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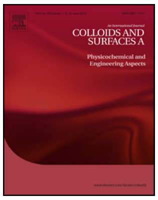

Design of an optimal middle phase microemulsion for ultra high saline brine using hydrophilic lipophilic deviation (HLD) method

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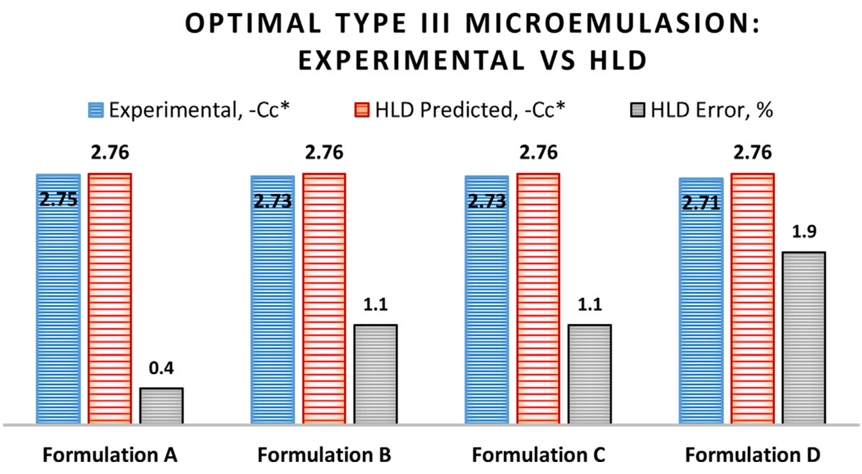
HIGHLIGHTS

- Binary mixtures of extended surfactants and ethoxy sulfates are optimized for 300,000 mg/L brine.
- Proposed surfactant formulations meets IFT and stability criteria for cEOR.
- The HLD method is found to be a promising tool for designing microemulsion systems for cEOR applications.
- Correct *K*-values and α_T values of surfactants play a crucial role in an accuracy of the HLD method.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, alcohol-free surfactant formulations incorporating sodium alkyl alkoxy sulfate surfactants and a sodium alkyl ethoxy sulfate surfactant are tested at 52 °C for reservoir brine having a total dissolved solids of above 300,000 mg/L with total hardness of about 13,000 mg/L. The optimized surfactant formulations show excellent aqueous phase stability, produce an ultra-low-interfacial tension (IFT) of 0.004 mN/m, and give fast coalescence rates of less than 30 min at reservoir salinity and temperature. Surfactant-only sand pack studies further validate the formulations by mobilizing about 60% of residual oil without mobility control. In addition, the hydrophilic lipophilic deviation (HLD) method is used to find the optimal surfactant/co-surfactant ratio (defined as the ratio giving the lowest IFT) at the reservoir salinity and temperature. Results show, first, that HLD constants measure at low salinity are applicable at high salinity and high hardness, and second, that the correct determination of surfactant head constant '*K*' and temperature constant 'α_T' governs the precision of the HLD approach as a surfactant selection tool for chemical enhanced oil recovery (cEOR) application. Results illustrate the potential of surfactant-only flooding to produce significant tertiary oil recovery.

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1. Introduction

The importance of the middle phase microemulsion and its relation to ultra-low interfacial tension and chemical enhanced oil recovery (cEOR) is well understood [1,2]. Many researchers have extensively studied this area and have developed surfactants that can produce this type of microemulsion at different reservoir conditions [3,4]. However, developing a surfactant formulation for sandstone reservoirs containing high total dissolved solids (TDS) brine (>200,000 ppm) is a challenging task [5]. Shown in Fig. 1 is the effect of high TDS on homogeneous single phase surfactant solution. The presence of monovalent and divalent cations, such as Na^+, K^+, Ca^{++}, and Mg^{++}, in the reservoir brine creates an unsuitable environment for the anionic surfactant by inducing surfactant precipitation or a two phase aqueous micellar solution [6,7]. Surfactant precipitation is the most common problem encountered at high TDS conditions. The counter-ions present in the aqueous solution may result in surfactant precipitation [8]. This situation can be exacerbated in the presence of a high concentration of divalent cations making it completely ineffective for cEOR application. The salting out of micelles or the formation of two phase aqueous micellar solution having both micelle rich and micelle poor phases can also be encountered at high salinity conditions [9]. Even though, at such condition, the surfactants are soluble in brine, it is highly undesirable for cEOR as it increases the IFT of the oil-water interface.

In recent years, surfactant formulations for high TDS brine are gaining popularity among industries because of growing onshore and offshore cEOR opportunities [3]. Industries prefer to use the produced reservoir brine or available water sources (for example, seawater in offshore) for cEOR technique. However, if the surfactant formulation developed for a cEOR process cannot survive the high TDS of the produced brine, it requires fresh water and water treatment facilities. This increases the overall project cost making cEOR projects less attractive, especially for small producers. Additionally, polymers that are normally used as mobility control agents in cEOR also become ineffective in high TDS brine [10–12]. There is, therefore, a need for an innovation of surfactant formulation for high TDS brine conditions for cEOR processes that do not require mobility control.

It is well known that the sodium alkyl alkoxy sulfate surfactants, also known as extended surfactants, are suitable for high salinity brines [3,13,14]. By definition, extended surfactants have polypropylene oxides (POs) or a mixture of polyethylene oxides (EOs) and polypropylene oxides (POs) inserted between the hydrophilic heads and lipophilic tails [15]. According to Winsor's *R* ratio [16], the best way to generate an optimal middle phase microemulsion, Type III, having equal amount of oil and water solubilized in the middle phase is to equally enhance surfactant–oil and surfactant–water interactions. These two interactions can be enhanced by making the surfactant's head group more hydrophilic and tail group more hydrophobic. However, there is a possibility a conventional surfactant loses water solubility because of increased tail group hydrophobicity [2] and is not desirable for cEOR application [14]. In contrast, extended surfactants can maintain their stronger interaction with both water and oil phase while generating ultra-low IFT and without losing water solubility due to the presence of polar groups in the EOs and POs [14]. One of the drawbacks of extended surfactant is the hydrolysis of sulfur-to-oxygen (S—O) bond, which is present between its sulfate head group and alkoxy chain, above 60 °C [17]. Therefore, surfactants having sulfonate or carboxylate head groups are suggested for reservoirs with higher temperature conditions [18]. Another class of surfactant, that is sodium alkyl ethoxy sulfate [19], is also reported to show promising results in high salinity brines. This class of surfactant is usually used as a co-surfactant in a surfactant mixture to enhance the overall hardness tolerance of surfactant mixture. Some authors also report the use of co-solvents such as short chain alcohols (*sec*-butanol and *iso*-propanol) to increase the solubility of surfactant in high salinity brine [20,21]. However, alcohols that are mostly used for eliminating gels/ liquid crystal formation in surfactant systems can adsorb together with the surfactant at the oil–water interface. In such cases, oil solubilization ability of the surfactant systems decreases and IFT increases which is undesirable for cEOR application [22]. Therefore, a careful consideration should be given in selecting surfactants and ingredients with the correct structure as this plays an important role in developing surfactant formulation for any cEOR process.

Most of the suggested formulations for high salinity brines are developed either for brines up to 21 wt% NaCl without hardness [19] or brines containing hardness up to 8500 mg/L with a total TDS of 165,000 mg/L [23]. In this work, surfactant formulations for reservoir brine having total TDS of over 300,000 mg/L with the total hardness of about 13,000 mg/L are reported. To date, this is the highest TDS brine that has been addressed in the cEOR literature. The alcohol free binary mixtures of extended surfactants and sodium alkyl ethoxy surfactant (sodium laureth sulfate) with three EOs are evaluated through phase behavior studies, IFT measurements, and sand-pack tests at reservoir conditions. Moreover, the concept of hydrophilic lipophilic deviation (HLD) equation is used as the surfactant selection tool for the purposed surfactant systems at constant TDS – the TDS of the reservoir brine – by varying the ratio of two surfactants, one more hydrophilic and one more hydrophobic.

2. Hydrophilic lipophilic deviation (HLD) concept

Salager et al. [24] first proposed the HLD concept as the thermodynamically derived correlation to describe microemulsion systems at the formulation conditions. Although, there are other correlations such as Winsor *R* ratio and HLB equation [25] to describe emulsion and microemulsuion systems as well as the overall hydrophilic-lipophilic attraction of the surfactants, the practical applications of such correlations are still limited. For example, the parameters of Winsor *R* ratio are almost impossible to estimate, whereas the HLB concept has its own limitations of not taking into account of both equilibrium and formulation conditions. The HLD equation closes this gap by overcoming the limitations of both the Winsor *R* ratio and HLB equation. The negative, positive and zero values of HLD represents Type I, II and III microemulsion systems, respectively. There are two forms of the HLD equation, one form of the HLD equation is for ionic surfactants and the other form of the HLD equation is for nonionic surfactants [24]. Since the surfactants that are used in this research are anionic, the HLD equation is written as:

$$\mathrm{HLD} = \mathrm{Cc} + \ln(S) - K\,(\mathrm{EACN}) - f\,(A) - \alpha_T\,(\Delta T) \tag{1}$$

where Cc determines the hydrophobicity of a surfactant, *S* is the salinity of the aqueous phase in grams of NaCl per 100 mL of solution, *K* is the constant whose value depends on surfactant head group and its hydrophilicity, EACN is the equivalent alkane carbon number of the oil used, *f*(*A*) is the alcohol constant, α_T is a temperature constant, and ΔT is the difference between formulation temperature, *T*, and the reference temperature, $T_{\mathrm{ref.}} = 25\,^\circ\mathrm{C}$.

Some researchers have reported that a change in system pressure results in changes to the optimal salinities [26] and have incorporated pressure correction factor in the HLD equation [27]. However, as our experiments were carried out at atmospheric pressure, we have neglected this term in our calculations.

At optimal condition, HLD is equal to zero and the salinity '*S*' represents the optimal salinity 'S^*'. Assuming $T = T_{\mathrm{ref}} = 25\,^\circ\mathrm{C}$, and if