THE EFFECT OF OILFIELD CHEMICALS ON THE SURFACE TENSION OF SURFACTANT SYSTEMS

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ABSTRACT

Treated sea water is the most significant source of water and surfactant floods. The various chemicals employed in treatment plants should be compatible with surfactant systems. Based on surface tension experiments, the activity of these chemicals is examined over a wide range of concentrations in different solutions, including distilled water, sea water by using three types of surfactant mixtures. For this purpose, the conventional chemicals of a typical water treatment plant, namely scale inhibitor, corrosion inhibitor, biocide, O2 scavenger, coagulant, and antifoam, were selected. The results show chemicals are completely compatible with the surfactant systems in concentrations utilized for an oilfield dosage. Scale inhibitor, O2 scavenger, and coagulant did not show any surface properties, but the positive effects of the other chemicals on the reduction of the surface tension were observed. The interaction of active chemicals was evaluated using response surface methodology. The results demonstrate that antifoam had more significant effects on the reduction of the surface tension than corrosion inhibitor and biocide.

Keywords: Oilfield Chemicals, Surface Tension, Surfactant, Response Surface Methodology, Water Flooding

INTRODUCTION

Surface tension is one of the most important parameters of surface chemistry. An accurate method to investigate the interaction and association of chemicals and biochemicals is the measurement of surface tension [1-3]. It can also be applied to thermal stability studies [4].

The surface tension of water arising from hydrogen bonds formed between water molecules can be changed by the act of surface active agents. A decrease in the surface tension values indicates the tendency of molecules of these agents towards adsorption at the water interface. The accumulation of molecules at the air–water interface is calculated according to the term of surface pressure (∂γ/∂log C). The high amount of accumulation of the molecules of the chemicals which act as surface active agents increases the surface pressure of the interface. Gibbs adsorption isotherm (Equation 1) calculates the maximum surface excess value (Γmax) of these mixtures.

\[
\Gamma_{\text{max}} = \left(\frac{1}{nRT}\right)\left(\frac{\partial \gamma}{\partial \ln C}\right)
\]

(1)
where, \( R \) is the gas constant, \( T \) is temperature, and \( C \) is concentration [5].

Surface and interfacial tension of injection fluids have a direct influence on the capillary forces of reservoir fluids, particularly in secondary (i.e. water flooding) and tertiary oil (especially chemical flooding) recoveries. It can be easily understood from the Young-Laplace equation for capillary tube (Equation 2):

\[
\Delta P = \frac{2\sigma \cos(\theta)}{R}
\]

where, \( \Delta P \) is the capillary pressure, \( \sigma \) is the surface tension, \( \theta \) is contact angle, and \( R \) is the pore radius [6,7].

The effects of various chemical additives on the surface and interfacial tension of different fluids have been investigated in the literature. Krumrine et al. studied the effect of alkaline additives on the surface tension, adsorption, and desorption of surfactants. The results showed that they could decrease the interfacial tension of alkaline-surfactant systems with a high pH value. Another positive effect is the reduction of surfactant retention in porous media. These effects can increase oil production from 40% to 70% [8].

Al-ghamdi and Nasr-El-Din carried out research on the effects of oilfield chemicals on the clouding point of anionic surfactants. A wide range of chemicals containing simple salts, alkalis, acids, polymers, scale and corrosion inhibitors, biocides, a mutual solvent, and a crude oil were selected. They concluded that these chemicals affected clouding point and the effect was dependent on the number of ethylene oxide groups of the surfactant [9].

Dabbousi et al. investigated the effect of oilfield chemicals on the surface tension of well stimulating fluids. A wide range of acidizing and stimulating additives were selected. They found that the surface tension of stimulating acids was a function of the type and concentration of acid and its additives. As an example, the effect of ionic surfactant on the reduction of surface tension was twice as marked as non-ionic surfactants. Furthermore, \( \text{H}_2\text{S} \) inhibitor decreased the surface tension of acid, while clay stabilizer had no considerable effect [10].

Amro evaluated the effect of scale and corrosion inhibitors on the well productivity in reservoirs containing asphaltene. The experiments were limited to these 2 chemicals at a constant concentration of 200 ppm. They demonstrated that corrosion inhibitors considerably reduced surface and interfacial tension, while scale inhibitors showed no significant effect [11].

Nasr-El-Din et al. measured the surface tension of completion fluids at temperatures up to 150 °C and densities up to 93 pcf. Furthermore, the effects of commonly used chemicals on the surface tension of completion brines were also investigated. They concluded that surface tension of completion brines increased linearly with salt concentration except for sodium formate solutions. Xanthan gum (except in the presence of sodium carbonate), non-ionic surfactants, methanol, and temperatures up to 150 °C decreased the surface tension of completion brines, while polyanionic cellulose and increasing pH had no significant effect [12].

Bataweel et al. evaluated the association of polymers and surfactants in terms of the surface tension variations and polymer-free aggregates. They measured the surface tension of amphoteric surfactants at different concentrations in the presence of polymer [2].

Saneifar et al. tested different types and concentrations of acid additives, including corrosion inhibitors, iron control agents, mutual solvents, methanol, acetic, and formic acids on the surface tension of spent acids at high temperature (up to 150 °C) and pressure (1000
psi). They concluded that corrosion inhibitors decreased surface tension of spent acid while other chemicals had no effect [13].

Previous researches concluded that surface properties of EOR, stimulation, and workover fluids are sensitive to the addition of pertinent chemicals. Therefore, the response of surface tension in the presence of different chemicals should be investigated comprehensively in individual processes from drilling to production operations. The effect of oilfield chemicals commonly used for the treatment of sea water on the surface tension of different injection fluids has not been considered yet. The objective of the current study is to evaluate the compatibility and effect of these oilfield chemicals on surfactant mixtures based on surface tension measurements. Thus the interactions of effective parameters are studied using response surface methodology.

Response surface methodology (RSM) consists of a collection of mathematical and statistical techniques, which can be well utilized when a response or a set of responses of interest are influenced by several associated variables. As a statistically designed experimental protocol, it is used for designing experiments, developing functional relationship between a response and a number of related factors through analyzing their interactions, and optimizing the levels of these factors to attain the best process performance [14-17].

MATERIALS AND METHODS

Chemical Preparation and Characterization

Common oilfield chemicals (industrial grade) used in the typical water treatment plant of offshore oilfields under water flooding were employed in this work. The main composition or basis of oilfield chemicals used in this study is presented in Table 1.

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**Figure 1: Schematic of the water treatment plant**

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Table 1: Characteristics of oilfield chemicals used in water treatment plant

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Main component</th>
<th>pH</th>
<th>σ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion inhibitor</td>
<td>Alkyl dimethyl benzyl ammonium chloride</td>
<td>8</td>
<td>33.8</td>
</tr>
<tr>
<td>Scale inhibitor</td>
<td>Phosphonic acid salts</td>
<td>5.5</td>
<td>57.3</td>
</tr>
<tr>
<td>Biocide</td>
<td>Aldehyde</td>
<td>4.5</td>
<td>40.1</td>
</tr>
<tr>
<td>O₂ scavenger</td>
<td>Ammonium bisulfite</td>
<td>5</td>
<td>75.7</td>
</tr>
<tr>
<td>Coagulant</td>
<td>Cationic polymer</td>
<td>6</td>
<td>57.6</td>
</tr>
<tr>
<td>Antifoam</td>
<td>Fatty acid ester</td>
<td>6</td>
<td>26.1</td>
</tr>
</tbody>
</table>

All the chemicals were in liquid state. Table 2 shows the analysis of sea water used in this study.

Table 2: Analysis of sea water

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>23000 mg/l</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3350 mg/l</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>166 mg/l</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2996 mg/l</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>267 mg/l</td>
</tr>
<tr>
<td>Na⁺</td>
<td>11750 mg/l</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>3.4 mg/l</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.42 mg/l</td>
</tr>
<tr>
<td>TDS</td>
<td>40270 ppm</td>
</tr>
<tr>
<td>Salinity</td>
<td>3.5%</td>
</tr>
<tr>
<td>pH</td>
<td>7.7</td>
</tr>
</tbody>
</table>

The type and concentration of surfactants (all from Merck) are listed in Table 3. One of the most important properties of surfactants is the critical micelle concentrations (CMC) [18]. This parameter is of interest for theoretical studies as well as practical applications [19]. Having this point of view, we selected the concentration of surfactants in the vicinity of their CMC (C₁₆TAB [20], Triton X100 [21], SDS [22]). After the preparation of surfactant mixtures, they were stored for 8 hours to stabilize.

<table>
<thead>
<tr>
<th>Surfactant type</th>
<th>Molecular weight (g/mmol)</th>
<th>Purity (%)</th>
<th>Concentration (M)</th>
<th>σ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₆TAB</td>
<td>364.46</td>
<td>&gt; 97</td>
<td>1.1 × 10⁻³</td>
<td>36.0</td>
</tr>
<tr>
<td>SDS</td>
<td>288.38</td>
<td>&gt; 85</td>
<td>8 × 10⁻³</td>
<td>34.6</td>
</tr>
<tr>
<td>Triton X100</td>
<td>646.86</td>
<td>98-100</td>
<td>2.4 × 10⁻⁴</td>
<td>30.1</td>
</tr>
</tbody>
</table>

**Design of Experiments**

In the first attempt, the effects of chemicals were evaluated. The compatibility of oilfield chemicals with surfactant systems and the determination of effective (active) chemicals which cause the variation of fluid surface tension were the objectives of the current experiments. For this purpose, five series of experiments were designed. In each one, the basic fluid was different, namely distilled water, sea water and sea water containing cationic, anionic, or nonionic surfactants.

Each chemical was evaluated in a wide range of concentrations because their concentration may change from one plant to another (25, 50, 100, 250, 500, 1000, 2500 ppm). Having 6 chemicals and 7 concentrations, the number of experiments reached 42 in each of the basic fluid.

For each individual experiment, a chemical with determined concentration was injected into 20 ml basic fluid using a micro syringe (Hamilton) and stirred for at least 1 minute to solve completely.

Following this, active components were selected to evaluate their interactions using RSM, central composite design (CCD). Design Expert 7 was used as the experimental design software package. The number and levels of factors were consequently determined by the results of the first part. To stabilize probable interactions, the prepared samples were stored overnight and then the surface tension was measured.

**Surface Tension Measurement**

The surface tension of the sample was
measured using Du Noüy ring method (Krüss K10). For this purpose, a sample was poured into a glass container and placed in a measurement zone. The measurement ring was zeroed in air after the ring was installed. Then, the ring was pulled down such that it was suspended on the surface of the liquid. Finally, the fine adjustment of the tensiometer was set to zero, the measurement was initiated, and terminated when the upward pulling force on the ring just balanced the downward force exerted by the fluid. All the measurements were carried out three times at ambient temperature and the average value was reported. As the experiments were performed on different days, for the calibration of the apparatus, the surface tension of distilled water (blank experiment) was measured as the last sample of the day.

RESULTS AND DISCUSSION

Effect of Oilfield Chemicals on the Surface Tension of Surfactant Systems

The goal of secondary and tertiary oil recoveries is production surveillance or the enhancement of recovery. Sea water is an appropriate source of water supply for chemical EOR methods. It must be treated to prevent formation damage, which is one of the biggest challenges of these methods. Water plants use different types of chemicals in the treatment process; thus their compatibility with EOR chemicals is important from an engineering point of view. The role of chemicals on the variation of the surface tension of injection fluids is a good indicator for the characterization of their compatibility.

In this study, the effects of 6 oilfield chemicals commonly used in water treatment plants on the surface tension of different injection fluids were evaluated. Distilled water was selected as one of the basic fluids due to better understanding of the effects of oilfield chemicals. Otherwise, the application of distilled or even fresh water is limited as an injection fluid.

The solubility (compatibility) of the chemicals was satisfying even in sea water and at high concentrations; however, antifoam, due to dispersion rather than dissolution, made an exception at concentrations higher than 250 and 100 ppm for distilled and sea water respectively. Fortunately, the applied dosage of this chemical in the treatment plant is less than its critical concentrations.

Scale inhibitor, coagulant, and O2 scavenger have no significant effect on the surface tension of different injection fluids. The surface tension of distilled water was measured as 71.8 mN/m at 25 °C (71.97 mN/m reported in the literature [23]). The addition of these chemicals did not affect the surface tension of distilled water, even at different concentrations. The surface tension of sea water was measured to be about 61 mN/m, which was not influenced by the presence of the above chemicals. The results were the same when the surfactant mixtures were investigated. The surface tension of C16TAB, Triton X100, and SDS at ambient temperature was measured approximately 36, 34.6, and 30.1 mN/m respectively (Table 3). Measurements indicated that even an increase in the concentration of these chemicals (up to 2500 ppm) did not change the surface tension of surfactant mixtures.

Phosphonic acids, as the main basis of scale inhibitors, are organic compounds which are known as effective chelating agents. They bind tightly to di-and trivalent metal ions, preventing them from forming oilfield scale. Current coagulant is composed of polyelectrolyte polymers. They aid the process of destabilization by charge neutralization. Once neutralized, particles no longer repel each other and can be brought together. Coagulation process before sand filters is necessary for the better removal of the colloidal-sized suspended particles. The
Figure 3 indicates that corrosion inhibitor had a positive effect on the surfactant systems. By adding this chemical, the surface tension of C16TAB, Triton X100, and SDS mixtures was finally reduced to 2.9, 1.2, and 3.1 mN/m respectively.

![Graph 3: Effect of corrosion inhibitor on the surface tension of surfactant mixtures](image)

Figure 3: Effect of corrosion inhibitor on the surface tension of surfactant mixtures

The main component of this corrosion inhibitor is alkyl dimethyl benzyl ammonium chloride (ADBAC). Due to the presence of hydrophilic and hydrophobic moieties within the same molecule, this organic corrosion inhibitor is identified as a surfactant (Figure 4).

![Graph 4: The surfactant feature of ADBAC molecule](image)

Figure 4: The surfactant feature of ADBAC molecule

The group of quaternary ammonium makes it a nitrogenous cationic surfactant, which leads to a reduction in the surface tension of the fluids studied. The application of surface active agents in the composition of corrosion inhibitors increases the inhibition efficiency [24]. The results of scale and corrosion inhibitors over a wide range of concentrations confirm the results obtained by Amro [11], although the concentra-
tions were kept constant (200 ppm) therein.

The effects of biocide are presented in Figures 5 and 6. Figure 5 shows that the surface tension of sea water was more sensitive to the variations of concentration compared to distilled water. It was reduced from 61 to 32 mN/m (29 units) and from 64 to 50 mN/m (14 units) for sea water and distilled water respectively over biocide concentration range.

Figure 5: Effect of biocide on the surface tension of distilled and sea waters

Considering the surfactant mixtures, the results of the corrosion inhibitor were repeated (Figure 6). The surface tension of C_{16}TAB was decreased to 1.2 mN/m, whereas the other mixtures had just changed 1 mN/m over biocide concentration range.

Figure 6: Effect of biocide on the surface tension of surfactant systems

There is a quaternary biocidal surfactant in the chemical composition of this biocide (5-10 %). Such components are often employed in the mixture of biocides [25]. It seems that surface activity of this biocide is assigned to this component.

Figure 7 shows that antifoam decreased the surface tension of distilled and sea water with similar trends. Antifoam had the most significant effect and reduced the surface tension to 28.5 mN/m. It hinders the formation of foam bubbles via severe reduction of the surface tension. This separates particles stabilizing foam from air-liquid surfaces and causes rupture of the bubbles.

Figure 7: Effect of antifoam on the surface tension of distilled and sea waters

Moreover, it had a greater effect on the surface tension of surfactant mixtures compared to corrosion inhibitor and biocide (Figure 8), although the mixture of Triton X100 containing lower concentrations of biocide revealed a slightly different trend. The values of reduction for three types of surfactants were measured 4.7 mN/m (C_{16}TAB), 4.7 mN/m (Triton X100), and 2.2 mN/m (SDS). The effectiveness of antifoam is attributed to its mechanism.

Several important points can be drawn from the results of these three chemicals, although further experiments may be required for more detailed discussion due to the industrial grade of the current oilfield chemicals and the nature of sea water, containing different types of salt.
First, their effects on the surface tension of distilled and sea water showed different trends. Although both corrosion inhibitor and biocide had quaternary ammonium components, their behaviors were completely different in distilled and sea water. However, trends were similar for antifoam. The solubility of surface active agents in the solvent plays a critical role in their stability and consequently their efficiency. Comparing the structure of these organic components, we find that they have different lengths of carbon chain. It is clear that organic components containing longer chains of carbon have less solubility in electrolyte solvents (e.g. sea water). In this case, ADBAC (the base of corrosion inhibitor) has longer chains of carbon in comparison with aldehyde (the base of biocide) and its solubility and stability in sea water decreases at higher concentrations. Therefore, the reduction of the surface tension of sea water containing corrosion inhibitor is less than sea water containing biocide over a range of concentrations. However, fatty acid ester (the base of antifoam) has very long chains. The turbidity of distilled and sea water started when 250 and 100 ppm of antifoam were added respectively. Hence antifoam is dispersed (insoluble) in sea and distilled water and it is resulted in the similar trends of the surface tension.

Second, their effects on the surface tension of surfactant mixtures were positive but insignificant compared to the distilled and sea water. On the other hand, the addition of these chemicals having surface active agents could help a further reduction in the surface tension of surfactant mixtures in the vicinity of CMC. Although the surface tension of surfactant mixtures becomes constant at CMC and higher concentrations (the general definition of CMC), they showed synergistic interactions with surfactant mixtures.

Interaction of Effective Parameters

The results of the previous experiments determined the active chemicals as follows: corrosion inhibitor, biocide, and antifoam. The interactions of these factors were studied using RSM, CCD method. Distilled water was selected as the base media for the preparation of chemical solutions. The range of variables was defined by zero as the minimum (coded -alpha) and CMC in distilled water as the maximum (coded +alpha) concentrations. Due to the incompatibility of antifoam at concentrations higher than 100 ppm, this concentration was assigned as the upper boundary of this factor, although its CMC was measured 500 ppm (Figure 7).

16 runs were designed and done, in which two additional measurements were performed for each experiment to confirm the reproducibility of the results (Table 4).

Perturbation plot helps with comparing the effects as shown in Figure 9. The response is plotted by changing only one factor over its range while holding the other variables constant (at their midpoints, coded 0). Figure 9 indicates that antifoam has the greatest effect on the reduction of the surface tension in the presence of other chemicals, because its curve shows both curvature and steep slope.

The interactions of chemicals are presented in Figures 10 and 11. The results show that the
interaction between antifoam and corrosion inhibitor was more important than its interaction with biocide.

Table 4: CCD runs and corresponding results

<table>
<thead>
<tr>
<th>Run</th>
<th>Factor1: Ccorr. inh. (ppm)</th>
<th>Factor2: Cbiocide (ppm)</th>
<th>Factor3: Cantifoam (ppm)</th>
<th>Response: surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>80</td>
<td>20</td>
<td>34.8</td>
</tr>
<tr>
<td>2</td>
<td>125</td>
<td>100</td>
<td>50</td>
<td>32.4</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
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<td>20</td>
<td>34.5</td>
</tr>
<tr>
<td>4</td>
<td>125</td>
<td>50</td>
<td>50</td>
<td>32.9</td>
</tr>
<tr>
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<td>50</td>
<td>32.3</td>
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<td>200</td>
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<td>9</td>
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<td>50</td>
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<td>10</td>
<td>50</td>
<td>80</td>
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<td>16</td>
<td>0</td>
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<td>50</td>
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</table>

Table 5: The analysis of variance for RSM model

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<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F value</th>
<th>p-value</th>
<th>Prob&gt;F</th>
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</thead>
<tbody>
<tr>
<td>Model</td>
<td>379.34</td>
<td>6</td>
<td>63.22</td>
<td>2.56</td>
<td>0.0996</td>
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</tr>
<tr>
<td>Residual</td>
<td>222.66</td>
<td>9</td>
<td>24.74</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Lack of fit</td>
<td>222.48</td>
<td>8</td>
<td>27.81</td>
<td>154.50</td>
<td>0.0621</td>
<td>-</td>
</tr>
<tr>
<td>Pure error</td>
<td>0.18</td>
<td>1</td>
<td>0.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 9: Perturbation plot of RSM model

Figure 10: Interaction of antifoam (C) and corrosion inhibitor (A)

Figure 11: Interaction of antifoam (C) and corrosion inhibitor (A)

CONCLUSIONS

An experimental study was conducted to examine the effect of oilfield chemicals used in water treatment plant on the surface tension of different water and surfactant systems. The following conclusions were drawn:

- All the chemicals had compatibility with fluids studied at the concentrations used in water treatment plant according to surface tension measurements;
- Corrosion inhibitor and biocide reduced the surface tension of distilled and sea water
considerably, while the most significant effect was related to antifoam;

- The interaction of antifoam with corrosion inhibitor was more important than its interaction with biocide;

- The addition of corrosion inhibitor, biocide, and antifoam showed a synergistic effect on the surface tension of surfactant mixtures (cationic, anionic, and nonionic);

- Scale inhibitor, coagulant, and O$_2$ scavenger had no considerable effect on the surface tension of distilled water, sea water, and three types of surfactant mixtures;

- In this study, the solubility and stability of effective chemicals were determinative parameters, while the variation of the surface tension was not sensitive to the type of surfactants.

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