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Systematic Phase Behaviour Study and Foam Stability Analysis for Optimal Alkaline/Surfactant/Foam Enhanced Oil Recovery

S.M. Hosseini Nasab* (Delft University of Technology) & P.L.J. Zitha (Delft University of Technology)

SUMMARY

Alkaline-Surfactant-Foam (ASF) flooding is a recently introduced enhanced oil recovery (EOR) method. This paper presents laboratory study of this ASF to better understand its mechanisms. The focus is on the interaction of ASF chemical agents with oil and in the presence and absence of naphthenic component and in-situ soap generation. The impact of alkali, IFT reduction, in-situ soap generation and oil acid number were systematically studied by measurement of phase behaviour, interfacial tension and foam stability. Phase behaviour results indicate the synergistic effect between the generated soap and synthetic surfactant, which gives wider range of optimal salinity in terms of IFT reduction. The novel alkali-surfactant formulation lowered IFT between oil and aqueous phase from nearly 30 mN/m to 10-1 - 10-3 mN/m. This means that chemical formulation can create low tension foam flooding with higher capillary number than conventional foam for displacing oil from porous media. In the foam stability analysis of ASF agent in the presence and absence of oil, several characteristics such as foam volume evolution, foam half decay time, liquid fraction of foam were measured over a wide range of surfactant, alkali, electrolyte and naphthenic acid concentration. Bulk foam stability tests demonstrated that stability of foam diminishes in presence of oil with high in-situ soap generation. The obtained results for foam stability in the presence of oil were successfully interpreted in terms of phenomenological theory of entering/spreading/bridging coefficient, lamella number and pseudo-emulsion film. The discussed method in this paper can be successfully applied to formulate high performance chemical agents for achievement of improved foam flooding according to reservoir fluid condition, i.e. properties of crude oil and formation water.
1. Introduction

Foam has shown promise as drive fluid for improved and enhanced oil recovery (IOR and EOR), particularly for shutting-off of unwanted gas production in production wells in the field applications in carbon dioxide (CO₂) and nitrogen (N₂) foam flooding, steam flooding (Holm, 2013; Mohammadi et al. 1989; Sohrabi & Farzaneh, 2013). Foam has greater apparent viscosity than displaced fluids by drastically lowering gas mobility, which is essential to improve volumetric sweep efficiency in gas flooding into oil reservoirs (Mannhardt et al., 2000; Sagar & Castanier, 1997). Foam improves volumetric sweep efficiency, especially in heterogeneous, but its microscopic displacement efficiency is low (Hirasaki et al., 2004; Li et al., 2010).

In reservoirs with high permeability contrast, strong foam will form in higher permeability zones leading to diversion of flow from high to low permeability zones (Cottin et al., 2012; Li et al., 2010). During field applications, foam may encounter varying conditions such as a range of oil saturations, different salinities. Foam should be designed to be stable in presence of oil. In cases where foam is injected into swept zones with low oil saturation, intermediate or low stability foam in presence of oil may be adequate (Mannhardt et al., 2000).

Foam has been identified also as an attractive alternative to polymer in the ASP flooding for either low permeability reservoirs with high salinity formation water (Lawson & Reisberg, 1980; Srivastava et al., 2009). Foam offers better properties over polymers for conformance issues. Alkali-surfactant-foam (ASF) flooding has been developed as new techniques which use foam as mobility control agent instead of polymer and also provides to low interfacial tension to increase the capillary number (Guo et al., 2012). Others have proposed similar processes under the name alkali-surfactant gas (ASG) or low tension gas (LTG) flooding (Szendak et al., 2013; Tang et al., 2014; Wu et al., 2010).

Surface active molecules, like surfactant and soap, adsorb onto the gas–liquid interfaces. They stabilised foam by inducing repulsive forces in the lamellae, modifying the viscoelasticity of gas-liquid interfaces and reduction of gas–liquid surface tension (Gauchet et al., 2014; Karakashev et al., 2012; Stubenrauch & Klitzing, 2003). This IFT reduction leads to increase of capillary number to improve the sweep efficiency (Kang et al., 2010; Yuqiang et al., 2008). The surface behaviour of the strongly interacting systems depends significantly on the electrolyte concentration, charge density and length of hydrocarbon chain in the surfactants (Campbell et al., 2011; Petkova et al., 2012; Worthen et al., 2013). Recently it was shown that the surface tension behaviour in the foam structures can also be influenced by mechanical agitation of the solutions (Campbell et al., 2011).

For water-flooded oil reservoirs, low IFT generating formulations, such as ASP and ASF chemical agents, are sought for EOR applications in order to mobilize residual oil which is trapped by capillary forces. Surfactant formulations reduce these capillary forces enabling the residual oil to be produced (Iglauer et al., 2010). A process based on surfactant phase behaviour screening has been described for evaluating potential EOR surfactants (Levitt et al., 2009). This approach is based on a well-established relationship between low interfacial tension and micro-emulsion phase behaviour. This work aims to find out high performance chemical system for ASF flooding, by investigating crucial parameters governing this process at bulk condition. The phase behaviour and foaming-ability of such selected chemicals was studied in detail in absence and in presence of model oil, with and without organic acid to find out the water and oil solubilisation ratio and interfacial tension behaviour versus salinity. We focused on the high molecular weight IOS surfactant for the all experiments. Towards the purpose of this study, then we performed a foam stability screening test to specifically address the impact of surfactant concentration, salt, alkali, oil saturation, interfacial tension (IFT) and in-situ soap generation. Then obtained results for foam stability in the presence of oil is discussed in terms of classical entering/spreading coefficient, oil solubilisation effect and stability of pseudo-emulsion film. Then the main conclusions of this study are drawn.

2. Theoretical Background:

2.1. Entering, spreading and bridging coefficient and lamella number

Several mechanisms of foam/oil interaction have been suggested in the literature. Three main models have emerged in attempts to predict foam stability in presence of oil: spreading and entering coefficients, lamella number, and pseudo-emulsion film models (Koczo and Lobo, 1988; Koczo et al.,...
Attempts to correlate spreading behaviour to foam destruction by oil, forms the basis for most of the work performed on oil destabilization mechanisms, where the spreading coefficient, $S$, for an oil-foam system is given by:

$$ S = \sigma_{gw} - \sigma_{ow} - \sigma_{og} $$

where $\sigma_{gw}, \sigma_{ow},$ and $\sigma_{og}$ are the foaming solution surface tension, initial foaming solution/oil interfacial tension and surface tension of oil phase, respectively. For oil at a gas/water interface the other two classical entering (E) and bridging (B) coefficients take the following forms

$$ E = \sigma_{gw} + \sigma_{ow} - \sigma_{og} $$

$$ B = \sigma_{gw}^2 + \sigma_{ow}^2 - \sigma_{og}^2 $$

Ability of oil drop to enter the gas–water interface, expressed by a positive entry coefficient $E$, is the necessary condition to rupture foam lamellae (Robinson & Woods, 1948). For $S$ positive oil spreads over the liquid gas interfaces, lowers the surface tension, increases the radius of curvature of the bubbles, alters the original surface elasticity, and also changes the surface viscosity. Thus the interfacial film loses its foam stabilizing capability (Harkins, 1941). When $S$ is negative oil does no spread and instead oil droplets form lenses at the gas–water interface, foam film may rupture once oil drop enters both surfaces of the lamella (Vikingstad et al., 2005). Under this condition oil might drop spans the film by making an unstable bridge (i.e., $B$ is positive).

Table 1 gives a summary of the foam stability prediction by the signs of the $E$, $S$ and $B$ coefficients.

<table>
<thead>
<tr>
<th>$S$</th>
<th>$E$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$+$</td>
<td>$+$</td>
</tr>
<tr>
<td>$-$</td>
<td>Stable foam</td>
<td>Stable foam</td>
</tr>
<tr>
<td>$+$</td>
<td>Stable foam</td>
<td>Unstable foam</td>
</tr>
</tbody>
</table>

Schramm and Novosad (Schramm & Novosad, 1990, 1992) proposed another mechanism for foam stability in terms of oil emulsification and imbibition in the foam structure. The main step of this mechanism is to form small oil droplets by emulsification, which allows oil droplets to move inside the foam structure. A dimensionless parameter, called lamella number ($L$), was proposed to describe foam stability. It was defined as a ratio of capillary pressure at Plateau borders to the pressure difference across the oil–water interface:

$$ L = \frac{\Delta P_C}{\Delta P_R} = \frac{r_o}{r_p} \frac{\sigma_{gw}}{\sigma_{ow} \theta_{ow}} $$

where $r_o$ is the radius of oil drop, and $r_p$ is the radius of the Plateauborder. Schramm and Novosad (Schramm & Novosad, 1990, 1992) found that the radius ratio was constant ($r_o/r_p = 0.15 \pm 0.01$) for all foams investigated. They defined three types of foam depending on the value of the lamellanumber ($L$): type A foam for $L < 1$, type B foam for $1 < L < 7$, and type C foam for $L > 7$. Table 2 presents a summary of the foam stability prediction by the lamella number theory.
## Table 2 Foam stability prediction by the lamella number theory.

<table>
<thead>
<tr>
<th>Type of Foam</th>
<th>Foam stability to oil</th>
<th>$E$</th>
<th>$S$</th>
<th>$L$ (→)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Quite stable foam</td>
<td>Negative</td>
<td>Negative</td>
<td>$L &lt; 1$</td>
</tr>
<tr>
<td>$B$</td>
<td>Moderately stable foam</td>
<td>Positive</td>
<td>Negative</td>
<td>$1 &lt; L &lt; 7$</td>
</tr>
<tr>
<td>$C$</td>
<td>Quite Unstable foam</td>
<td>Positive</td>
<td>Positive</td>
<td>$L &gt; 7$</td>
</tr>
</tbody>
</table>

### 2.2. Surfactant Phase Behaviour

The main objective of surfactant phase behaviour is selection of chemical formulation for a specific chemical EOR application. In this paper for all experimental investigations IOS surfactant was used as this type of surfactant has been shown low interfacial tension and relatively stable foam property at low concentration (Guo et al., 2012). Falls et al. (1994) reported using of high carbon number IOS surfactant as one of the components of the formulation used in the White Castle ASP pilot.

IOS formulations with high water/oil solubilisation ratio at optimal salinity gave the best performance among other types of surfactant in the core floods experiments reported by Sanz and Pope (1995). It was also found that high molecular weight internal olefin sulfonate (IOS) surfactants perform exceptionally well with the difficult oils in terms of providing efficient micro-emulsion compared to many other types of surfactants. In oil/brine/surfactant mixtures, IOS surfactants do not exhibit the tendency to form the liquid crystals, gels and ordered structures in spite of lacking branching (Barnes, Dirkzwager, Smit, & Smit, 2010; Zhao et al., 2008).

Phase behaviour tests include the aqueous stability test, salinity scan and oil scan. Micellar phase which are clear and composed of surfactant, brine, and oil at thermodynamically stable condition, is called “micro-emulsion” (Bourrel & Schechter, 1988; Quintero et al., 2011). Micro-emulsion phase changes from type I (oil in water), type II (water in oil) and type III (a bicontinuous oil/water phase) as the salinity increases (Winsor, 1954). The transition of micro-emulsion can be represented by a volume fraction diagram, which demonstrates an understanding of the sensitivity of the surfactant solution behaviour to additional electrolytes (Sheng, 2011).

For anionic surfactants, increasing the salinity causes a characteristic transition from type I to type III to type II. Healy et al. (1976) first developed a correlation between oil and water solubilisation ratios and the interfacial tension between the micro-emulsion and each excess phase. The concept of optimum salinity was introduced as corresponding to the salinity where an equal amount of oil and water are solubilized in the middle phase (type III) micro-emulsion. The intersection of the plots of $V_o/V_\text{s}$ and $V_w/V_\text{s}$ as a function of salinity occurs at the optimum salinity, and is defined as the optimum solubilization ratio $\sigma$. Huh (1979) developed a theoretical relationship between interfacial tension IFT and the oil/water solubilisation ratio as follow:

$$\gamma = \frac{C}{\sigma^2}$$  \hspace{1cm} (5)

where $C$ is approximately 0.3 dynes/cm for typical crude oils and surfactants. When the optimum solubilisation ratio $\sigma$ equal or larger than 10, the IFT at optimum salinity is on the order of $10^3$ dynes/cm or less, which is sufficiently low to mobilize the majority of residual oil. Therefore, in this paper we use a target optimum solubilisation ratio of 10 or higher for micro-emulsion phase behaviour screening.

### 2.3. Role of Alkali in Chemical EOR

Alkalis used in chemical flooding interact with carboxylic acids in the crude oil generate in-situ surfactants, wettability alteration and reduce surfactant losses (Ojukwu et al., 2013). The alkali-oil chemistry is described by partitioning of the naphthenic acid between the oleic and aqueous phases and subsequent hydrolysis in the presence of alkali to produce a soluble anionic surfactant $A^-$. 

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DeZabala et al. (1982) suggested a chemical model for the alkali-oil saponification. Acid existed in oil phase by interaction with alkali will have some aqueous solubility and will distribute itself between the oleic and aqueous phases represented by Eq.6:

\[
HA_o + NaOH \leftrightarrow NaA + H_2O
\]  

(6)

where HA\(_o\) is the oleic-phase acid, HA\(_w\) is the aqueous phase acid. Water-soluble anionic surfactant (A\(^-\)) can be produced from oleic-phase acid HA\(_o\) by the following hydrolysis and extraction equation:

\[
HA_o \leftrightarrow HA_w
\]  

(7)

\[
HA_w \leftrightarrow H^- + A^-
\]  

(8)

The generated A\(^-\) ion will adsorb at oil-water interfaces and lower the interfacial tension.

The acid dissociation constant (K\(_A\)) for Eq. 6, the partition coefficient of the molecular acid K\(_D\) and the dissociation constant of water (K\(_W\)) are as the following:

\[
K_A = \frac{[H^+][A^-]}{[HA_w]} 
\]  

(9)

\[
K_D = \frac{[HA_w]}{[HA_o]}
\]  

(10)

\[
H_2O \leftrightarrow H^+ + OH^-
\]  

(11)

\[
K_w = \frac{[H^+][OH^-]}{}
\]  

(12)

An increase in [OH\(^-\)] results in a decrease in [H\(^+\)]. pH is defined as –log[H\(^+\)]. At high pH, the concentration of soap in the aqueous phase is (Sheng, 2011):

\[
[A^-] = \frac{K_A K_D [HA_o]}{[H^+]} = \frac{K_A K_D [HA_o]}{[OH^-]} K_w
\]  

(13)

3. Experimental
3.1. Materials and methods

Brine containing 0.5 M sodium chloride (NaCl, Fisher Scientific) in de-ionized water (pH = 6.8 ± 0.1) was used to prepare the surfactant solution. The alkaline solutions were a mixture of sodium carbonate (Na\(_2\)CO\(_3\)) and sodium chloride that were obtained from Fisher Scientific Company with ACS purity. Nitrogen gas with a purity of 99.98% was used to generate foam. Normal hexadecane (n-C\(_{16}\), Sigma–Aldrich) as model oil was used to investigate the effect of oil on foam stability. Hexadecane as model oil was used in the presence and absence of naphthenic acid which was Decanoic Acid, where in situ soap is generated by interaction of alkali from surfactant solution with acidic component of oleic phase. The Decanoic Acid (99% pure) is an organic acid that was supplied from Sigma. In this work, 1.0 weight percent of Decanoic acid dissolved in n-hexadecane was used which has the total acid number (TAN) of 3.0 determined using ASTM method D664.
The commercial internal olefin sulfonate (IOS) was selected for this study. The IOS surfactants used in this study were prepared by Shell Chemical Company from internal olefins with carbon chain C20-24. The synthesis steps of IOS surfactant and the chemical structures formed were described by Barnes et al. (2008, 2012). These surfactants are designated by the abbreviation IOS 20–24. The surfactant solution was prepared using brine containing 0.5 M sodium chloride (NaCl, Fisher Scientific) in de-ionized water (pH = 6.8 ± 0.1).

3.2. Micro-emulsion Phase Behaviour Tests:

Water, oil, and surfactant were weighed into pipettes using an analytical balance, taking into account their densities. Phase behaviour samples were prepared in volumetric tubes by adding equal amounts of aqueous chemical formulation and hydrocarbon. The samples were mixed well for several hours, and were allowed to equilibrate for at least three weeks at temperature conditions T = 60 °C and atmospheric pressure. Typically, they were removed from the oil bath briefly several times during equilibration, shaken by hand a few times, and replaced. This procedure was continued until phase volumes remain unchanged. The phase characteristics of each system were recorded (i.e. the relative volumes of the aqueous and oleic phases, and, if present, the middle phase) (Wu et al., 2010).

3.3. Surface and Interfacial tension measurements:

The surface and interfacial tensions (ST and IFT) were measured using a KSV Sigma tensiometer by the DuNouy ring method. The gas above oil and water was air. The measurements were conducted for a sufficiently long time to obtain a constant value. All measurements were also performed at ambient temperature (21 ± 1 °C) and atmospheric pressure.

The ultralow interfacial tension (IFT) between oil-phase and water-phase were measured using a SITE100 spinning drop tensiometer (Kruss). In the cases where alkaline or/and surfactants were added to the water phase, the rotation speed was sufficiently high to ensure that the length of the oil drop is larger than four times its diameter. The IFT was determined with a built-in software system according to the following equation (Su, 2012):

$$\sigma = 3.42694 \times 10^{-7} (\rho_w - \rho_o) \omega^2 D^3$$

where \(\sigma\) is the interfacial tension in dyne/cm, \(\rho_w\) and \(\rho_o\) is the density of water (out) and oil (drop) phase in g/cm³, respectively, \(\omega\) is the rotational velocity in RPM, \(D\) is the measured drop width (diameter) in mm, and \(L\) is the length of the oil drop in mm.

3.4. Static FoamScan tests:

The foaming properties of the selected surfactant, from the phase behaviour study, were tested by using the FoamScan apparatus (IT Concept, France). Foam was generated in the apparatus by sparging nitrogen gas through a porous glass frit into a fixed amount of surfactant solution (50 ± 1 cm³) and at a fixed gas flow rate of 16 ± 1 cm³/min. The gas flow stopped automatically when foam volume reached a pre-set value of 150 cm³. The foam volumes during of generated foam as well as the subsequent foam drainage are monitored by images of the column, which are constantly recorded by a CCD camera throughout the experiment. The amount of liquid volume in the foam was measured by conductivity measurements at the different heights of the foam column. A pair of electrodes at the bottom of the column was used to measure the amount of liquid, which was not present in the foam. The schematic of FoamScan instrument is demonstrated in the Fig. 1.
The following parameters were measured in experiments with the FoamScan: foam volume generated during gas sparging (foamability), decay of foam volume after stopping gas sparging (foam stability) and also the amount of liquid volume in the foam structure. The foamability of the surfactant solutions was described by the foam capacity ($FC$) and foam maximum density ($MD$) coefficients. In fact, the main advantage of the FoamScan is its ability to measure simultaneously the liquid volume in the foam and parameters like $FC$ and $MD$ which allow us to extract additional information on the processes that destroy the foam. The $FC$ coefficient is the ratio of foam volume at the end of gas sparging to the total gas volume injected. When the generated foam is stable, the $FC$ coefficient is higher than unity. When the generated foam is not stable during the foaming process, the $FC$ coefficient is less than unity, meaning that part of the injected gas has not been retained in the foam column. The $MD$ coefficient was used to characterize the liquid retention in the generated foam and defined as a ratio of the liquid volume in the foam to the final foam volume (Simjoo et al., 2013).

3.5. Experimental Procedure:

Firstly chemical systems containing surfactant, alkali, electrolyte, organic acid and model oil were tested in phase behaviour experiment to identify the composition of the chemical slug and drive for ASF flooding. In order to identify micro-emulsion phase boundary, Winsor phase behaviours of brine-Surfactant-oil systems were performed under specific condition of salinity, surfactant concentration, oil type as demonstrated in the Table 3. Two types of micro-emulsion were generated one from surfactant, alkaline/surfactant (AS) solution with n-hexadecane and another type is alkaline/surfactant (AS) solution with acidic mixture of n-hexadecane. For the salinity scan test in phase behaviour study, we used the water/oil ratio equal to one. Information relevant to the observed type of various phase behaviours (such as Winsor I, Winsor II or Winsor III) was visually observed at equilibrium condition.
### Table 3 Overview of the all phase behaviour experiments performed in this study.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Changing Parameters</th>
<th>Surfactant Concentration (wt%)</th>
<th>Electrolyte Type</th>
<th>Oil Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl Concentration</td>
<td>0.5</td>
<td>NaCl</td>
<td>n-Hexadecane</td>
</tr>
<tr>
<td>2</td>
<td>NaCl Concentration</td>
<td>0.5</td>
<td>Na₂CO₃/NaCl</td>
<td>n-Hexadecane</td>
</tr>
<tr>
<td>3</td>
<td>NaCl Concentration</td>
<td>0.5</td>
<td>Na₂CO₃/NaCl</td>
<td>n-Hexadecane +Decanoic Acid</td>
</tr>
<tr>
<td>4</td>
<td>NaCl Concentration</td>
<td>1.0</td>
<td>NaCl</td>
<td>n-Hexadecane</td>
</tr>
<tr>
<td>5</td>
<td>NaCl Concentration</td>
<td>1.0</td>
<td>Na₂CO₃/NaCl</td>
<td>n-Hexadecane</td>
</tr>
<tr>
<td>6</td>
<td>NaCl Concentration</td>
<td>1.0</td>
<td>Na₂CO₃/NaCl</td>
<td>n-Hexadecane +Decanoic Acid</td>
</tr>
</tbody>
</table>

Foamability and foam stability of different systems considered in the phase behaviour study were examined by investigating effect of several parameters. First effect of surfactant concentration on the stability of IOS foam in the absence and presence of oil phase was investigated, where oil saturation was 5 volume percent. Then toward understanding the impact of oil saturation on foam stability, generated foam containing 1.0 wt% IOS was exposed upon different volume concentration of n-hexadecane.

The amounts of liquid volumes until reaching maximum value were measured, which obtained at different times depending on the surfactant concentration and oil saturation. In the next step, to demonstrate effect of salt and alkaline on the foam stability, half decay time of foam column generated using the 1.0 wt% IOS surfactant throughout the range of salt and alkaline concentration. Finally effects of in-situ soap generation and acid number on the stability of foam were investigated. All of foamability and foam stability experiments performed in this study are listed in Table 4.

### Table 4 Overview of the all foamability and foam stability experiments performed in this study.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Changing Parameters</th>
<th>Surfactant Concentration (wt%)</th>
<th>Electrolyte Type</th>
<th>Oil Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Surfactant Concentration</td>
<td>0.1 up to 2</td>
<td>NaCl</td>
<td>Without Oil</td>
</tr>
<tr>
<td>2</td>
<td>Surfactant Concentration</td>
<td>0.1 up to 2</td>
<td>NaCl</td>
<td>n-Hexadecane</td>
</tr>
<tr>
<td>3</td>
<td>Oil Saturation</td>
<td>1.0</td>
<td>NaCl</td>
<td>n-Hexadecane</td>
</tr>
<tr>
<td>4</td>
<td>NaCl Concentration</td>
<td>1.0</td>
<td>NaCl</td>
<td>Without Oil</td>
</tr>
<tr>
<td>5</td>
<td>Na₂CO₃ Concentration</td>
<td>1.0</td>
<td>Na₂CO₃</td>
<td>Without Oil</td>
</tr>
<tr>
<td>6</td>
<td>Na₂CO₃ Concentration</td>
<td>1.0</td>
<td>NaCl/ Na₂CO₃</td>
<td>n-Hexadecane +Decanoic Acid</td>
</tr>
</tbody>
</table>

### 4. Results and Discussion
#### 4.1. Phase behaviour investigation

Fig. 2 and 3 show the plots of solubilisation parameters \((V_o/V_s)\) and \((V_w/V_s)\) for three systems, where \(V_o\), \(V_w\), and \(V_s\) are volumes of oil, brine, and surfactant in the micro-emulsion phase, as estimated from
Fig. 2 illustrates phase behaviour of system containing 0.5 % active weight percent surfactant and Fig. 3 similar to Fig. 2 shows dependence of solubilisation parameter on salinity for the 1.0 wt% IOS surfactant equilibrate with hexadecane. In these two figures, data points of oil solubilisation ratio are connected with dashed line while water solubilisation ratio by dot line, and where two lines dedicated to each system intersect each other considered to be optimal point. Optimal salinity, where the two solubilisation parameters have equal values (V/Vs) is shown in Fig. 2 and 3, and for all examined system optimal salinities, solubilisation parameters (measured at optimal salinities) and optimal IFT are summarized in Table 5, 6. IFT at optimal salinity were obtained according to Chun-Huh’s theoretical relationships as given in equation (5) which correlates the solubilisation parameter and IFT of middle-phase micro-emulsion (type III).

**Figure 2** Solubilisation ratio of oil and water for systems containing 0.5 wt% IOS 2024 surfactant solution contacting hexadecane model oil with variation of NaCl concentration. ○ standard system 1; △ system containing 1% Alkali, ◊ system containing Alkali and Decanoic acid. —— connecting oil solubilisations ratio; —— connecting water solubilisations ratio.
Figure 3 Solubilisation ratio of oil and water for systems containing 1.0 wt% IOS 2024 surfactant solution contacting hexadecane model oil with variation of NaCl concentration. ○ standard system 1; △ system containing 1% Alkali, ◇ system containing decanoic acid. — connecting oil solubilisations ratio; ---connecting water solubilisations ratio.

Table 5 Experimental data of phase behaviour study for three type of chemical systems containing 0.5 wt % IOS20-24 surfactant at optimal condition.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Electrolyte</th>
<th>Oil Phase</th>
<th>Optimal Salinity (wt% NaCl)</th>
<th>Optimal Solublization Ratio</th>
<th>IFT at Optimal Salinity (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl</td>
<td>Hexadecane</td>
<td>3.27</td>
<td>5.9</td>
<td>9.19 E -3</td>
</tr>
<tr>
<td>2</td>
<td>NaCl- Na₂CO₃</td>
<td>Hexadecane</td>
<td>2.6</td>
<td>7.1</td>
<td>6.35 E -3</td>
</tr>
<tr>
<td>3</td>
<td>NaCl- Na₂CO₃</td>
<td>Acidic</td>
<td>1.12</td>
<td>15.95</td>
<td>1.19 E -3</td>
</tr>
</tbody>
</table>

Table 6 Experimental data of phase behaviour study for three type of chemical systems containing 1.0 wt % IOS20-24 surfactant at optimal condition.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Electrolyte</th>
<th>Oil Phase</th>
<th>Optimal Salinity (wt% NaCl)</th>
<th>Optimal Solublization Ratio</th>
<th>IFT at Optimal Salinity (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaCl</td>
<td>Hexadecane</td>
<td>4.15</td>
<td>9.75</td>
<td>3.37 E -3</td>
</tr>
<tr>
<td>2</td>
<td>NaCl- Na₂CO₃</td>
<td>Hexadecane</td>
<td>3.54</td>
<td>10.5</td>
<td>2.9 E -3</td>
</tr>
<tr>
<td>3</td>
<td>NaCl- Na₂CO₃</td>
<td>Acidic</td>
<td>1.92</td>
<td>19.9</td>
<td>6.86 E -4</td>
</tr>
</tbody>
</table>

Table 5 and 6 show the phase behaviour results that compare the optimal salinity, solubilisation ratio and IFT values of systems with and without alkali contacting with acidic and not acidic model oil.
The measured data indicate that the addition of both alkalis and surfactant to the water phase does not reduce the IFT substantially as also shown in Fig. 2. A much great reduction can be obtained by the generation of in-situ soap in the system. As a rule of thumb, systems that give larger oil recovery factors in porous media exhibit an IFT of nearly $10^{-3}$ dyne/cm. Indeed, values of $(V/V_s)$ exceeding 10 should lead to sufficiently low tensions for good recovery, a criterion met by all system containing 1.0% wt surfactant. However for system of 0.5 wt% we can only see for system with acidic oil where there is soap generation assisted IFT reduction.

This data suggests that this particular model oil develops with 1.0 wt % IOS surfactant lower interfacial tension than 0.5 wt%, and will be mobilized easier in the displacement experiments. As we made goal to design a chemical formulation for ASF flooding, this data indicate that impact of presence of alkali, soap generation and surfactant concentration on range of optimal salinity, solubilisation parameters and IFT values. This series of experiments can show the importance of high values of oil/water solubilisation ratio and consequently effect of amount of IFT reduction in displacement of oil in ASF flooding in the latter porous media experiment for the our future works. Moreover, the results indicates that use of suitable IOS surfactants is a promising approach for designing surfactant EOR processes for ASF flooding. This shows that this type of IOS surfactant can be used over a range of salinities that gives high solubilisation of oil at their optimal salinities.

4.2. Foamability and foam stability tests

4.2.1. Effect of Surfactant Concentration and Oil Saturation

This section is concerned with the effect of surfactant concentration with and without contacting oil and also effect of oil saturation on the foamability and foam stability. Firstly to investigate effect of the IOS surfactant concentration on the stability of foam, IOS concentration has been varied from 0.1 to 2.0 wt % IOS but in all other experiments the IOS concentration was kept constant at 1.0 wt%. Fig. 4 shows the evolution of liquid volume holdup in the foam as a function of time during foam generation and drainage after switching off airflow, varying surfactant concentration. Fig. 5 shows similar experiments in presence of oil. To gain further insight into effect of oil saturation on the foam properties, foam capacity ($FC$) and maximum density ($MD$) were measured as demonstrated in Fig. 6.

![Figure 4: Effect of IOS surfactant concentration in the absence of oil phase illustrated by the change in the liquid volume of foam during foam generation and after termination of gas sparging as a function of time. The initial liquid volume of the generated foam is 50 cm$^3$ and maximum volume of generated foam from IOS surfactant in the presence of oil phase using the foam scan are illustrated.](image-url)

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Figure 5 The change in the liquid volume of foam during foam generation and after termination of gas sparging as a function of time for the various oil saturation. The initial liquid volume of the generated foam is 50 cm\textsuperscript{3} and maximum volume of generated foam from 1wt\% IOS surfactant in the presence of oil phase using the foam scan is illustrated.

Data in Fig. 4 show that IOS foam grows linearly with time during foam generation. This indicates a stable build-up of foam volume. Thus from a straight line in the foam volume profile is inferred IOS foam evolution not to be affected by the destruction processes such as coalescence, gravity drainage, Ostwald ripening during foaming generation (Carey & Stubenrauch, 2009; Tcholakova et al., 2011). Fig. 4 also shows that liquid hols-up increases with surfactant concentrations. This can be explained
by the fact that the bubble size decreases with increasing surfactant concentration as visually observed during the experiments. Maximum volume of liquid inside the foam structure was increased as the oil saturation increased (Fig. 5). This observation can be supported by the variation of $FC$ and $MD$ (Fig. 6). A higher liquid volume in the foam is expected to lead to a larger drainage rate for the same surfactant solution and similar experimental conditions, which is indicated in Fig. 7 by depicting half decay time of 1.0 wt% IOS surfactant solution contacting with the range of oil saturation. In this case the foam generated in the presence of higher oil saturation has a higher $V_{L,max}$, which, in turn, leads to a higher drainage rate and a faster decrease of volume of foam compared to that generated foam interacting with lower oil saturation (Carey & Stubenrauch, 2009).

**Figure 7** Effect of different oil saturation of n-hexadecane on the foam half decay time generated from 1.0wt% IOS.

**Figure 8** Effect of IOS surfactant concentration on the foam half decay time in the absence and presence of 5.0 volume percent of n-hexadecane.
**Figure 9** Effect of the IOS surfactant concentration on the foam capacity (FC) in the absence and presence of 5 volume percent n-Hexadecane. The initial surfactant solution volume of the generated foam is 50 cc and in the case of presence of n-Hexadecane, oil saturation is 5 volume percent.

Fig. 8. displays half decay time $t_{1/2}$ in the presence of oil is systematically lower, and it increases with surfactant concentration. Foam stabilized 0.1 wt% IOS was the least stable, with the $t_{1/2}$ which nearly 1/2 compared to foam in absence of oil. As shown the FC coefficient is larger than unity even for the foam stabilized by a low surfactant concentration of 0.1 wt% (Fig. 9). The FC coefficient for foam in the presence of oil is systematically lower than that in the absence of oil. The difference in the FC coefficients can be attributed to the gas sparging time. Recall that the FC coefficient was defined as a ratio of foam volume at the end of gas sparging, to total volume of gas injected. This infers injection of a larger volume of gas, and resulting a smaller value of the FC coefficient (Simjoo et al., 2013). From the data in Fig. 9 it can also be seen that the MD coefficient of freshly generated foams as a function of surfactant concentration in the absence and presence of n-hexadecane. The MD and FC coefficients increased with surfactant concentration and oil saturation.

### 4.2.2. Effect of Salt and Alkaline

Illustrated in Fig. 10 concentrations of salt and alkaline increase up to 5.0 wt%. This is the considered the limit concentration for the application of generated IOS foam in the ASF flooding according to the results of optimal salinity from phase behaviour study (section 4.1). From Fig. 10 it can be seen that addition of salt (NaCl) and alkali (Na$_2$CO$_3$) to the IOS foaming system can have some effect on the reduction of the foamability and foam stability. Maximum density of the generated foam also decreases which means ability of foam to hold the liquid volume inside the foam diminishes (Fig. 11.). Such effects have been associated to the cationic-anionic-type interaction between the anionic moiety of the IOS surfactant and cation ion of the salt and alkali, resulting in screening the repulsive forces between the ionic head group. Consequently this causes the reduction of the repulsion between the surfactant layers or the opposing film interfaces, which in turn leads to faster film drainage. Therefore the change in foam height with electrolyte concentration might be associated with the change in the micelle structure from spherical shape to other more complex structures.
4.2.3. Role of Soap Generation

The effect of surface tension on the transients of foam drainage is shown in Fig. 12. The figure shows the foam volumes versus time for varying combinations of alkali concentration in the aqueous phase and acid number in oleic phase. It can be seen that by increasing alkali concentration from 0.5 wt% to 1.0 wt% stability of foam increases. This can be interpreted by the fact more amounts of in-situ soap generation in the system helps to stabilize foam, because addition of alkali means more amount of in situ soap generation. But for the surfactant solution containing 2.0 wt% alkali, rate of drainage is
larger than system containing 1.0 % alkali (Fig. 12). Thus drainage is faster and the extent of drainage larger for the cases with high amount of soap generation. This can be explained by the fact that the gas-liquid interface is more mobile at smaller surface tension, which tends to increase the rate of liquid drained out of the plateau border. This dropping of liquid occurs during initial liquid holdup and also drainage. At smaller surface tensions, the driving force due to gradient of plateau border suction (which opposes gravity) is smaller and, therefore, the rate of foam drainage is greater. Thus uneven thinning and instabilities of the film might happen which will cause accelerating film drainage and rupture.

![Graph showing foam volume as a function of time for different alkali concentrations with and without acid](image)

**Figure 12** Foam volume as a function of time for 0.5 wt% IOS foam contacting n-hexadecane in the absence and presence of naphthenic acid (Decanoic acid). Effect of in situ soap generation and surface tension on the stability of foam illustrated.

The reason for the observed behavior is not completely clear. This observation could be also interpreted by the rapid spreading of an oil drop that has a low surface tension over the lamella and subsequently can cause pre-mature rupture by providing weak spots. The spreading oil by augmenting the curvature radius of the bubbles lowers the original surface elasticity and surface viscosity. Thus the interfacial film loses its foam stabilizing capability.

### 4.2.4. Entering, spreading and bridging coefficient and lamella number:

Table 7 displays entering, spreading, bridging coefficients and lamella number obtained by combining the measured ST, IFT between surfactant solution/model oil, surfactant solution/air and model oil/air. The purpose of obtaining these phenomenological parameters was to get insight for any correlation between aforementioned coefficients and bulk foam stability in the presence of oil. All the surfactant solutions exhibit a positive entering coefficient ($E>0$), indicating favourable conditions for n-hexadecane and acidic n-hexadecane to enter the gas–water interface. Thus foam stability will be determined by the magnitude and sign of the spreading $S$ and bridging $B$ coefficients.

Among the systems studied, system 1, 2 provide the negative spreading coefficients, but these systems showed the largest positive $B$ coefficients. This indicates that generated foam should be relatively stable in the presence of n-hexadecane, which is in very good agreement with the observed decay behaviour in Fig. 8.
Table 7 Entering, spreading, and bridging coefficients and lamella number for different studied systems in the presence of n-hexadecane. Surfactant concentration was fixed at 1.0 wt%.

<table>
<thead>
<tr>
<th>System</th>
<th>Entering Coefficient (mN/m)</th>
<th>Spreading Coefficient (mN/m)</th>
<th>Bridging Coefficient (mN/m)^2</th>
<th>Lamella Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 IOS/Hexadecane</td>
<td>22.85</td>
<td>-2.59</td>
<td>784.899</td>
<td>0.4224</td>
</tr>
<tr>
<td>2 IOS-Alkali/Hexadecane</td>
<td>30.64</td>
<td>-6.48</td>
<td>1106.712</td>
<td>0.304</td>
</tr>
<tr>
<td>3 IOS/Acidic Hexadecane</td>
<td>13.62</td>
<td>13.62</td>
<td>440.594</td>
<td>0.812</td>
</tr>
<tr>
<td>4 IOS-Alkali/Acidic Hexadecane</td>
<td>10.74</td>
<td>10.74</td>
<td>468.236</td>
<td>4.172</td>
</tr>
</tbody>
</table>

Foam stability can be examined further by comparing the value of lamella number. System 1, 2 exhibit a lamella number less than unity, which corresponds to type A foam. According to Table 2, type A foam is a very stable foam in the presence of oil with a negative S coefficient. However, this is not in line with the calculated E and S coefficients in Table 7, and also not with the observed foam stability in Fig. 8, particularly for the cases with the absence of organic acid (Decanoic acid), which was rather sensitive to the oil phase.

The spreading coefficients calculated from interfacial tension measurements for the acidic model oils were positive for the IOS surfactant (Table 7). By theory, in such a situation the oil would spread at the surface and break the foam. If the spreading coefficient were negative, the literature suggests that the oil would remain a droplet at the surface, and this defines a necessary condition for stable foam (Koczo et al., 1992; Nikolov et al., 2013). Systems 3 and 4 had positive spreading and entering coefficients, indicating type C foams. Foam stability in the presence of the acidic oils does not seem to be governed by this type of classification. For all IOS foams generated in the presence of oil the bridging coefficient was large and positive (Tables 5). This indicates that the bridging mechanism may induce film rupture. System 4 exhibited type-B foam behaviour which indicates foam stability in the presence of soap generation could be related to transport properties within the foam.

Previous work has shown that type-B foams have the capacity to transport more oil than type-A or type-C foams by carrying emulsified oil droplets inside the foam structure while retaining a moderate degree of stability to oil (Vikingstad et al., 2005). Thus we could conclude that a negative spreading coefficient is not a necessary condition for stable foam, and stability of foam in the presence of oil could be attributed to transport properties within the foam lamella (Vikingstad et al., 2006). Based on the coefficients, IOS foam is predicted to generate more stable foams when mixed with soap generated by interaction of alkali and naphtenic acid of oil phase.

Conclusion

1- A surfactant formulation which gives ultralow interfacial tensions at the optimum salinity and has good foaming characteristics was experimentally investigated.
2- Phase behaviour study of particular system in this work demonstrated the impact of presence of alkali, soap generation and surfactant concentration on range of optimal salinity, solubilisation parameters and IFT values.
3- Impact of alkali on foam stability could be attributed either to screening the repulsive forces between the ionic head group resulted from cationic-anionic-type interaction or the change in the micelle structure from spherical micelles to other more complex structures.
4- Solubilisation ratio of 10, as criterion to get the sufficiently low tensions for good recovery, met by all systems containing 1.0 wt% surfactant. However for system of 0.5 wt% we can only see for system with acidic oil where there is soap generation assisted IFT reduction.
5- High amount of in-situ soap generation resulted diminishing foam stability.
The classical phenomenological parameters such as spreading and entering coefficients have been used with some success and similarities in trend, but foam performance does not correlate the foam stability to oil for all experiments.

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