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Effect of ionic strength on crude emulsification and EOR potential of micellar flood for oil recovery applications in high saline environment

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ABSTRACT

Micellar flooding is one of the chemical oil recovery techniques in which micelle action emulsifies the crude oil to be mobilized in form of emulsion from a subsurface porous media. However, the subsurface conditions such as high ionic strength and temperature are challenges to the successful use of micellar flood owing to the deterioration of micelle action suggesting no crude emulsification. The ionic compounds dissociate into different ions that may further affect micelle action *via* loss in viscosity and pressure drop, increased water cut, and mobility contrast between micellar flood and displaced oil. Thus, investigation leading to the successful use of micellar flood, context to crude emulsion, in extreme salinity and temperature is vital to extend the use of chemical methods in new reservoirs. In this work, a typical surfactant sodium dodecyl sulfate (SDS) solution with critical micelle concentration (0.8 wt%) was tested to emulsify a fresh crude oil in the presence of varying ionic strength (0–4 wt%, $NaCl/CaCl_2$ and temperature (40–98 °C). The efficacy of SDS micelles to produce crude emulsion significantly reduced with increasing salt concentration as reported through microscopic, rheological, and flooding experiments, particularly for divalent salt ($CaCl_2$) than monovalent salt (NaCl). The increase in temperature (> 40 °C) further curtailed the growth of crude emulsion, mainly due to enhanced droplet coalescence; thus the use of micellar flood is critical in a reservoir enriched with high salinity and high temperature. Salinity effect on emulsion viscosity is reported through rheological measurements. The study highlighted important aspects of surfactant flooding and is a forward step towards the use of SDS based micellar flood at complex reservoir conditions.

1. Introduction

The major reservoirs of the world are in their declining stage of production and there have been no significant oil and gas discoveries lately (Sharma et al., 2015). Thus, improving oil mobilization from the current reservoirs holds the key to meet the global energy demands. After water flooding, chemical methods such as micellar or surfactant flooding is one the most effective tools to improve the mobilization of trapped oil from the reservoir (Sheng, 2015). The use of surfactant in oilfield has been considered a good practice to formulate chemical solution of improved properties (Healy and Reed, 1977). Widespread attention has been given to these processes due to significant advantages of improved flow behavior and reduced interfacial tension (IFT) (Hirasaki et al., 2011). The micellar flooding refers to the injection of a chemical slug of surfactant that induces micelles which emulsify the trapped crude oil, and generates small droplets to be recovered at the surface in form of crude oil-in-water (o/w) emulsion (Nedjhioui et al., 2005; Tichelkamp et al., 2016). Thus, the surfactant helps to produce o/w emulsion of crude oil during the micellar flooding process (Bai et al., 2014). Although micellar flooding has demonstrated great potential in improving the oil production, the successful application of micellar flooding is still associated with challenges especially to the use of surfactant in emulsifying the crude oil and the ability to form micelles under *in-situ* reservoir conditions of high salinity (Tabray et al., 2013; Bera et al., 2017). The conventional surfactant flooding techniques have shown unsuccessful results in salt dominated reservoirs (Puerto et al., 2012) thus, these techniques need investigations for their successful applications, particularly in oil and gas industry.

In micellar flooding, the surfactant is added at critical micelle concentration (CMC) to generate sufficient number of surfactant micelles in solution (Domínguez et al., 1997). These micelles finally adsorb at the interface of oil-water and reduce IFT to improve the oil

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mobilization. Importance of surfactant in chemical methods for micellar flooding (Sheng, 2015) and other methods such as surfactant-polymer (Yan et al., 2016), alkaline-surfactant (Bai et al., 2014) and alkaline-surfactant-polymer (Panthi and Mohanty, 2013) flooding has been reported in numerous literature. Among the chemical slug types used after water flooding, alkaline-surfactant-polymer solution has been proven as the outstanding displacing fluid to recover the remaining oil from either the technical or economics point of views (Le Van and Chon, 2016). The performances of micellar flooding and alkaline-surfactant-polymer flooding was compared, showing the two processes are similar on the basis of oil volume recovered per unit mass of the chemical used and micellar flooding is the superior process on the basis of total oil recovered after water flooding (Thomas and Farouq, 2001). Various surfactants *viz.,* alkylmethylnaphthalene sulfonate surfactants (Zhao et al., 2007), alkyl-branched sulfate and ethoxy sulfate surfactants (Varadaraj et al., 1991), branched alcohol propoxylated sulfates (Jayanti et al., 2002), alkyl polyglycoside surfactants (Iglauer et al., 2004), and gemini surfactant (Chen et al., 2005) has been developed and explored for oil production in oil and gas industry. However, most of the surfactant flooding projects were carried out in normal reservoir conditions and rarely investigated for reservoirs exhibiting high temperature ($> 90\,^{\circ}C$) and high salinity ($\geq 20 \times 10^4$ mg/L) conditions (Yuan et al., 2015). High temperature may lead to thermal stability issues in micellar solution resulting precipitation, degradation, and possible plugging of the pore spaces by the surfactant (Tabray et al., 2013). Therefore, most of the surfactant flooding projects have proved unsuccessful at higher temperature (Negin et al., 2017).

Similarly, salinity affects the surfactant flooding process by influencing parameters such as phase behavior, surfactant adsorption, precipitation, and phase entrapment (Yuan et al., 2015). Surfactant used in the presence of low salinity called as smart water surfactant flooding has shown better results of oil mobilization (Khanamiri et al., 2016). But, the surfactants show extremely limited tolerance to hard brines (Tabray et al., 2013). Even the lone presence of monovalent cations like Na^+ in connate water can hamper the aqueous surfactant flooding performance (Healy and Reed, 1977). Divalent cations like Ca^{2+} and Mg^{2+} are highly undesirable and can cause surfactant precipitation and pore throat blockage hence reducing the permeability of the formation (Negin et al., 2017). Higher percentage of divalent ions in the reservoir brine may lead to enhanced surfactant retention in the pore spaces owing to ion exchange in the crude oil/brine/rock system (Gupta, 1982). Nelson, 1981 reported that anionic surfactants are more sensitive to divalent cations than monovalent cations and may undergo severe hydrolysis and precipitation, particularly at low surfactant concentration. Surfactant flooding demonstrates the best performance when an optimum salinity level is maintained for the surfactant used during the process (Negin et al., 2017). Optimum salinity is defined as the salinity where surface forces is reported to be at minimum energy level and all surfactant micelles are in equilibrium (Hirasaki et al., 2011). Although the effectiveness of low salinity is obvious, some shortcomings come out in the use of micellar flooding at high salt concentration. This indicates that the salt concentration exceeding certain limit may degrade surfactant micelles in solution as demonstrated (Iyota and Krastev, 2009). Salt ions exceeding 0.5 M significantly adsorbed on surfactant micelles and weakened the electrostatic repulsion which consequently allowed micelles to aggregate in solution (Iyota and Krastev, 2009). Micelles aggregation may decrease the possibility of micelle reaction with trapped crude oil, and the occurrence of obtaining o/w emulsion in micellar flooding will decrease. This indicates that surfactant flooding in presence of high salinity behaves as normal water flood with no additional oil mobilization. It is also true that the formation of o/w emulsion depends on pH environment (Negin et al., 2017). Choi et al. (2014) investigated the effect of varying pH on the droplet size; his study revealed that increasing pH significantly reduced the droplet diameter and improved the emulsion stability. This indicates that the successful use of surfactant flooding may be anticipated at alkaline levels as low pH reduces the surfactant interfacial adsorption which results in no emulsion as demonstrated (Choi et al., 2014). Thus, the investigation leading to examine the effects of high temperature and high salinity on micellar flooding is an important aspect for its possible application in complex reservoirs.

Another criterion of studying the stability of o/w emulsion is rheology. Such investigation can provide important information on emulsion droplet interaction and its flow behavior in reservoir during injection of micellar solution (Sharma and Sangwai, 2015). Several studies have been conducted to investigate the rheological behavior of o/w emulsions (Otsubo and Prud'homme, 1994; Binks et al., 2005). However, comprehensive information regarding the effects of harsh reservoir conditions on rheological behavior of crude oils produced during micellar flood still eludes the current literature as far as we are aware. Therefore, in this study, the use of sodium dodecyl sulfate (SDS) based micellar solution to emulsify the crude oil for oil mobilization from a synthetic sand-pack of fair porosity and permeability saturated with varying concentration (0, 0.5, 1.0, 2.0, 3.0, and 4.0 wt%) of monovalent (NaCl) and divalent ($CaCl_2$) salts is reported. This is required to create *in-situ* subsurface equivalent saline environment (different ionic strength) in sand-pack during the injection of SDS micellar solution to mobilize the crude oil. The temperature during the experimental study was varied from 40 to 98 °C. The rheological behavior was studied through the investigation on crude emulsion viscosity in the presence of different salinity and temperature. Effect of pH on emulsion stability has also been reported. Finally, oil displacement tests were performed to quantify the improved crude oil recovery which in our knowledge has not yet been addressed before.

2. Experimental work

2.1. Materials

Salts *viz.,* NaCl (purity 99.5%) and $CaCl_2$ (purity 99.5%) in powder form were supplied by Sisco Research Laboratories, India. Surfactant SDS (purity 90%) was obtained from Ranbaxy Fine Chemicals Limited, India and used as received. SDS (purity ~ 90%) used in this work is a conventional detergent which contains ingredients such as, 5–15% anionic surfactants; oxygen-based bleaching agents, *viz.*, < 5% non-ionic surfactants, phosphonates, polycarboxylates; and zeolites in very less amount. Hydrochloric acid (purity 35–38%) was supplied by S D Fine-Chem Private Ltd. Mumbai. All chemicals were of analytical grade and used as received. Aqueous solutions were prepared by using an accurate analytical weighing balance (Mettler Toledo, Mumbai, Model-AL204 with a repeatability of ± 0.0001 mass fraction) and an industrial mixer (Oster Grinder, Model-MCPRO6WSO with mixing speed ranges from 9000 to 18000 rpm). Deionized water, obtained from Millipore® Elix-10 purification apparatus, was used to prepare all aqueous

Table 1
Compositional details and physical properties of the crude oil used in this study.

Fluid	Saturate wt (%)	Asphaltene wt (%)	Resin wt (%)	Aromatic wt (%)	Acid number (mg of KOH/g)	Base number (mg of KOH/g)	Pour point (°C)
Crude Oil	64.6	18.4	12.9	4.1	1.92	2.82	37
	Viscosity: 4.2 mPa s (60 °C) and 2.6 mPa s (98 °C), Density: 0.84 gm/cc (60 °C) and 0.83 gm/cc (98 °C)						
	API gravity: 37.92 (60 °C) and 40.49 (98 °C)						