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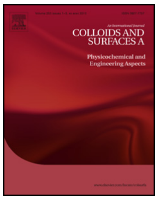

Improved oil recovery by reducing surfactant adsorption with polyelectrolyte in high saline brine

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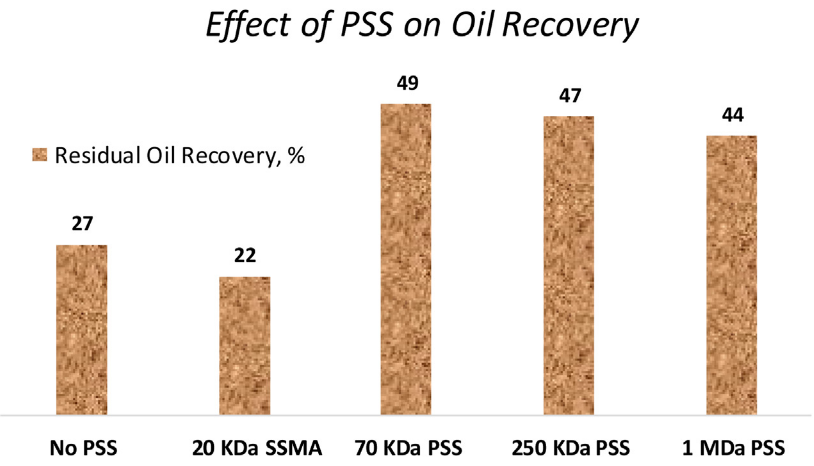
HIGHLIGHTS

- Surfactant adsorption is higher on Berea sandstone reservoir rock at high saline brine, over 300,000 mg/l TDS.
- Addition of polyelectrolyte, polystyrene sulfonate (PSS), minimizes surfactant adsorption.
- Surfactant-only flooding yields improved oil recovery from sand packs that are pre flooded with PSSs.
- 20 KDa SSMA reduces surfactant adsorption but negatively impacts oil recovery.

GRAPHICAL ABSTRACT



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ABSTRACT

Surfactant adsorption on reservoir rock is one of the biggest challenges of chemical enhanced oil recovery (cEOR) techniques. This problem can become severe in high saline brine environments. In this work, the efficacy of a polyelectrolyte, polystyrene sulfonate (PSS), as a sacrificial agent for lowering surfactant adsorption from reservoir brine that has totally dissolved solids (TDS) of over 300,000 mg/l is investigated. Four different molecular weight PSSs are evaluated through equilibrium and dynamic adsorption studies carried out on Berea sandstone and Ottawa sand. Results show significant reduction in surfactant adsorption after PSSs addition. The effects of surfactant/PSS addition techniques, sequential and simultaneous, on surfactant and/or PSS adsorptions are also studied. Sand pack studies are conducted to evaluate the effect of PSS-minimized surfactant adsorption on oil mobilization/recovery. Results show substantial improvement in oil recovery in the presence of PSS, suggesting a potential as a sacrificial agent in cEOR.

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1. Introduction

In surfactant aided chemical enhanced oil recovery (cEOR) techniques, an injected surfactant solution mobilizes trapped oil by lowering the interfacial tension (IFT) of the oil-water interface [1–3]. This technique is proven to recover trapped oil that cannot be extracted using the traditional water flooding method [4]. Despite the potential of surfactant-based hydrocarbon extraction, there are still challenges that need to be addressed to make this process economically feasible. Included in those challenges is the issue of surfactant loss due to adsorption on reservoir rock [5,6]. Surfactants that are adsorbed on an oppositely charged rock surface do not lower the IFT of the oil-water interface, and therefore are not available to participate in oil mobilization. This phenomenon lowers the overall efficiency of surfactant based cEOR techniques and increases the cost of projects. Therefore, it is necessary to mitigate surfactant loss on mineral rocks to make cEOR processes economically viable.

The physical adsorption of ionic surfactant on oppositely charged mineral oxide exhibits a low surface coverage region (Region “1” in Fig. 1) at low surfactant concentration [7,8] which is described by Henry’s law [9]. At any surfactant concentration above the critical admicelle concentration (CAC), the low coverage region enters a region of sharp positive slope (Region “2” in Fig. 1) where the formation of surfactant aggregates such as hemimicelles (monolayers), admicelles (bilayers), or mixture of both may take place [8,10]. The formation of a bilayer/admicelle, which is the result of surfactant hydrophobic tail-tail interaction, then starts to slow down surfactant adsorption due to saturation of high energy patches on the surface, and enters into the region (Region “3” in Fig. 1) where bilayer patches are slowly filled until a complete bilayer is formed [11] or the CMC is reached. This then leads to the plateau region [12] (Region “4” in Fig. 1) where surfactant adsorption is constant for any concentration of surfactant above the critical micelle concentration (CMC) because the monomer concentration of the surfactant does not change as more micelles are added to the solution. Although the formation of the surfactant partial bilayer prevents additional surfactant adsorption, this is not desirable for a cEOR process because the amount of surfactant that is required to form such a bilayer might be above the economical limit. Therefore, surfactants having the same charge as the reservoir rocks are generally used to minimize surfactant bilayer/admicelle formation. For example, anionic surfactants are typically used for the negatively charged surfaces of sandstone reservoirs and cationic surfactants should most likely be used for positively charged carbonate reservoirs. However, due to complexities of the reservoirs, including rock composition, the presence of clays, high brine salinity, multivalent ions, and even pH, there is still a possibility of significant surfactant loss due to adsorption.

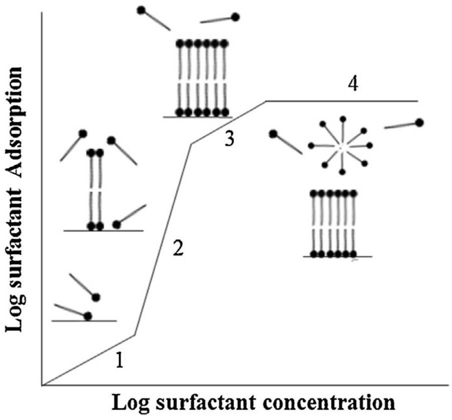

Fig. 1. Surfactant adsorption isotherm.

Efforts have been made to minimize the surfactant adsorption on rock or soil surfaces. Alkalis such as sodium hydroxide or sodium carbonate are typically used as a chemical agent to lower the adsorption of anionic surfactants [13,14]. Addition of alkali increases the pH, resulting in an increased net negative surface charge, and thereby reduces the adsorption of anionic surfactants due to electrostatic repulsion. In spite of a positive influence of alkali in lowering adsorption of anionic surfactants, it is limited to reservoirs with low TDS brines; this is mainly because alkalis are sensitive to divalent cations, Ca^{2+} and Mg^{2+}, and the elevated level of such ions present in high TDS brine causes alkali to precipitate and thus make it ineffective [15]. Other alternatives include using fresh water or using a water treatment plant, which also increase process complexity and cost.

Several authors have reported the application of polyelectrolytes as sacrificial agents in reducing adsorption of ionic surfactants on oppositely charged surfaces [16,17]. It is believed that polyelectrolytes, when adsorbed on the surface, cover positive sites and eliminate electrostatic-attraction driven surfactant adsorption. ShamsiJazeyi et al. [16] studied the effect of sodium polyacrylate on adsorption of anionic surfactant. They observed that higher molecular weight (>4500 Da) sodium polyacrylates significantly reduce the adsorption of anionic surfactant on both Berea sandstone and Carlpool dolomite rock surfaces. ShamsiJazeyi also claimed that the presence of surfactant does not affect the adsorption of polyacrylate due to its low desorption and high surface coverage nature. Additionally, they observed that increasing salinity as well as Ca^{2+} ions elevate surfactant adsorption on Berea sandstone even in the presence of polyelectrolyte. Experiments performed by Weston et al. [17] showed that addition of another anionic polyelectrolyte, polystyrene sulfonate (PSS), on a positively charged metal oxide, alumina, and cationic polyelectrolyte, polydiallyl dimethyl ammonium, on a negatively charged metal oxide, silica, reduced the adsorption of anionic and cationic surfactants, respectively. Weston also observed that a sequential addition methodology – addition of polyelectrolyte followed by surfactant – is more effective in reducing surfactant adsorption than simultaneous addition, where polyelectrolyte and surfactant are added together. The hypothesis proposed for this observation is that during sequential addition, the polyelectrolyte does not have to compete with surfactant to adsorb on the metal oxide surface.

It is well known that an increase in electrolyte concentration of a solution increases the adsorption of anionic surfactants [18]. Even though polyelectrolytes are proposed to significantly minimize surfactant adsorption on rocks or metal oxides, their effectiveness in high electrolyte/TDS (>200,000 mg/l) reservoir brine condition is yet to be studied. A possible explanation may be the difficulties in developing surfactant formulations that remains stable in a very high TDS solution. This work hopes to close such a gap and demonstrate that polystyrene sulfonates (PSSs) can be used as a sacrificial agent in minimizing adsorption of anionic surfactant –in a sandstone reservoir that has brine with total TDS of over 300,000 mg/l and total hardness (Ca^{2+} and Mg^{2+}) of about 13,000 mg/l.

2. Experimental

2.1. Materials

Polystyrene sulfonates (PSS) with four different molecular weights (MWs) i.e., 20 kDa (25% active), 70 kDa (30% active), 250 kDa (30% active), and 1 MDa (25% active) are the anionic polyelectrolytes used in this study. These polyelectrolytes are commercially available and were provided by Akzo Noble Inc. Nashville,