Evaluation of Surfactant Synthesized from Waste Vegetable Oil to Enhance Oil Recovery from Petroleum Reservoirs

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Abstract

Minimizing the loss of chemicals due to adsorption unto the rock materials during injection into petroleum reservoirs is critical to improve the economics and environmental footprint of the process and ensure its wider application. In this study, adsorption of a surfactant formulated from waste vegetable oil (SEMES) and two commercial surfactants, cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) onto common reservoir materials, at various concentrations, salinity and pH is compared. Indirect method of residual equilibrium concentration measurement was employed to obtain the adsorption isotherm of the surfactants on kaolin, silica, alumina and ilmenite. They were found to adsorb strongly onto the materials while stabilization in the region above the CMC was observed. At constant salinity, cationic surfactant adsorbed more strongly on the materials than the anionic surfactant. With increasing pH, the adsorption of SDS and SEMES decreased while the opposite was the case with the cationic surfactant, CTAB.

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Keywords: Crude oil; Petroleum reservoir materials; Waste vegetable oils; Chemical enhance oil recovery; Surfactants; Sodium epoxidized methyl ester sulfonate; Adsorption,

1. Introduction

Surfactant flooding is a widely employed chemical enhanced oil recovery (CEOR) process to manipulate the phase behaviour of petroleum reservoir fluids so as to counteract the high capillary force trapping oil in the pores of the reservoir \cite{1, 2}. The surface active chemical promote the formation of microemulsions at the crude oil and the displacing fluid (most often water) interface \cite{3, 4}, thus causing a significant lowering of the fluids interfacial tension (IFT). This is required to efficiently mobilize a substantial percentage of the residual oil to enhance overall crude recovery \cite{5}. The major problem that affects the efficiency of the CEOR processes is the loss of surfactant through interaction with reservoir rock \cite{6}, along with surfactant partitioning into the oil interface \cite{7}.

In surfactant-water-solid systems, surfactant loss via adsorption unto the reservoir rock bed depends on the rock properties, the nature of the surfactant, temperature, salinity and pH \cite{8}. High adsorption of surfactants onto the reservoir rock causes surfactant loss thus imparting the economic viability of the CEOR project \cite{9}. To enhance residual oil recovery using surfactant flooding, it is crucial to have a broad understanding of adsorption of

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surfactants unto the reservoir materials. An important factor which has been the focus of numerous investigations is the behaviour of surfactant mixtures at solid-liquid interfaces [10]. Surfactant adsorption has been shown to increase as the surface charge of the reservoir rock increases [11]. Various studies have investigated the effects of pH and salinity on the adsorption of surfactants [12-14] also. Generally, addition of alkali to raise the pH will change the surface charge and alter the adsorbed quantity while salinity will alter the electrical potential of surface sites for adsorption [13].

In determining surfactant adsorption in dispersed systems, a known quantity of surfactant is added to the system and allowed to reach equilibrium. Afterwards, the dispersed solids are separated and the surfactant concentration in the solution measured [15]. Surfactant adsorption is obtained using eqn 1.

\[
\Gamma = \frac{(C_i - C_e) \times M_s}{M_e} \times 10^{-2}
\]

where, \(\Gamma\) is the adsorption density (mg/g), \(C_i\) is the initial surfactant concentration (ppm), \(C_e\) is the equilibrium surfactant concentration in solution (ppm), \(M_s\) is the mass of the surfactant solution (g) and \(M_e\) is the mass of the dry absorbents (g).

This study investigated the adsorption characteristics of a surfactant formulated from waste vegetable oil, on different reservoir materials. This was compared to that of commercial anionic, sodium dodecylsulfate, and cationic, cetyltrimethyl-ammonium bromide surfactants. Adsorption on the emerging drilling mud weighing agent, ilmenite was also investigated.

2. Experimental Procedures

Sodium epoxidized methyl ester sulfonate synthetized from waste vegetable oil, an anionic surfactant, sodium dodecylsulfate (SDS) and a cationic surfactant, cetyltrimethyl-ammonium bromide (CTAB) were employed. The alkalinity was adjusted with NaOH while NaCl solution was used for salinity adjustment. The surfactants were of research grade and were used as received. The adsorbents material (to represent reservoir rock materials) used are alumina, silica, kaolin (Sigma Aldrich, 98%) and ilmenite (Tronox SA) obtained from South Africa ore was used as the drilling fluid weighing agent. The clay materials were dried in a convection electric oven at 120 °C overnight to eliminate water and any other adsorbed substances.

Static adsorption experiments were employed to measure the adsorption characteristics of the surfactants from aqueous solution onto the adsorbent surfaces. Initial surfactant concentrations prepared in 2 wt. % NaCl was varied between 50 and 600 ppm. The absorbent-dispersed surfactant solution samples were maintained as a mass (solid-liquid) ratio of 1:20. The absorbent-surfactant solution mixtures were agitated (240 rpm) for 24 h at room temperature and ambient pressure. After equilibration, the surfactant-solid system was filtered. Residual surfactant concentration was measured before and after contact with the reservoir materials. The equilibrium concentrations of the surfactants were evaluated to determine the maximum quantity of adsorbed onto reservoir material. The amount adsorbed (adsorption density) was expressed as the unit of mass of surfactant adsorbed per gram of solid absorbent (mg/g). The effects of pH and salinity on the adsorption capacity of the adsorbent were also investigated. To adjust the required pH, values of the maximum adsorption of the surfactant solutions were considered and NaOH solutions ranging from 0 - 1 wt. % were used. The salinity of the solution was altered with NaCl solution.

3. Findings and Discussions

The adsorption isotherm for SDS, CTAB and SEMES on the representative reservoir rock materials and the weighing agent at ambient temperature, pH 6 and solution salinity of 2 (vol %) is presented in Figure 1.
At alkali concentration > 0.6 wt. %, the adsorption of the surfactant on kaolin reached saturation at ~0.431 mg/g. SEMES showed similar adsorption characteristics to the anionic SDS with the addition of alkaline chemical but its adsorption plateau is reduced more significantly at NaOH concentrations of 0.2 to 1 wt.%. However, in case of CTAB, as the pH of the solution increased, the adsorption capacity also increased. This is due to the fact that the cationic surfactant positively-charged head groups are strongly attracted at high pH with negatively-charged kaolin clay surface. It can be concluded that anionic surfactant adsorption on mineral rock surfaces can be minimized by adjusting the pH of the solution which is crucial to the economic viability of surfactant use in CEOR processes.
Fig. 2. The effect of alkali concentrations on the adsorption isotherms at ambient temperature

Generally, enhanced oil recovery (EOR) is carried out using brine injection which contains hard ions. Hence, it is essential to study the effect of divalent ions on surfactant adsorption. Adsorption isotherms for SDS, CTAB and SEMES at different salinities on synthetic kaolin clay are presented in Fig. 3. An increase of the adsorption plateau of the anionic surfactants (SDS and SEMES) with increase in the equilibrium amount of hard ions can be observed.

Fig. 3. Adsorption Isotherm of SDS and CTAB at different NaCl salt concentrations at ambient temperature

The addition of salts of multivalent cations may in some instances result in a substantial increase in the anionic surfactants adsorption while causing a decrease in the adsorption capacity of cationic surfactants [7]. When the concentration of NaCl is increased, there was a consequent decrease in the electrostatic repulsion between the adsorbed surfactant species and the absorbent. This results in an increase of adsorption capacity of anionic surfactants. Thus, there is a monotonic increase in the adsorption capacity of SDS and the synthesized surfactant SEMES as more NaCl solution is added. This is attributed to the fact that the concentration of divalent ions (Na+) in the solution increases with increase in the added quantity of sodium chloride. However, a different trend was observed with CTAB, increase in the NaCl salt concentration caused the electrostatic attraction between the adsorbed surfactant species to fall resulting in the decrease of the adsorption capacity for CTAB (see Fig. 3).

4. Conclusions

In summary, the amount of adsorption in terms of mass per unit surface area varies with different minerals. From this study, it can be concluded that cationic surfactant has a tendency to be strongly adsorbed to silica > kaolin > ilmenite surfaces compared with the anionic and the formulated SEMES. At low surfactant concentrations, the adsorption of cationic surfactants is induced by electrostatic forces of interaction on diaspore as well as ion exchange, thus making them to adsorb readily on kaolinite, silica and ilmenite mineral surfaces. With increase in the surfactant concentration, adsorption on the surface of reservoir materials particles increases until the saturation point
is reached. With pH and salinity, the adsorption capacity of anionic surfactant is favoured by increase in salinity while the adsorption capacity of cationic surfactant is favoured by increase in alkalinity of the system at ambient temperature. In reservoirs containing mineral surface with a net negative surface charge, anionic surfactants are better suited for chemical flooding. In the same way, cationic surfactants are favored for use in reservoirs with a positive net surface charge. These results show that sodium epoxidized methyl ester sulfonate formulated from waste vegetable oil can potentially be used as a substitute surface tension agent for commercial surfactants during chemical enhanced oil recovery operations.

Acknowledgements

The authors acknowledge the financial support provided by Cape Peninsula University of Technology for this research.

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