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Research paper

Modification of bentonite clay by a cationic surfactant to be used as a viscosity enhancer in vegetable-oil-based drilling fluid

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ABSTRACT

Bentonite clays may be used as additives in drilling fluids aiming at viscosity correction. A surface modification procedure with the purpose of dispersing the clay in the organic phase of a vegetable-oil-based drilling fluid was performed. The fluids were prepared using soybean oil, lauryl alcohol triethoxylate, brine, bentonite modified by hexadecyl trimethylammonium bromide (CTABr), and barite. The clay modification step was performed using three different concentrations of cationic surfactant. To evaluate the surface modification of the clays, surface tension measurements and determination of contact angles on soybean oil with the capillary rise method were performed. A factorial design 2^3 with triplicate center point was conducted to evaluate the influence of the concentration of CTABr in clay modification, viscosity enhancer concentration in the composition of the drilling fluid and temperature on the rheological properties of the fluid: plastic viscosity, apparent viscosity, thixotropy and yield strength. As higher amounts of quaternary ammonium cations were adsorbed on clay surface, a decrease of the contact angle was observed, suggesting an increasing affinity for soybean oil. The study of the effect of independent variables showed that temperature is the most influential factor in the rheological properties of the prepared fluid.

1. Introduction

The surface modification of clays enables to improve their adsorption properties and widen their application (Bergaya and Lagaly, 2001), such as clay organophilization by ion exchange with quaternary ammonium ions, which is commonly used to make dispersible clays in organic solvents (Klapyta et al., 2001; Rodrigues et al., 2010; Yilmaz and Yapar, 2004).

The increasing affinity between the clay and the interested organic phase involves decreasing the contact angle between them. The contact angle expresses the wetting ability of the fluid on the solid surface, with $\theta = 0°$ representing perfect wettability and $\theta = 180°$ representing the non-wettability condition (Amarasinghe et al., 2014). The direct measurement of contact angles for liquids on sprayed solid particles is not possible, thus the indirect calculation is performed (Siebold et al., 1997).

Drilling fluids are commonly "muds", or solids dispersions in aqueous or oily solution, water-based muds (WBM) or oil-based muds (OBM), respectively, in the presence of one or more surfactants (Balhoff et al., 2011). In oil well drilling, bentonite is added to drilling fluids to control the viscosity, to help the transfer of gravel from downhole to the surface, and to prevent drilling fluid filtration through the pores of the producing formations (Kelessidis et al., 2006).

Hermoso et al. (2014) evaluated the effect of the nature and concentration of viscosity enhancer on the rheological properties of OBM under high pressure and concluded that the viscous flow behavior of the investigated OBM is strongly influenced by the nature and concentration of the organophilic clay. Silva et al. (2014) studied the modification of bentonite by nonionic surfactants with the objective to use them as dispersants in the composition of organic-based drilling fluids, and observed an efficient intercalation of nonionic surfactants and chemical compatibility between diesel or kerosene and the modified organoclays.

The growing interest in developing non-aqueous drilling fluids with low toxicity and good performance under extreme conditions of temperature and pressure encourages research in this area. Dias et al. (2015) investigated the utilization potential of starch derivatives modified with vinyl esters of fatty acids as filtrate control additives in invert-emulsion drilling fluids and concluded that the developed formulations are able to compete technically with the drilling fluid standard, the performance of these materials being associated with the degree of chemical modification of the polysaccharide.

This study aims at obtaining an organophilized bentonite capable of dispersing into the continuous phase of a soybean oil-based drilling fluid. The choice of the vegetable soybean oil as a substitute for the

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traditionally used diesel oil and paraffin is justified because it is less aggressive to the environment. To evaluate the surface modification of the clays, surface tension measurements and determination of contact angles on soybean oil with the capillary rise method were performed, besides the rheological analysis of the obtained fluid.

2. Material and methods

2.1. Materials

The bentonite was obtained from the NERCON Company (state of Paraíba, Brazil). This bentonite was been modified with CTABr (brand: VETEC; molecular weight: 364.45 g/mol; purity 99%). n-Hexane PA A.C.S. (brand: SYNTH; density at 25 °C: 661 kg/m^3; surface tension at 25 °C: 18.4 mN/m; viscosity at 25 °C: 0.326 mPa s) was used as a reference for determining the contact angle. In the preparation of drilling fluid, lauryl alcohol triethoxylate (non-ionic surfactant, purity: 97%; density at 25 °C: 950 kg/m^3), barite (barium sulfate) as a heavyweight additive, soybean oil (density at 25 °C: 920 kg/m^3; surface tension at 25 °C: 33.3 mN/m) and sodium chloride P.A. A.C.S. (brand: SYNTH; molecular weight: 58.44 g/mol) were used.

2.2. Surface modification of the bentonite

The bentonite modification method consisted in the interlayer cation exchange between ions present in the clay structure by cations of quaternary ammonium salt in aqueous solution. The cation exchange with alkylammonium ions is well known as the preferred method for the preparation of organoclays (Paiva et al., 2008).

The procedure, adapted from Yilmaz and Yapar (2004), consisted in preparing solutions of CTABr in distilled water. Solutions were prepared at different concentrations, taking the critical micelle concentration (c.m.c.) into account: 30% below c.m.c., at the c.m.c and 30% above c.m.c. 4.16 mass% of clay was added to the surfactant solution. Each sample was stirred at 750 rpm (propeller agitator, brand: Fisatom; model: 713D), during 20 min at 80 °C (heater plate; brand: Fisatom; model: 752 A). After this stage, the solution was filtered, the obtained clay transferred to an oven (dry heat oven, brand: Nova Técnica; model: NT515; maximum temperature of 250 °C, controlled by electromechanical thermostat; accuracy: ±15 °C) at 60 °C during 48 h. Subsequently, the clay was crushed and placed on a fine mesh sieve to be added to the drilling fluid. The filtrates were used to measure surface tensions and to determine the surfactant concentration that remained in solutions.

2.3. Evaluation of surface modification of the clay

The determination of surface tension was performed with a tensiometer (SensaDyne Fluid Surface Tensiometer, brand: SensaDyne Instrument Division; model: QC6000), which uses the maximum bubble pressure method, through which is pumped an inert gas (nitrogen) by means of two capillaries of different diameters. Nitrogen is pumped through a cylinder connected to the tensiometer. Surface tension values were plotted vs. CTABr concentration in order to compare the values of surface tensions of the filtrates and, therefore, determine the amount of adsorbed surfactant in each modified clay.

Furthermore, the determination of the contact angle of soybean oil on the clays subjected to the surface modification process, and on the original bentonite was performed through capillary rise method, with a tensiometer (Processor Tensiometer; Brand: KRÜSS; Model: K100C). The procedure consisted in introducing the clay into a cylindrical glass tube (50 mm height and 10 mm inner diameter) having, at the bottom, a filter paper fastened with a perforated threaded cover, through which the liquid ascends. The tube filled with solid was positioned on top of the tensiometer, using a metal support connected to a micro scale. Approximately 50 mL of solvent were placed at the bottom of the tensiometer, coupled to a lifting system. The equipment performs the ascent of the container with liquid until the tube base touches the liquid surface, initiating the mass transfer measurement as a function of time.

n-Hexane was used as a reference for the determination of the contact angle between the clays and the oil, using the adsorption method in the KRÜSS tensiometer, based on Eq. (1) (Washburn, 1921).

$$h^2 = \frac{r\gamma_L \cos\theta}{2\eta}\, t \tag{1}$$

where h represents the cylinder height, r the effective capillary radius, γ_L and η the surface tension and the kinematic viscosity of the liquid phase, respectively, t the time and θ the contact angle between porous solid and liquid phases.

Automatic mass measurements are more accurate than visual observations of the liquid front height (Siebold et al., 1997), and these can be related as follows:

$$w = \epsilon\rho\pi R^2 h \tag{2}$$

where w corresponds to the liquid mass, ε the porosity, ρ the liquid density and R the inner radius of the tube.

Combining Eqs. (1) and (2):

$$w^2 = \frac{\left[\left(\epsilon\pi R^2\right)^2 r\right]}{2}\frac{\rho^2\gamma\cos\theta}{\eta}t \tag{3}$$

The term C_w (Eq. (4)) is a geometric factor, constant if the packaging and particle size are constant (Siebold et al., 1997).

$$C_w = \frac{\left[\left(\epsilon\pi R^2\right)^2 r\right]}{2} \tag{4}$$

Substituting Eq. (4) into Eq. (3):

$$w^2/t = C_w\frac{\rho^2\gamma\cos\theta}{\eta} \tag{5}$$

Writing cosθ as a function of C_w:

$$\cos\theta = \frac{(w^2/t)\eta}{C_w\rho^2\gamma} \tag{6}$$

Relating a partially wettable solvent (pm) with another fully wettable (m) ($\cos\theta = 1$), it is possible to obtain Eq. (7).

$$\cos\theta = \frac{(w^2/t)_{pm}\eta_{pm}\gamma_m\rho_m^2}{(w^2/t)_m\eta_m\gamma_{pm}\rho_{pm}^2} \tag{7}$$

The calculation of the contact angle was performed through Eq. (7) and that of C_w through Eq. (6), considering the fully wettable solid in n-hexane ($\cos\theta = 1$). Determinations of densities (pycnometry), viscosities (Thermo Cientific rheometer) and surface stresses (tensiometer Kruss K100) for soybean oil and n-hexane were performed at 25 °C.

2.4. Composition of drilling fluids

The composition of the drilling fluids was 2 mass% sodium chloride solution (35,000 mg/L), 28 mass% lauryl alcohol triethoxylate and 70 mass% soybean oil. The fluid preparation consisted in adding the viscosity enhancer additive (bentonite) to the oily phase, under stirring. After 24 h at rest, the saline solution, the surfactant and barite were added to the previous mixture and left under stirring (Hamilton Beach Mixer; Brand: Fann; Model: HMD200) during 15 min at 16,000 rpm. The