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Influence of surfactant and electrolyte concentrations on surfactant Adsorption and foaming characteristics

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ABSTRACT

Surfactant adsorption and foaming characteristics are influenced by surfactant concentration and presence of inorganic electrolytes. Hence, it should be possible to optimize the performance of the surfactants in subsurface applications by understanding the influence of these parameters on surfactants. This study investigates the adsorption of sodium dodecyl sulfate (SDS) on kaolinite as a function of surfactant concentration and added electrolyte (NaCl, $CaCl_2$ and $AlCl_3$) concentration. Influence of temperature on the electrolyte and surfactant interactions was also examined. Adsorption isotherms were obtained using surfactant concentrations higher and lower than the critical micelle concentration (CMC). Surfactants adsorption on kaolinite was determined using a surface tension technique and two phase titration methods. Adsorption data were analyzed by fitting with Langmuir and Freundlich adsorption isotherms. The foam was generated by dispersing CO_2 gas into the surfactant solution through a porous stone. Foam half-life and the rate of foam collapse as function of time was monitored. The adsorption of SDS by kaolinite increases with the increasing concentration of NaCl and $CaCl_2$ and decreasing temperature. However, adsorption in presence of $AlCl_3$ shows different behavior. The adsorption remains constant irrespective of the increasing $AlCl_3$ concentration. Results show that the adsorption of SDS onto kaolinite in presence and absence of salts follows the Langmuir isotherm models. Salts containing trivalent ions and divalent ions ($AlCl_3$ and $CaCl_2$) were found to increase SDS adsorption on kaolinite and decrease bubbles stability compared to salts containing mono ions (NaCl). The order of increase in surfactant adsorption and bubble coalescence in presence of salts is as follows: $AlCl_3 > CaCl_2 >$ NaCl. There was an optimum surfactant concentration corresponding to maximum foam stability beyond which there was either a reduction or no significant changes in foam stability. This concentration decreases in presence of salts, except for $AlCl_3$ and high concentrations of NaCl (5 wt%) and $CaCl_2$ (1 wt%). The presence of salt improved foam generation and bubble stability at SDS concentration below the CMC. Above CMC, the bubble coalescence inhibition and foam stability decreased in the presence of salt. Decrease in surfactant surface tension and CMC, the screening effect of electrostatic double layer (EDL) by salts and the ability of SDS to form a complex with divalent (Ca^{2+}) and trivalent (Al^{3+}) cations are critical factors affecting SDS adsorption and foaming behaviors in presence of $AlCl_3$, $CaCl_2$ and NaCl salts. The results of this study have wide applications in the design, implementation and optimization of chemical EOR in the field.

1. Introduction

Surfactants, due to their favorable physicochemical properties have wide applications in several engineering and industrial processes (Bera et al., 2013). The adsorption and foaming characteristics of surfactants remained an important subject of active research in various fields such as surface and colloid chemistry, enhanced oil recovery (EOR) and biochemistry (Bournival et al., 2014; Firouzi and Nguyen, 2014a). Surfactants are used in several applications to generate stable foams due to their ability to prevent bubble coalescence by stabilizing the thin liquid films between two bubbles (Bournival et al., 2014). In chemical EOR applications, surfactants are very essential materials for oil-water interfacial tension and capillary forces reduction. The adsorptions of surfactants on clay minerals can results in loss and decrease in surfactant concentration, which may reduce the quantity of surfactant molecules available for the reduction of oil-water interfacial tension during surfactant flooding (Bera et al., 2013). Surfactant loss can also reduce the available surfactant molecules that can adsorb at the air-

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water interface of the foam to stabilize the foam lamellae. Hence, the effectiveness of surfactant and foam flooding EOR depends on the extent of surfactant adsorption on reservoir rock surfaces and clay minerals.

The success of surfactant applications for EOR depends on the foaming and adsorption properties of surfactant in presence of resident reservoir brines in porous media. Inorganic salt influences the adsorption of surfactant molecules on clay minerals and gas-liquid interface of surfactant-stabilized foam. Ions of different valences have different effects on surfactant foaming and adsorption properties as a result of their influence on the screening of the electrostatic charge (Behera et al., 2014). Besides electrolytes concentration, several physicochemical properties such as pH and temperature, which affects surfactant dissolution and precipitation behavior, also affects surfactant adsorption properties (Lv et al., 2011). Previous studies of surfactant adsorption on reservoir rocks and clay minerals reported in literatures shows that the adsorptions of cationic and nonionic surfactants are higher than that of anionic surfactants. Effects of different parameters on surfactant adsorption from solution onto reservoir rocks have also been investigated (Amirianshoja et al., 2013; Bera et al., 2013; Førland et al., 1996; Gogoi, 2009; Lv et al., 2011; Muherei and Junin, 2009; Muherei et al., 2009; Paria and Yuet, 2007; Sánchez-Martín et al., 2008; Zhang and Somasundaran, 2006). Results show that surfactant adsorption increases with decreasing pH for anionic and nonionic surfactant. For the cationic surfactant, adsorption increases with increasing pH.

Gogoi (2009) found that the adsorption of Na-lignosulfonate onto the reservoir rocks increases with increasing NaCl concentration and decreasing pH. Bera et al. (2013) conducted comprehensive studies of the influence of different parameters on surfactants adsorption onto sand surface. Their results show that surfactants adsorption increases with increasing NaCl concentration, adsorbent dose and decreasing temperature. They reported that there is a threshold surfactant concentration, beyond which, there was no increase in surfactant adsorption on sand particles irrespective of the increasing adsorbent dose and surfactant concentrations. Results of previous studies of surfactant adsorption on reservoir rocks and clay minerals have been analyzed by fitting the data with various adsorption models such as Linear, Langmuir, Temkin, Freundlich, Redlich-Peterson and Sips isotherm models. Ahmadi et al. (2012) reported that the adsorption isotherm of Zyziphus spina-christi onto rock surface can be adequately predicted using a Langmuir model. Bera et al. (2013) demonstrated that the adsorption isotherm of sodium dodecyl sulfate (SDS) on sand surface follows the Langmuir isotherm and pseudo-second order kinetics models.

Sodium dodecyl sulfate (SDS) is of special interest among surfactants for EOR applications because of their low adsorption on reservoir rock and the high stability of SDS-stabilized foams. The extent of SDS adsorption on reservoir rock and clay minerals depends largely on the type of electrolytes and the mineralogical composition of the adsorbent. Kaolinite is one of the major clay minerals with complex mineralogical composition and surface properties. Both positive and negative sites co-exist on kaolinite surfaces (Totland et al., 2011; Xu et al., 1991; Yu et al., 2007). Most of the previous studies of influence of electrolytes on SDS adsorption to kaolinite surface have been limited to influence of sodium chloride (NaCl) on surfactant adsorption isotherm. The influence of mono-, di-, and trivalent cations on SDS adsorption to kaolinite is yet to be fully understood. Reported studies of influence of temperature on SDS adsorption to kaolinite were conducted in absence of salts. There is still paucity of information on the impact of temperature on the electrolyte and surfactant interactions. Since Sodium dodecyl sulfate (SDS is widely used in oil field applications, it is essential to gather information regarding the effect of salts on this surfactant in order to optimize its performance in subsurface application.

Generally, electrolyte concentration also influence SDS-stabilized foam generation and stability through its effects on the maximum disjoining pressure of the liquid films and electrostatic double layer (EDL) (Ruckenstein and Bhakta, 1996). The influence of electrolytic salt concentration on foam generation, bubble coalescence and foam lamellae stability has been investigated by researchers (Del Castillo et al., 2011; Firouzi and Nguyen, 2014b; Karakashev et al., 2008; Liu et al., 2005; Mannhardt and Svorstøl, 2001; Nguyen et al., 2012; Quinn et al., 2014; Rojas et al., 2001; Vikingstad and Aarra, 2009; Xu et al., 2009). Some of the researchers reported that, there is a significant inhibition of bubble coalescence at salt concentration above a certain critical concentration called the transition concentration (Del Castillo et al., 2011; Firouzi and Nguyen, 2014b, 2014c). Results of Rojas et al. (2001) studies showed that the addition of salts greatly reduces the stability of foams generated with anionic surfactants. Bournival et al. (2014) reported that foaming activities is only improved by the addition of sodium chloride at low surfactant concentrations. Xu et al. (2009) found a decrease in bubble size and an increase in stability of SDS-stabilized foam with increasing NaCl concentration until a threshold NaCl concentration (0.25%) were attained. Further studies on this subject will be necessary to establish consistent results. Moreover, the role of salts containing mono-, di-, and trivalent ions on the SDS-foam generation, propagation and stability is not yet explicit.

Results of some studies of the influence of surfactant concentration on foam generation, stability and bubble coalescence in presence and absence of salts are also reported in literatures (Farzaneh and Sohrabi, 2015; Rojas et al., 2001; Simjoo et al., 2013; Szekrényesy et al., 1992; Wang and Chen, 2013; Wang and Mulligan, 2004a). Some of the researchers reported that foam stability increases with increasing surfactant concentration while others reported an increasing foam stability with the increasing surfactant concentration until a threshold concentration is attained. The latter emphasized that foam stability either decreases or remains the same from this surfactant concentration and beyond. Despite these results, Influence of SDS concentration at concentration below and above the critical micelle concentration (CMC) on foam generation and stability remains unknown.

Motivated by the limitations of the previous studies, this present work has been designed to experimentally study the influence of surfactant (SDS) and electrolytes (NaCl, $CaCl_2$ and $AlCl_3$) concentrations on the adsorption of sodium dodecyl sulfate (SDS) onto kaolinite and the foaming properties of the SDS-stabilized foam. These salts represent the major monovalent, divalent and trivalent cations, and the major anion found in reservoir brines. Influence of temperature on surfactant adsorption isotherm in presence and absence of salt will be investigated. Adsorption data will be analyzed by fitting with Langmuir and Freundlich isotherm models. The morphology of the bubbles will be analyzed with Leica EZ4 HD stereo microscope (Leica Microsystems, Switzerland) in order to determine the bubble size distribution and micro-bubbles lamellae in absence and presence of salts. Surfactants adsorption will be determined using a surface tension and two-phase titration method for surfactant concentrations above and below the surfactant monomer saturation (CMC). Foam stability will be determined by monitoring the foam half-life and the total collapse of the foam height as a function of time. The resulting changes in the surface tension and the CMC of the surfactant at different salt concentrations will be used to explain the foaming and adsorption behaviors.

2. Materials and methods

2.1. Materials

An anionic surfactant, sodium dodecyl sulfate (SDS) was used for this study. The surfactant ($C_{12}H_{25}NaO_4S$) was supplied by Scharlau Chemie S. A. It has a molecular weight of 288.38 g/mol and a purity of 95%. Three salts were used to investigate the effect of electrolyte concentrations on surfactant adsorption and foaming properties.