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Microemulsion and phase behavior properties of (Dimeric ammonium surfactant salt – heavy crude oil – connate water) system

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ABSTRACT

Fundamentally, recovery methods of untapped crude oils require injection of foreign material(s) in the reservoir, which subsequently promote(s) the displacement of residual oil. In chemical enhanced oil recovery (EOR), the microscopic sweep efficiency depends primarily on achievement of a low interfacial tension. The present work investigates into the surface tension and phase behavior properties of microemulsion developed from a contact between a dimeric ammonium salt surfactant achieve an ultra-low interfacial tension (IFT) was compared with a conventional polysorbate surfactant commonly used in chemical EOR. At fairly low concentration, dimeric surfactants achieved an IFT of order of 10^{-3} mN/m. Salinity tolerance and IFT were significantly altered not only by the heaviness i.e. API of the crude, but also by the reservoir conditions. Moreover, alkane carbon number (ACN), introduced in this work, revealed that modeling a micellar slug formulation solely based on chemical composition of the crude and/or its nature could be misleading. Presence of divalent ions was found to promote the increase in IFT rather to a shift to a lower value. Also, a relative low adsorption of micellar slug was found in both dolomite and Berea sandstone. However, active head of the dimeric surfactant showed a preferential attachment to carbonate rock while low interactions were observed for sandstone. Lastly, the present study has highlighted an inhibiting acidity activity for dimeric ammoniums salt surfactants.

1. Introduction

The terminology microemulsion (ME), reported to be first used by Schulman et al. (1959) to describe a multiphase system consisting of water, oil, surfactant and alcohol, which forms a transparent solution (Schulman et al., 1959). Subjected to debates, Schulman's definition was later modified by Danielsson and Lindman (1981). They proposed, what is thought to be, the most effective and complete definition of ME. ME was then referred as a system consisting of water, oil and amphiphilic material which is optically isotropic and thermodynamically stable (Danielsson and Lindman, 1981).

Over past decades, ME flooding has been gaining prominence in the petroleum industries especially for extraction of residual oil after primary and secondary recovery processes. Pioneered by Holm (1971) who reported a high extraction efficiency at elevated temperatures using sodium sulfates, systematic studies on MEs for oil recovery have been investigated therefrom (Holm, 1971). The use of surfactants were reported to alter greatly the oil-brine interface which subsequently modified the surface properties of the petroleum fluids (Healy et al., 1976; Reed and Healy, 1977). Moreover, MEs are reported to be commercially viable primarily because of (i) their lower energy requirements(Magdassi et al., 2003), (ii) their potential to develop an ultra-low interfacial tension (IFT) Bera et al., 2012 and (iii) high interfacial area (Bera and Mandal, 2015). From a thermodynamic point of view, MEs are relatively stable compared to emulsions (Alade et al., 2016). Aforementioned singular properties have been applied in various areas of engineering including food novel drug delivery systems, use of CO_2 as a solvent, synthesis of nanoparticles and enhanced oil recovery (EOR) (Sjoblom et al., 1996; Heitz et al., 1996; Paul and Moulik, 2001; Henle et al., 2007). The latter application is the scope of this work.

As far as the micellar slug for oil recovery is concerned, it is important to highlight that for the surfactants investigated for most of the case they were (i) anionic (Iglauer et al., 2004, 2010b), (ii) monomeric and (iii) were used mainly for on light and medium crudes oils. Also, literature has shown that if a Gemini

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surfactant[1] was rather used as micellar solution (micellar slug), an ultra-low IFT (order of 10^{-3} mN/m) as well as promising rheological properties compared to monomeric surfactants could be achieved (Gao and Sharma, 2013). It would be judicious to extent aforediscussed properties to extraction of heavy crude oils[2] although chemical EOR is not the primary method to extract stranded heavy fractions. Also, it should advisable to report that achieving an ultra-low IFT is just a part of the research focus when chemical EOR is considered. In fact, the crux of the problem also lies upon deep profile control. Therefore, this paper aims at developing a micellar slug from of dimeric surfactants for a possible application in recovery of heavy crude oils.

Zana (1996) showed in his work that both micellization and solubilization of dimeric type surfactants were much lower compared to their corresponding monomers (Zana, 1996). It was further proven that an ultra-low IFT was achieved in ME even at fairly low concentration. These findings contrasted with the belief that a minimum of 1 wt.% surfactant/cosurfactant (weight of active surfactant/100 g of micellar solution) was required to develop the desirable IFT. When an ultra-low IFT is reached, the capillary forces that hold stranded crude oil inside the pore throats of reservoir rocks are tremendously reduced. In other words, a large surface area is provided. As a result, the mobilization of the residual phase is allowed (Iglauer et al., 2010b). However, the overall effectiveness of oil displacement, by means of ME flooding, lies upon the macroscopic sweep and the microscopic displacement efficiencies (Iglauer et al., 2010a; Chou and Shah, 1981).

The dependence of reservoir environment and the composition of the micellar slug with the efficiency in developing an ultra-low IFT is well established. In fact, the increase in reservoir water salinity decreases the solubility of Gemini surfactant (Shah and Schechter, 1977). ME is, thence, expected to span from a lower phase (*l*) termed as type II (−) to an upper phase (*u*) or type II (+) through a middle phase (*m*) or type III Winsor, 1954. Another terminology uses Winsor type I to describe an *l*-phase and Winsor type II an *u*-phase (Reed and Healy, 1977). Throughout this work, the terminology defined by Winsor (1954) was adopted. In a typical type II (−) system, dimeric surfactant forms an oil-in-water (O/W) ME in the aqueous phase while a water-in-oil (W/O) ME is predominant in the oleic phase in a type II (+). Both are unfavorable for an EOR application, as the ultra-low IFT desirable cannot be achieved. In a type III, however, a bicontinuous phase containing surfactant, water and dissolved hydrocarbons is developed. This case is highly desirable (Pillai et al., 1999). Not only salinity and surfactant concentration are said to alter properties of MEs, but also various parameters including cosurfactant type, molecular structure of Gemini structure, type of crude oils, reservoir temperature and to a least extent the reservoir pressure (Healy et al., 1976; Jones and Dreher, 1976; Cayias and Schechter, 1976; Pintér and Wolfram, 1981; Novosad, 1982; Puerto and Reed, 1983).

The present investigation, rather extensive than exhaustive, presents the properties of a ME formulated from a contact of dimeric cationic ammonium salt, heavy crude oil and connate water. Herein will be discussed in a broad picture the effects of natural oil reservoir parameters on such ME, their stability in the reservoir conditions as well as the micellar solution retention. Ultimately, the present work targets to evaluate the potential of cationic dimeric surfactants as micellar slugs for heavy crude oil recovery.

2. Materials and methods

2.1. Materials

Physical and chemical properties of the petroleum fluids and surfactants used in this work are summarized in Tables 1 and 2 respectively. The complete list of suppliers and the purity of the chemicals is outlined in Appendix A of the supplementary file of this manuscript.

2.1.1. Dead crude oils at 25 °C

Two dead heavy crude oils (SK-3H and SK-2H) were selected as candidate petroleum fluids for this investigation. Prior experimental phase, both were centrifuged for 2 h at 4000 rpm to ensure a complete dewatering and the removal of any form of emulsified oil. A synthetic light crude oil (SK-1H) was prepared from hexadecane, decane and ethylbenzene at a fixed ratio of 60/30/10 (% volume).

2.1.2. Connate water

Brine (or connate water) was introduced in this research to model reservoir saline water trapped between the interstices of porous reservoir rock formations. Six different compositions of brine solutions were prepared (Table 1). Four including W_1 to W_4 were composed primarily on monovalent ions (Na^+ and Cl^-). W_5 and W_6 were composed of both monovalent and divalent ions (Ca^{2+} and Mg^{2+}). Sodium chloride, calcium chloride and magnesium chloride hexahydrated were used as raw materials to prepare the saline water solutions. It should be pointed out that W_5 and W_6 were scaled from actual reservoir water.

2.1.3. Surfactants and cosolvents

Two lyophilized dimeric ammonium salt surfactants namely trimethylene-1,3 bis-(dodecyldimethylammonium bromide) and trimethylene-1,3-bis(hexadecyldimethylammonium bromide) were used to prepare micellar solutions. To compare surface tension alteration of the proposed micellar slugs, a micellar solution from a non-ionic polysorbate (Tween 20) was prepared as well. The selection of a non-ionic polysorbate was done solely based on its broad use as conventional polymer for chemical EOR (Iglauer et al., 2004; Wu et al., 2010). The surfactants were used without any further form of purification. Cosolvents (or cosurfactants), used to enhance surfactant solubility, were selected among those, which have shown satisfactory results during the solubility test. The details of that experiment as well as the results are presented elsewhere (Nguele et al., 2015). Throughout this study, the concentrations of micellar solution will be expressed in wt.% i.e. weight of active surfactant/100 g of micellar solution.

2.2. Methods

2.2.1. Phase behavior test

2.2.1.1. Solubilization parameters determination. A salinity scan test was performed to investigate the microemulsion phase behavior and to compute its inherent parameters. For a given surfactant/cosurfactant formulation, following experimental sequence was used:

(1) Introduce an equal amount of heavy crude oil and brine solution in a graduated test tube with cap.
(2) Add a defined amount of micellar solution prior prepared. We used 1 ml in this work.
(3) Shake the tube test at a constant speed for a minimum of 2 h. We used a Vortex Genie 2 (Scientific Industries, USA).
(4) Allow the ME thence formed to equilibrate in an oven. In this work, the ME was kept at 40 °C, 5% higher than the oilfields from which the heavy crude oils were drilled.

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[1] A Gemini surfactant consists of two identical hydrophobic chains linked together with a spacer.

[2] In 2013, the recovery potential of heavy grades of crude oil were estimated at 5 trillion barrels worldwide (Abdul-Hamid et al., 2013).