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Journal of Petroleum Science and Engineering

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

Experimental investigation of rheological properties in zwitterionic-anionic mixed-surfactant based fracturing fluids



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ARTICLE INFO

Article history:

Received 20 November 2015

Received in revised form

7 March 2016

Accepted 2 May 2016

Available online 3 May 2016

Keywords:

Rheological properties

VES

FF

Mixed surfactant

Nano-particle

Proppant

ABSTRACT

Zwitterionic-anionic mixed surfactant systems offer synergistic interactions in aqueous medium due to polymorphism of self-assembly structures that have combined properties of surfactants in the mixture. In this paper, a comparative study is done on rheological properties of Viscoelastic Surfactant (VES) based fracturing fluids (FF) developed from CAPB+NaOA/iso-amyl alcohol/clove oil/water and CAPB+SDS/iso-amyl alcohol/clove oil/water systems. Static and dynamic rheological tests indicated superior viscoelastic properties of the former system (26% and 28% C/S) at a relatively low %C/S in contrast to the latter system (28% and 30% C/S). The addition of alkali (0.1% NaOH) and SiO₂ nano-particles in the fluid further intensified the viscoelastic properties. The 0.1% SiO₂+0.1% NaOH+28% C/S VES fluid developed from CAPB+NaOA/iso-amyl alcohol/clove oil/water offered good apparent viscosity stability for 120 min at 103 °C and 100 s⁻¹ under different test pressures (2068, 4137 and 6205 KPa) that is suitable for conducting fracturing job and to suspend proppants. Unlike in diesel oil, the miscibility test evidenced solubility of the VES fluids in water. These VES fluids provided satisfactory proppant suspension capabilities in the presence of three proppants (20/40 mesh size) at different test temperatures (70–100 °C).

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1. Introduction

Hydraulic fracturing is a technique to stimulate oil and gas production with the aim to increase well productivity by the creation of fractures in the reservoir formation (Dantas et al., 2006; Bohlooli and Pater, 2006; Zhang and Chen, 2010; Liu et al., 2010). The technique involves the pumping of FF under a high differential pressure along with proppants to keep the created fractures open with proppants after the cessation of pumping (Gidley et al., 1989; Goel et al., 2002). The rheology of non-Newtonian FF exhibits a complex nature when injected in these natural porous formations that encompasses several possible models, like the Power law model which provides the simplest relationship between stress and strain (Ciriello et al., 2013; Longo et al., 2015). The proppant-laden fractures improve the permeability of the reservoir formation by establishing a highly conductive path for the reservoir fluids to flow to the wellbore. After proper placement of proppants in the fractures, the viscous FF needs to break down into a low viscosity fluid so that it can flow back to the surface with the reservoir fluids and the oil well can be put on production without much delay (Dantas et al., 2006). In order to maximize the profit by exploiting these reservoirs, the proper fracture

orientation is required that exhibits a longer effective half-length (King, 1983; Luo et al., 2014).

Unlike polymer based gels, the VES based fracturing gels prepared from low-molecular weight molecules provides the advantage of being broken into a low viscosity fluid, when exposed to hydrocarbons or formation water (Khair et al., 2011; Al-Sadat et al., 2014; Yang, 2002). The VES fluids do not develop filter cake in the fractures that leads to high cost, as large amount of fluid is required for a particular fracturing job (Liu et al., 2010). These fluids also offer low thermal stability in comparison to polymer based fluids. Consequently, these limitations of the VES fluids can be overcome by cross-linking with nano-particles that would help in the development of filter cake and increase the thermal stability (Baruah et al., 2015a).

VES gels developed from surfactants include anionic, cationic, zwitterionic and non-ionic (Al-Sadat et al., 2014; Xing and Rankin, 2013; Yusof and Khan, 2013; Javadian et al., 2013). Zwitterionic surfactants have the combined presence of anionic and cationic centers in their heads, that are expensive but has higher thermal stability than the other surfactants (Pan et al., 2015; Sullivan et al., 2006). Anionic surfactants are negatively charged that provides the advantage of being economical and has the ability to water wet sandstone reservoirs. Anionic surfactant is more biocompatible and degradable than cationic surfactants, but faces the application limitation in high temperature regions (Yixiu et al., 2015; Al-Sadat et al., 2014). Mixed surfactant systems have gained great interest

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Nomenclature

VES	Viscoelastic surfactant	CMC	Critical micelle concentration
FF	Fracturing fluids	%	Percent weight
%C/S	Percent of co-surfactant to mixed surfactant concentration	CAPB+NaOA	Cocamidopropyl betaine+ sodium oleate
C/S	Co-surfactant to mixed surfactant ratio	CAPB+SDS	Cocamidopropyl betaine+ sodium dodecyl sulfate
		v_p	Average settling velocity
		IFT	Interfacial tension
		ISP	Intermediate strength proppants

because of polymorphism of self-assembly structures accessible through simple tuning of composition that have combined properties of the various surfactants in the mixture (Silva et al., 2013; Lu et al., 2015). When anionic and zwitterionic surfactants are mixed in a definite ratio, this mixed surfactant system will offer synergistic behavior, that will provide biocompatibility with reservoir formation, better biodegradability and performance (Khair et al., 2011; Thampi et al., 2014; Ghosh et al., 2011).

In our previous work, a comparative study on the rheological properties was performed for single (anionic) and mixed (anionic-zwitterionic) surfactant systems in the presence of iso-amyl alcohol/pine oil/water. Next, we have tried to develop water based VES fluids from a single anionic surfactant with two different branched alcohols (co-surfactants) having the same carbon number. Later, we have worked on the development of FF from two anionic surfactants, three co-surfactants, clove oil and water.

In this present study, we endeavored to develop a zwitterionic-anionic mixed surfactant based FF that exhibited suitable viscoelasticity, adequate apparent viscosity stability, miscibility with water and satisfactory proppant suspension capabilities under specific operating conditions. Two anionic surfactants (sodium dodecyl sulfate, SDS and sodium oleate, NaOA) and a zwitterionic surfactant (Cocamidopropyl betaine, CAPB) were selected for the development of the VES based FF. The VES fluids were developed from two quaternary systems consisting of mixed surfactant (CAPB+NaOA or CAPB+SDS), iso-amyl alcohol as the co-surfactant, clove oil as the oil phase and water as the aqueous phase. Pseudo-ternary phase diagrams were plotted for both the quaternary systems to outline the gel region. A point within the gel region is selected for the preparation of VES fluid. Static and dynamic rheological studies of the VES fluids were investigated in the absence and presence of alkali and nano-particles. In contrast to our previous work, the effects of time and pressure on the apparent viscosity of VES fluids were conducted for 120 min at 100 s^{-1} and $103\text{ }^\circ\text{C}$. Miscibility test and static proppant suspension test of the VES fluids were determined under different operating temperatures. Unlike the use of only sand as proppants in our preceding work, three types of proppants were utilized in this present study to determine the proppant settling velocities in the VES fluids at different test temperature.

2. Experimental method

2.1. Materials

Sodium dodecyl sulfate (SDS, >85%), 3-methyl butane-1-ol (iso-amyl alcohol, >98%) and sodium hydroxide (NaOH, >98%) were all received from Loba Chemie Pvt., Ltd. Sodium oleate (NaOA, >82%) and clove oil were procured from Sigma–Aldrich. Cocamidopropyl betaine (CAPB, ≥35%) was acquired from Alpha Chemicals Pvt. Ltd., Navi Mumbai, India. Silicon dioxide (SiO_2) nano-particles, 15 nm in size were obtained from SRL Pvt., Ltd. Distilled water was used for sample preparation.

2.2. Critical micelle concentration and pseudo-ternary phase diagram

Critical Micelle Concentration (CMC) is the surfactant concentration above which amphiphilic molecules spontaneously assemble into micelles (Baruah et al., 2015b). The CMC of mixed surfactant (CAPB+NaOA and CAPB+SDS) systems in the presence of co-surfactant (iso-amyl alcohol) and alkaline (0.05% and 0.1% NaOH) aqueous medium can be determined by the Interfacial tension (IFT) measurement methods. The CMC values of mixed surfactant system are the point of intersection between the decreasing and increasing/flat curves of IFT versus surfactant concentration (Baruah et al., 2015b). A programmable tensiometer (Kruss GmbH, Germany, model: K20 Easy Dyne) was utilized to determine the IFT of the different concentrated surfactant solutions at $30 \pm 1\text{ }^\circ\text{C}$ under atmospheric pressure by the Du Nouy ring method. The platinum ring of the tensiometer was cleaned with acetone and flame dried before each measurement and the standard deviation did not exceed $\pm 0.1\text{ mN/m}$. Three repeated runs were carried out for each experiment to ensure reproducibility of the results.

The gel region was determined for the development of FF by plotting the pseudo-ternary phase diagrams for CAPB+NaOA/iso-amyl alcohol/clove oil/water and CAPB+SDS/iso-amyl alcohol/clove oil/water systems. The mixing ratio of CAPB with NaOA (or SDS) is 1:2. The co-surfactant to mixed surfactant ratio (C/S) was fixed at 1:2 (or 0.5) and the phase diagram was constructed using a water titration method fixed at $30 \pm 1\text{ }^\circ\text{C}$ under atmospheric pressure. The ratio of oil to the C/S was varied from 1:9 to 9:1 by weight. 1 ml of water was added to the mixture consisting of mixed surfactant, co-surfactant and oil at their specific weight ratios which was stirred in a magnetic stirrer at a moderate speed (Thampi et al., 2014). The mixture systems were equilibrated for 30 min to produce a stable system that were visually differentiated and classified according to Winsor's classification (WI, WII, WIII and WIV). The 30 min is taken as the sufficient time for phase separation of the mixture, as beyond this time period, no further separation was noticed. The addition of 1 ml of water was continued until a Winsor II fluid system was obtained. Pseudo-ternary phase diagram was constructed by plotting the weight percent of C/S, oil and water. The error associated with this method was 1–2%. The procedure for the construction of pseudo-ternary phase diagram is summarized in Fig. 1.

2.3. Preparation of VES gels

A point was selected within the gel region for the development of fracturing gel from the pseudo-ternary phase diagrams. The gel was prepared using a mechanical stirrer, where all the chemicals in the liquid form ((iso-amyl alcohol), clove oil, water, CAPB) were added in a beaker and was continuously stirred. The SiO_2 nano-particle induced VES fluid was prepared by dispersing the nano-particles in distilled water by using ultrasonic water bath at 60 Hz for 3 h and about 0.04 wt% of SDS surfactant was added to stabilize the dispersion of SiO_2 nano-particles in water. To this mixture,

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