Applied Clay Science 143 (2017) 89–100

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

Understanding the clay-PEG (and hydrophobic derivatives) interactions and their effect on clay hydration and dispersion: A comparative study

Santiago Villabona-Estupiñán, Jorge de Almeida Rodrigues, Regina Sandra Veiga Nascimento *

Laboratório de Fluidos e Materiais Poliméricos Multifásicos- FLUMAT, Pólo de Xistoquímica, Instituto de Química, Universidade Federal do Rio de Janeiro, Hélio de Almeida St., 40, Cidade Universitária, Rio de Janeiro, Brazil

ARTICLE INFO

Article history:
Received 17 November 2016
Received in revised form 15 March 2017
Accepted 15 March 2017
Available online xxxx

Keywords:
Adsorption
Drilling fluids
Clay hydration
Hydration inhibitors
Poly(ethylene glycol)
Structure-performance relationship

ABSTRACT

In oil and gas well drilling, the effective minimization of clay-water interactions is an essential function that water-based drilling fluids must meet in order to maintain the integrity of the shale formations as well as suitable rheological properties. In this work, the protective effect of poly(ethylene glycol) 2000 (PEG2000) and two hydrophobic derivatives on the hydration and dispersion of reactive clay materials was investigated. Thus, conventional inhibition tests were combined with adsorption measurements and analyses by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and thermogravimetry (TGA) in an attempt to establish structure-performance relationships. It was found that both PEG2000 and its hydrophobic derivatives can strongly adsorb, in equimolar amounts, on mineral clay following a Langmuir type behavior, in which bilayers are formed in the clay interlayer region at surface saturation. It was found that the PEG backbone rules the adsorption process, while the hydrocarbon tails of the hydrophobically modified products do not play a decisive role. However, it was verified that hydrocarbon tails play a central role in the mechanism of inhibition of clay particles hydration. Bentonite inhibition test revealed that the incorporation of two hydrocarbon tails at the PEG2000 chain ends duplicate the performance of oligomer, regarding the product with just one tail.

1. Introduction

Properties emerging from clays and organic molecules interactions have been extensively studied and explored as powerful tools in a series of applications such as delivery systems for drugs (Park et al., 2008; Joshi et al., 2009) and fertilizers (Pereira et al., 2012; He et al., 2015); electrically (Khaldi et al., 2014; Dahou et al., 2016), thermally and mechanically (Ojijo et al., 2012) modified materials and fire retardants (Ribeiro et al., 2009; Li et al., 2010). In oilfield chemistry, the interaction between clays and organic molecules plays a very important role, mainly in respect to design and treatment of drilling fluids. Organically modified clays are usually used as rheology modifiers in non-aqueous drilling fluids (NADF), providing the required shear thinning behavior (Jones, 1983). Depending on their structure, polymers may interact with clays resulting in enhanced rheological and colloidal properties of water-based drilling fluids (WBDF), performing as bentonite extenders (Luckham and Rossi, 1999) or flocculants (Shiver, 1984).

One of the main technical concerns in drilling operations consists of keeping the wells stability. While using WBDF, reactive shale formations are especially problematic due to the high tendency of smectite from clay minerals to hydrate. With progressive hydration, reactive shales swell and disaggregate, weakening the walls of the well. Such events are part of a general problem known as wellbore instability, which in extreme cases may induce wellbore collapse, and therefore the loss of the drilling assembly, well side-tracks or total abandonment of the well (Anderson et al., 2010). On the other hand, the incorporation of drilling solids from reactive shales leads to a negative impact on the rheology of the fluid. Despite a high load of fine particulate solids not being considered a critical technical problem, it makes the fluids reconditioning more expensive (Caenn et al., 1988). The solution to these problems includes the use of distinct water-soluble or dispersible polymeric or oligomeric additives which interact with shale formation and drill cuttings through different mechanisms, keeping them whole and compact. Among the most commonly used shale inhibitors are the cationic and nonionic systems. Given their exceptional inhibitory characteristics, the former were introduced in WBDF expecting to replace the environmentally restricted NADF (Beihoffer et al., 1992). However, it has been established that they are toxic to aquatic ecosystems (Roddie et al., 2004; Costa et al., 2014). In addition, they suffer a high loss caused by depletion, are incompatible with anionic additives and are relatively expensive to produce. On the other hand, nonionic oligomers such as polyalkylenegycols (PAG), also known as polyols or polyglycols, are presented as a viable alternative, both from the

---

* Corresponding author.
E-mail address: rsandra@iq.ufrj.br (R.S.V. Nascimento).

http://dx.doi.org/10.1016/j.clay.2017.03.021

functional point of view and of economic and environmental perspectives (Reid et al., 1995). PAG are versatile systems that may play multiple roles such as drill lubrication, bit balling prevention, loss of circulation control and shale hydration inhibition. The latter property, especially, has attracted more attention. When properly engineered, WBDF based on PAG are highly inhibitory, stable, environmentally friendly and often cost-effective (Bloys et al., 1994).

There are several mechanisms that try to explain the effect of PAG as shale inhibitors: 1) increase of filtrate viscosity, which reduces the rate of filtrate invasion through formations; 2) reduction of water activity (chemical potential of water), creating an osmotic flow that leads to dehydration of formations; 3) pore blocking by thermally activated mud emulsions (TAME), which block the passage of the filtrate into the formations; and 4) adsorption within clay interlayer space, displacing water from these environments and reducing the hydration of clays (van Oort, 2003). All these mechanisms, except the fourth, depend strongly on specific conditions such as: 1) relatively high PAG concentration, to provide a significant increase in filtrate viscosity; 2) addition of salts at appropriate concentrations together with PAG to effectively reduce water activity; and 3) once inside the formation pores, the PAG fluids must become turbid when reaching a certain temperature called the cloud point (CP). However, it is known that PAG are able to reduce the tendency of shales to hydrate even when they do not meet such conditions. For example, some PAG are able to inhibit shale hydration at temperatures below CP (Reid et al., 1993; Boek et al., 1998) and at low concentrations, in low salt concentrations (Brady et al., 1998; Liu et al., 2006). These facts suggest that the mechanism based on adsorption plays an important role in stabilizing shales in WBDF. Therefore, the adsorption phenomenon is used as starting point for this study.

The literature review showed that there has been little emphasis on the pursuit of understanding the correlations between the structure and performance of PAG and their derivatives in respect to clay hydration and its consequences. In the last two decades, a small number of theoretical and experimental studies, based on the adsorption mechanism, have made some contributions in this regard. These studies suggest that the inhibitory performance of PAG can be improved by alternating hydrophilic and hydrophobic segments composed of monomer or oligomeric units (Boek et al., 1998; Liu et al., 2004; Bains et al., 2001), by the introduction of hydroxyl groups between hydrophobic segments (Bains et al., 2001) or by the presence of primary amino terminal groups (Hodder et al., 2010; Suter et al., 2011; Peng et al., 2013). Using another approach, in a previous study by our group, we showed that the ability of poly(ethylene glycol) (PEG) as a shale inhibitor was improved by attaching hydrocarbon segments at the ends of the oligomer chain. The percentage of cuttings recovered after the hot-rolling dispersion test increased with the length of the alkyl chain attached to the PEG400 (de Souza et al., 2010). However, the mechanism involved in this process is not fully understood yet nor is how the clay-hydrophobized PEG interaction results in shale inhibition. In the context of sustainable development, the inhibitory potential of hydrophobically modified PEG is attractive to the design of WBDF because of their relative low cost, low toxicity and biodegradability (Johansson and Svensson, 2001). Obviously, the fundamental understanding of their mechanism of inhibition and structural factors influencing their performance will definitely help in improving this kind of privileged structures.

The purpose of this work was to contribute to the understanding of how hydrophobized PEG exerts inhibitory effect. For this, it was decided to study products obtained by the hydrophobization of PEG2000 with one and two chains of oleic acid. The reasons for choosing these systems were: 1) oleic acid is a long chain fatty acid that could enhance the inhibitory performance of the products, as suggested by de Souza et al., 2010 and 2) preliminary tests showed that oleates of PEG2000 were those who exhibited appropriate physicochemical properties to perform the study. Systems having PEG chains of lower molar mass exhibited limited solubility. On the other hand, products with PEG segments of greater molar mass, although soluble in water, could significantly alter the rheological behavior of fluids.

Studies were conducted initially by performing conventional inhibition tests. In order to correlate the molecular structure with the results obtained in the performance tests, adsorption measurements were carried out on bentonite and the Bent/PEG complexes obtained were studied by FT-IR, XRD and TGA.

2. Experimental

2.1. Materials

Two types of clay materials were used in this study: Calumbi Shale (CS) and bentonite (Bent). These materials were chemically characterized by X-ray fluorescence. Their compositions are as follows, in terms of mass% of the respective oxides. CS: SiO_2 (57) Al_2O_3 (17), CaO (1.2), MgO (3.2), K_2O (3.4), TiO_2 (0.78), Na_2O (0.64), and Fe_2O_3 (7.1); Bent: SiO_2 (57) Al_2O_3 (19), CaO (1.2), MgO (2.5), K_2O (0.32), TiO_2 (0.15), Na_2O (1.8), and Fe_2O_3 (3.6). Samples of CS were collected from a natural outcrop of Calumbi located in the Brazilian Northeast (Sergipe State). Bentonite (Bent) and poly(ethylehe glycol) methyl ether 2000 (mPEG2000) and poly(ethylehe glycol) 2000 (PEG2000) were purchased from Sigma-Aldrich, Brazil. Oleic (OA) and *p*-toluenesulfonic (*p*TsOH) acids, toluene and NaOH were provided by Vetec Quimica, Brazil. PEG2000dioleate (OA-PEG2000-OA) and mPEG2000monooleate (mPEG2000-OA) were synthesized. NaOH was used in the experiments to adjust the pH in 10, in order to better represent the characteristics of the alkaline WBDF environment.

2.2. Methods

2.2.1. Synthesis of hydrophobized products

The synthesis of mPEG2000-OA and OA-PEG2000-OA was carried out through the esterification of mPEG2000 and PEG2000, respectively, as described by Rodrigues and Nascimento (2010). A mixture of reagents in the molar ratios of 1:1:0.01 (mPEG2000:AO:*p*TsOH) or 1:2:0.02 (PEG2000:AO:*p*TsOH) was stirred and heated to boiling and refluxed for 12 h while collecting water distilled as an azeotropic mixture of toluene/water in Dean-Stark trap. The reaction mixture was cooled to room temp and the products precipitated were washed several times with toluene. The remaining solvent was removed by vacuum distillation. The hydrophobized products were characterized by FT-IR spectroscopy (in KBr disks) and ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si). The spectra are presented in supplementary data.

2.2.2. Cuttings hot-rolling dispersion test

This test was conducted following the procedure described by Beihoffer et al. (1990), with some slight variations. 50 g of CS, previously granulated and selected between 4 and 8 mesh, were added to stainless steel aging cells containing one laboratory barrel equivalent (350 mL) of PEG solution at 30 g/L. The pH was adjusted to 10. All solutions were evaluated along with a control sample containing only water and shale. After heating the samples in a roller oven at 65.5 °C for 16 h, the resulting material was passed through a 30 mesh sieve to recover the remaining shale. Tests were performed in duplicate.

2.2.3. Bentonite inhibition test

The bentonite inhibition test was based on the general procedure described by Patel et al. (2002). While shearing, 7.0 g of Bent was added to 350 mL of PEG solution at 30 g/L. Then the pH was adjusted the pH to 10. The mixture was subjected to shearing for 30 min and transferred to the roller oven in stainless steel aging cells. After heating at 65.6 °C for 16 h, the suspensions were cooled to room temperature and the apparent viscosity (*AV*) and the yield point (*YP*) were determined with a Fann 35A® viscometer. A new amount of Bent was added and the previous procedure repeated for several days until the