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Phase behaviour and thermodynamic properties of lamellar liquid crystal developed for viscoelastic surfactant based fracturing fluid

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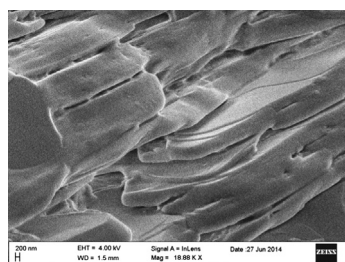
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HIGHLIGHTS

- Developed VES fluid exhibited shear thinning nature.
- Addition of alkali and salt improved the viscoelastic nature of the fluids.
- Comparison on effect of organic and inorganic salt on the developed VES fluid.
- Nano-particles participated in improving the thermal stability of VES gels.

GRAPHICAL ABSTRACT

FESEM image of air dried 500 ppm SiO₂ + 2% HCOONa + 0.1% NaOH + 34% C/S VES fluid sample at 200 nm scale.



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ABSTRACT

Phase behaviour of SDS/iso-amyl alcohol/pine oil/water and SDS/*tert*-amyl alcohol/pine oil/water systems were investigated for the development of viscoelastic surfactant (VES) based fracturing fluids having lamellar structures. The effects of co-surfactant, alkali, salt and nano-particle on rheology and thermodynamics of the lamellar liquid crystals were investigated. In contrast to *tert*-amyl alcohol, the use of iso-amyl alcohol as co-surfactant facilitated the formation of water-based gels. However, with subsequent addition of alkali, salt and nano-particles, VES fluid indicated an improvement in viscoelastic properties. Decrease in viscosity was observed with increase in temperature and shear rate. The developed VES fluids were miscible in water and nano-particle induced VES fluid exhibited satisfactory proppant suspension capability.

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1. Introduction

Surfactants play important roles in many petroleum reservoirs/well treatment problems because of their unique properties to reduce surface tension, change wettability, disperse corrosion inhibitors and mobilize residual oil (Chen et al., 2013; Liu et al., 2014; Mitra et al., 2006). VES fluids developed from surfactants

are commonly used in petroleum industry, especially in enhanced oil recovery (EOR) and well stimulation operations like hydraulic fracturing (Chai et al., 2007; Drexler et al., 2012; Iglauer et al., 2010). Hydraulic fracturing is a technique that aims to improve the productivity of oil wells, by pumping fluid under a high differential pressure to create fractures which, in turn, improves the conductivity of the formation rock (Hossain and Rahman, 2008; Liu et al., 2010). Fracturing fluids are usually pumped along with proppants to keep the created fractures open upon cessation of pumping (Malhotra and Sharma, 2012). These solid-laden fractures improve the permeability of formation by

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providing a highly conductive path for fluids to flow from the reservoir into the well (Bajpai et al., 2010).

The use of surfactant based fracturing fluids in the pay zone offers significant advantages over polymer based fracturing fluids, especially due to their non-damaging effects on the reservoir (Zanten, 2011). Viscoelastic surfactant (VES) based fluids are composed of low molecular weight surfactants that can form elongated micelle structures. These can provide sufficient viscosity for fracturing of formation without the use of polymer additives (Huang and Crews, 2009). VES fluid breaks down easily when it comes in contact with formation fluids and leaves very little or no residue, after a fracturing job is completed; thus eliminating the need for remedial measures which greatly reduce the operating cost and time. However, application of VES fluids is still limited mainly due to two reasons—(a) their inability to form a filter cake causing large amounts of fluid loss into the formation and (b) low thermal stability of VES fluids compared to polymers. In the recent years, nano-particles have attracted growing interests in the oil and gas industry, because of their great potential to cross-link with VES fluids, thereby forming filter cake on the formation face and enhancing the thermal stability of the fluid.

In the presence of oil and water, surfactant molecules have the capability to self-assemble into a variety of micro-structures, including rod-like, spherical, inverted micelles, vesicles, flexible bilayers, hexagonal phase etc. that have strong influence on rheological properties (Kumaran et al., 2001; Trickett and Eastoe, 2008). Due to their amphiphilic nature of surfactant molecules which consists of a hydrophilic head and a hydrophobic tail, they can distribute their head and tail parts to the corresponding polar and non-polar solvents and form a monolayer film between them (Pan et al., 2015; Salager et al., 2012; Schrader et al., 2013; Zhang and Wei, 2013). Certain surfactants when added to aqueous solutions form viscoelastic fluids by entanglement of these micelles (Paul et al., 2014). For a fluid to have a proper viscosity and elasticity under given conditions, proper micelles formation and entanglement of the micelles are required, so the surfactant structure should satisfy certain geometric requirements having sufficient length or interconnections for adequate entanglement (Chen and Abad, 2008). The association can be correlated with molecular geometry and packing parameter (Yang, 2002). These wormlike entangled micelles increase the viscosity of fluids like polymers. However, unlike polymers, these VES fluids made of micelles have the advantage to break and re-form under shear (Sharma et al., 2009). The reduction of head-group repulsions of micelles by counter-ions is another important aspect of micelle formation from ionic surfactants.

In our previous work, we have reported a comparative study on the rheology of the VES-based gels prepared from single surfactant (anionic, Sodium lauryl sulphate) and mixed surfactant (zwitter-ionic, Cocamidopropyl betaine and anionic, Sodium lauryl sulphate) systems (Baruah et al., 2014). In the present study, we endeavoured to develop water-based gel from an anionic surfactant (SDS) in the presence of two different co-surfactants namely, iso-amyl alcohol and *tert*-amyl alcohol, in a system consisting of pine oil and water. Branched alcohols having the same carbon number ($C_5H_{12}O$) were selected for comparing the formation of water-based gel. For this, pseudo-ternary phase diagrams were plotted separately to determine the gel region for the two co-surfactants. The effect of alkali (sodium hydroxide, NaOH) on rheological properties of VES gels, in the presence of inorganic (potassium chloride, KCl) and organic (sodium formate, HCOONa) salts, was investigated in details. The effect of SiO_2 nano-particle addition on the VES fluid properties was also studied in order to improve the thermal stability and leak-off property of the fluid. Static and dynamic rheological tests were carried out with respect to temperature and shear rate. Miscibility test of the developed

VES fluids was carried out in the presence of water and diesel oil. A proppant settling test was conducted at increasing temperature in order to get an indication of the proppant suspension capabilities of the VES fluid.

2. Experimental

2.1. Materials

Sodium Lauryl Sulphate (SDS, $CH_3(CH_2)_{11}OSO_3Na$, > 85%), 3-methyl butane-1-ol (iso-amyl alcohol, $(CH_3)_2CHCH_2CH_2OH$, > 98%), 2-methyl butane-2-ol (*tert*-amyl alcohol, $CH_3CH_2C(CH_3)_2OH$, > 99%), sodium hydroxide (NaOH, > 98%), sodium formate (HCOONa, > 90%) were all procured from Loba Chemie Pvt. Ltd., Mumbai, India. Inorganic salt, potassium chloride (KCl, > 99%) was obtained from the Merk Specialities Private Limited, Mumbai, India. Silicon dioxide (SiO_2 , > 99.5%) nanoparticle of 15 nm, size was procured from SRL Pvt. Ltd., Mumbai, India. Pine oil was used as the organic phase and distilled water was used for sample preparation.

2.2. Pseudo-ternary phase diagram and critical micelle concentration (CMC)

Pseudo-ternary phase diagrams were plotted for SDS/iso-amyl alcohol/pine oil/water and SDS/*tert*-amyl alcohol/pine oil/water systems that help in the determination of aqueous dilutability and the range of composition that form mono-phase region. The co-surfactant to surfactant (C/S) ratio was fixed at 1:2 (or 0.5). The phase diagram was constructed using a water titration method fixed at 30 ± 1 °C. 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 surfactant, co-surfactant and oil at their specific weight ratios which was stirred in a magnetic stirrer at a moderate speed. The mixture systems were equilibrated for 30 min to differentiate the various phases being obtained, that were based on visual assessment and was classified according to Winsor's classification (WI, WII, WIII and WIV). 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.

Interfacial tension (IFT) measurement is one of the important methods for determining the CMC of surfactants. The interfacial tension of the different concentrated surfactant solutions was measured by a programmable tensiometer (Kruss GmbH, Germany, model: K20 EasyDyne) under atmospheric pressure and temperature of 30 ± 1 °C 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 ± 0.1 mN/m.

2.3. Preparation of viscoelastic surfactant based fluids

A point was selected in the gel region of the phase diagram. VES fluid was simply made by mixing the aqueous phase, oil, co-surfactants simultaneously, with the help of a mechanical stirrer in a beaker. The nano-particle induced VES fluid was prepared by dispersing the nano-particles in a beaker consisting of only water that was stirred for 5 min. To this mixture, co-surfactant and oil was added subsequently. The anionic surfactant in the powder form is added slowly into the continuously stirred mixture in order to avoid the formation of lumps in the prepared gel. Alkali, salts were added into the systems in weight percents of the aqueous phase. The VES fluids were prepared at 30 ± 1 °C.

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