with a density of 0.92 g/cm³ at 25 °C; ethanol or hydrous ethyl alcohol fuel (HEAF) (ethanol: 92.6 to 93.8%, water: 6.2 to 7.4%, and gasoline: 30 mL/L) with 96% purity, 4% water (96°GL) and commercial anhydrous ethanol (99% purity).

The clays were dried at 60 °C for 24 h controlling its moisture to not achieve a value lower than 10%. After drying, the clays were deagglomerated and sifted through a mesh sieve of 0.074 mm. The proportion of the surfactant used in this study was 16.6% and 23.0% of the weight of dry clay. The surfactant was used separately (TA20 or TA50) and also in combination (50% TA20 + 50% TA50). The organophilization process involved the use of 3.6 L of deionized water and 150 g of clay; the mixture was stirred for 20 min (at 17,500 rpm), after which the nonionic surfactant was added. The pH was adjusted to 7.0 with a 2 N HCl solution and stirring was continued for another

20 min (at 1600 rpm), after which the system was filtered. The organoclays were washed three times with deionized water (pH 7.0) to remove excess surfactants. Each washing process used 3.6 L of deionized water. Previous research (Ferreira, 2005) indicated that this procedure is adequate to remove the surfactant not incorporated. After the cleaning process, the material was oven-dried at 60 °C for a period of 24 h to 96 h. Lastly, the organophilized clay was ball milled and sifted through a mesh sieve (0.074 mm).

The organophilized bentonites were examined by X-ray diffraction (Shimadzu D6000), to evaluate the variation in basal interplanar spacing. The analyzed samples were sifted through a mesh sieve of 0.045 mm and the XRD analysis was performed using CuKα radiation, fixed time scanning mode (step of 0.02° 2θs⁻¹ and present time of 0.6 s), divergence slit and anti-scatter slit of 0.5° and receiving slit of 0.15 mm, using monochromator and 40 kV and 30 mA as working conditions. The experimental error window is approximately ±0.03 Å at 2θ of 28.2°.

The percentage of surfactant incorporated into the clay was determined by thermogravimetric analysis (TGA) (Shimadzu, 60H), by subtracting the weight loss of the natural clays from their respective organophilic clays in the range equivalent to the decomposition of the nonionic surfactant, between 180 °C and 1000 °C. The analyzed samples were sifted through a mesh sieve of 0.074 mm, heated up to 1000 °C using a heating rate of 10 °C/min, under nitrogen atmosphere up to 600 °C and under air up to 1000 °C. Sample masses of 10 mg were used.

After organophilization, the swell index of the clays in the aforementioned liquid organic dispersion media was analyzed, as specified by the ASTM D 5890-11 standard (2011) (using a drying temperature of 60 °C and organic media instead of water in the procedure). This analysis was based on studies by Valenzuela Diaz (1994), who classified organoclays as follows: zero swelling—values equal to or lower than 2 mL/g; intermediate swelling—values ranging from >5 to <8 mL/g; and high swelling—values of >than 8 mL/g. This method indicated that the medium under study is compatible with the organophilic clays obtained.

The organic-based drilling fluids were prepared as follows: 336 mL of liquid organic medium and 84 mL of a saturated NaCl solution (0.395 g/mL) were placed in a Hamilton Beach N5000 blender and blended for 5 min, producing the base-fluid (an emulsion). The media that showed the best results in the swelling test, diesel and kerosene, were used in the analysis of viscosity. Then, 2.4 g, 6.0 g, 9.6 g and 13.2 g of organoclays were added to 420 mL of base-fluid emulsion and the mixtures were blended for another 20 min, producing drilling fluids with four clay concentrations. The resulting fluid was placed in a rotary oven heated to 66 °C, where it was aged for 16 h. The apparent viscosity (AV) and plastic viscosity (PV) were then determined according to the standards of Petrobras (2011), using a FANN 35A viscometer.

3. Results and discussion

XRD patterns of samples Bent1, Bent2, Bent3 and Bent4, with and without the addition of the TA20, TA50 and TA20 + TA50 nonionic surfactants, are depicted in Figs. 2 and 3. Note that the non-modified clays presented a basal reflection at the 2θ angle ranging from 5° to 6°, which corresponds to a distance d₀₀₁ between layers ranging, approximately, from 14 Å (1.4 nm) to 15.5 Å (1.55 nm). The addition of 16.6% and 23.0 wt.% of surfactant caused this reflection to shift to lower angles of about 2°, corresponding to distances d₀₀₁ in the range of 40–58 Å between the clay platelets. This indicates a considerable increase in the distance between layers and demonstrates the effective occurrence of intercalation in the clay interlayer spaces. This behavior indicates that adsorption occurred not only at the edges or outermost surfaces of the clay mineral layers in the bentonites but also penetrated between layers, despite the long carbon chains of the additives used.

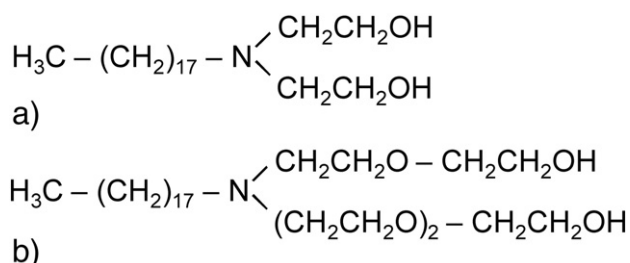


Fig. 1. Surfactants used in this work: a) TA20, b) TA50.

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