



Research paper

A novel nonionic surfactant for inhibiting shale hydration

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ABSTRACT

The demand for cost effective and environmentally shale inhibitor is increasing in drilling industry. This paper reports for the first time the use of *Zizyphus spina-christi* extract (ZSCE), a newly developed nonionic surfactant, for inhibiting shale hydration. The adsorption behavior of ZSCE onto shale cuttings was determined through conductivity technique. Adsorption isotherm coincides with the characteristics of Freundlich isotherm. The inhibitive property of ZSCE was assessed through a number of inhibition evaluation methods. All experimental findings verify that ZSCE can act as a potential shale inhibitor; nevertheless, its inhibitive potential has no significant improvement at concentrations above the CMC. Moreover, ZSCE has a better performance compared to potassium chloride and polyamine. According to compatibility tests, the ZSCE is compatible with conventional water-based drilling fluids (WBDF) additives. Scanning electron microscopy (SEM) observations clearly indicate the stability of sodium bentonite particles in ZSCE aqueous solution. The hydrogen bonding between hydrophilic tail of ZSCE molecules and oxygen atoms available on silica surface of clay, which results in formation of hydrophobic shell on the clay surface, is believed to be the main inhibition mechanism for ZSCE. This research paves the way for selection and implementation of surfactants, especially plant-based, as shale inhibitors in WBDF.

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1. Introduction

According to the statistics, wellbore instabilities could result in a waste of US\$ 1 billion per year worldwide (Zeynali, 2012), thereby profoundly impact the success of drilling operations (Cheatham Jr., 1984; Lu, 1988; Van Oort, 2003). Reasons for wellbore instability problems are both mechanical and physico-chemical effects. Mechanical effects, which are time independent, are a direct result of drilling operation (Zeynali, 2012). However, physico-chemical effects are time dependent (Lal, 1999; Osuji et al., 2008; Zeynali, 2012) and are a direct result of solid–fluid interaction (i.e. shale and drilling fluid). Shales, as fine-grained sedimentary rocks with laminated layered characteristics and high clay contents (Diaz-Perez et al., 2007), contribute to almost three-fourths of the formations encountered in drilling operations and are responsible for 90% of wellbore stability problems (Steiger and Leung, 1992). The swelling and dispersion properties of a reactive shale strongly depends upon the type and percentage of its swelling clay minerals (Steiger, 1982; Fam and Dusseault, 1998; Dehghanpour et al., 2012). Studies of clay swelling are most often focused upon sodium saturated smectites owing to their high swelling potential and their occurrence frequencies during drilling operations (Anderson et al., 2010). When water-sensitive shales contact with water-based drilling fluids (WBDF), they adsorb water and swelling occurs (Boek et al., 1995; Stamatakis et al., 1995; Hensen and Smit, 2002), resulting in

compressive strength reduction, indentation hardness of shales (Chenevert, 1970) and consequently a number of serious operational problems (O'Brien and Chenevert, 1973; Bol et al., 1994; Lomba et al., 2000; Akhtarmanesh et al., 2013). It has been reported that these problems eventually could lead to suspension of the well prior to reaching the target (Tan et al., 1997).

In drilling fluid terminology, the “inhibition” term covers all the mechanisms that can reduce or eliminate swelling, dispersion, and clay–water interactions (Khodja et al., 2010). Although oil-based drilling fluids (OBDF) provide superior inhibition performance, their utilization to control water-sensitive shales has been restricted owing to environmental limitations and their high cost (Tambach et al., 2004; Chegny et al., 2008). Therefore, the use of WBDF with oil-based drilling fluids performance has attracted a lot of interest within the industry. In order to overcome the problems associated with shale instability, different chemicals namely shale inhibitors have been added to conventional WBDF which provide shale stability via a number of mechanisms.

Potassium chloride, commonly shale inhibitor, has a high performance in inhibiting shale hydration owing to the appropriate cationic size and hydrational energy (Pruett, 1987). However, it has several disadvantages including failing WBDF at concentration above 1 mass% according to the mysid shrimp bioassay test (Anderson et al., 2010), adversely affecting the environment, high disposal cost (Zhong et al., 2011), and higher corrosion rates like any high salinity aqueous solution (Clark et al., 1976). Although the main function of natural-based water soluble polymers such as Guar Gum and Xanthan Gum in WBDF is viscosifier, it has been reported that they could provide limited shale stability (Annis and Smith, 1996). Quaternary amine compounds are

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often used as high performance shale inhibitor but several drawbacks including their toxicity, flocculation of fluids with high solid concentration, and incompatibility with anionic drilling fluid additives restrict their applications (Patel et al., 2007). An experimental study of the adsorption of polyamine onto three different clay minerals suggested that polyamine could suppress the hydration and swelling potential of montmorillonite effectively (Blachier et al., 2009). Nevertheless, it showed very limited ability to inhibit clay or shale hydration under high temperature conditions due to weakening of hydrogen bonding between the amino groups and tetrahedral siloxane surfaces of montmorillonite (Xuan et al., 2013). The ability of polyetheramine compounds in suppressing the hydration and swelling potential of clay or shale has already been investigated (Qu et al., 2009; Wang et al., 2011; Zhong et al., 2011, 2012). Recent efforts have elucidated the high applicability of dopamine (Xuan et al., 2013), bis(hexamethylene)triamine (Zhong et al., 2013), copolymers (Liu et al., 2013; Liu et al., 2014) in inhibiting clay or shale hydration. Very recently, a natural clay inhibitor taken from Henna leaf extract, known as a natural dye, has been found to exhibit superior performance in suppressing the swelling potential of sodium bentonite in aqueous solution (Moslemizadeh et al., 2015).

Two major utilizations of surfactants in petroleum industry are in enhanced oil recovery (EOR) techniques and drilling fluids. In EOR, surfactants have been identified as well stimulators, which aim to boost in displacement efficiency during oil recovery owing to their ability in lowering the oil/water interfacial tension (Hirasaki et al., 2011; Bera et al., 2013; Olajire, 2014). They are entered in WBDF for shale stability, emulsification of oil in water, prevention of differential sticking, and detergency to avoid cuttings sticking to drill bit (Quintero, 2002). Among three well known surfactants (i.e. anionic, nonionic, and cationic), the two kinds of nonionic and cationic surfactants could adsorb onto the surfaces of swelling clays owing to silanol groups and negative charges on the clay surfaces, thereby suppressing the clay hydration (Cui and Van Duijneveldt, 2010). As discussed earlier, most of the previously introduced shale inhibitors are chemical-based and no adequate investigations on the plant-based materials to control shale stability are available in the literature. Therefore, introduction of non-toxic and cost effective shale inhibitors is currently very important for both research and industry sectors. In the last few years, several studies have been undertaken on the use of *Zizyphus spina-christi* as a novel nonionic surfactant in EOR applications (Ahmadi and Shadizadeh, 2012, 2013a,b,c; Safian-Boldaji et al., 2013; Zendejboudi et al., 2013). However, employing this surfactant in WBDF to restrain shale hydration has not yet been reported in the literature. Several aspects such as environmentally friendly, low cost and availability could be considered as assets for this surfactant. This article reports for the first time the application of *Z. spina-christi*, as a novel nonionic surfactant, in WBDF for inhibiting shale hydration. In this connection, a wide range of characterization methods were implemented to assess the applicability of this novel nonionic surfactant in WBDF: adsorption onto crushed shale sample and critical micelle concentration (CMC) determination via conductivity and pH techniques, various inhibition evaluation methods, scanning electron microscopy (SEM) observations, and compatibility tests. Results from this study are presented and discussed in detail throughout the article and the outcomes of this study can be implemented for appropriate selection of surfactants in WBDF for inhibiting shale hydration.

2. Experimental section

2.1. Materials

2.1.1. Novel nonionic surfactant

The *Z. spina-christi* (Fig. 1) is a shrub, sometimes a tall tree, reaching a height of 20 m and a diameter of 60 cm; its bark is light-gray, very cracked, and scaly. In addition, the leaves of this tree are glabrous on upper surface and finely pubescent below (Jinous and Elaheh, 2012).

The leaves of *Z. spina-christi* which locally known as “Sedr” and “Konar” have been used for washing the hair and body (Nafisy, 1989; Amin, 1991). *Z. spina-christi* is commonly found in Jordan, Iran, Iraq and Egypt. In Iran, it has been widely distributed in East, South, North-East and central regions. Saponins, biosurfactants, are mainly produced by plants and less frequently by marine organism and insects (Thakur et al., 2011). These biosurfactants could present in more than 500 plant species (Hostettmann and Marston, 2005; Güçlü-Üstündağ and Mazza, 2007). It has been reported that the concentration of saponins in *Z. spina-christi* is fairly high (Kjellin and Johansson, 2010). The molecules of saponins (Fig. 2) are both hydrophobic and hydrophilic components; hydrophobic part is composed of triterpenoid and steroid or steroid-alkaloid while hydrophilic part is composed of saccharide residues. The hydrophilic part is connected to hydrophobic part via glycoside bonds (Stanimirova et al., 2011).

For the purpose of this study, novel nonionic surfactant was extracted from the leaves of *Z. spina-christi* by spray dryer method (Niessen, 2002; Mujumdar, 2007; Chiou and Langrish, 2007) as useful technique for converting a liquid, slurry, or low viscosity paste to a dry solid in one unit operation (Pordel Shahri et al., 2012). The extracted powder, *Z. spina-christi* extract (ZSCE), which contains high amount of saponins and flavonoids (Ahmadi and Shadizadeh, 2012) was used in this study. The properties of ZSCE are presented in Table 1 (Hostettmann and Marston, 2005; Güçlü-Üstündağ and Mazza, 2007; Kjellin and Johansson, 2010; Stanimirova et al., 2011; Ahmadi and Shadizadeh, 2013b).

2.1.2. WBDF additives

Potassium chloride (Merck), sodium chloride (Merck), green starch, low viscosity polyanionic cellulose (PAC-LV), Xanthan Gum (XC-polymer), partially hydrolyzed polyacrylamide (PHPA), barite, caustic soda, and clouding glycol were provided by National Iranian South Oil Company.

2.1.3. Minerals

Two minerals, shale cuttings and sodium bentonite, were used in this study. Shale cuttings were taken from depth of 2877 m, Ahwaz oilfield, Iran. The cation exchange capacity were determined according to the methylene blue test and found as 18 meq/100 g and 63 meq/100 g for shale cuttings and sodium bentonite, respectively. The semi-quantitative mineral compositions of shale cuttings and sodium bentonite were determined through X-ray diffraction (XRD, Table 2). In addition, X-ray fluorescence (XRF) was carried out on the sodium bentonite to characterize its chemical composition (Table 3). LOI demonstrates loss on ignition that is related to the volatile components.

2.2. Methods

2.2.1. CMC and adsorption measurements

Based on the properties of the surfactant in solution, there are a number of methods to determine the CMC of surfactants in aqueous phase including electrical conductivity, thermal conductivity, interfacial tension, gravimetry, surface tension (Ahmadi and Shadizadeh, 2013b), and pH. To assess the CMC of the ZSCE in the aqueous phase, conductivity and pH techniques were carried out. For this intent, at the first the master surfactant solution with concentration of 80,000 ppm was prepared by uniformly adding ZSCE powder to the deionized water and mixing via the magnetic stirrer for 2 h. Then, lower ZSCE concentrations on the wide range of 1000–80,000 ppm were derived by appropriate dilution of master ZSCE concentration, 80,000 ppm, using deionized water. Conductivity and pH of solution was determined from high concentration to low concentration using Sartorius professional meter PP-20. Finally, CMC of the ZSCE were figured out from plotting conductivity and pH versus relevant ZSCE concentration. CMC value corresponds to the concentration observed at the inflection point of the curves.

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