Effect of Salinity, pH, and Temperature on Stability of Gas Condensate in Water Emulsions Using Different Surfactants

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ABSTRACT: Light hydrocarbons in water emulsions are formed in many gas refinery wastewaters, and its stability depends on some parameters such as temperature, pH and salinity. In this study, different surfactants have been used to prepare gas condensates in water emulsion along with four surfactant kinds namely, Span 80, Tween 80, CTAB, SDS and Span 80 and Tween 80 mixture. For this purpose, the effects of temperature (25 and 60° C), pH (3, 5, 7 and 11) and salinity (2, 10 and 26 wt. % NaCl in water) on the stability of the emulsion have been studied. In order to evaluate the stability of these emulsions, the droplet size distribution was measured by an optical microscope. The results confirm that the increasing of salinity, as well as temperature of non-ionic surfactants (Such as Span 80 and Tween 80), lead to more stability of the emulsion. The increasing temperature didn’t have dominant effect on the stability of those emulsions which contain the ionic surfactants i.e., CTAB and SDS. Those emulsions formed by the combination of Span 80 and Tween 80 are more stable than the other ones. Results of the investigation the effect of pH on the emulsion stability clear that the emulsions are less stable at high pH than other ones.

KEYWORDS: Stability; Gas condensate in water emulsion; Droplets size distribution; Surfactant.

INTRODUCTION
An emulsion is an association of two liquids which are immiscible normally and one liquid dispersed in the other one in the form of droplets [1-2]. Correspondingly, an emulsion is a homogenous mixture of very fine droplets that are suspended in each other [3-5]. Oil and water emulsions called water-in-oil and oil-in-water emulsions depending on continuous and dispersed phases. Oil droplets in oil–water emulsions can remain in suspension for a relatively long time depending on charges of surface, specific gravity, surface tension and solubility characteristics [1-2, 6-7].

Emulsions are fundamental in many applications (food processing, petroleum and detergent industries) and industrial products (foods, pharmaceuticals or cosmetics). In specific, Oil-in-Water (O/W) emulsions are used in industrial operations involving two immiscible fluids and emulsifier agents which allow emulsion formation and stabilization [8-9]. The emulsion of hydrocarbon components in water is found, usually in the wastewater of refineries in which there is a small fraction of gas condensates in water [10]. In order to increase emulsion stability, which is a key factor for
its commercial applications, the use of emulsifiers such as proteins or surfactants is essential [11-13]. The role of emulsifiers in emulsion formation and stabilization has been extensively described in the literature of food colloids [14].

An aqueous phase, an oil phase and a surfactant (Surface active agents) are required to prepare an emulsion solution. If these two phases are mixed with surfactant using an agitator, an emulsion mixture is prepared [15-17]. When a surfactant is added in a negligible amount, water surface tension decreases considerably. Chemical structure of these materials often consists of a relatively long molecule with an hydrophobe end and a hydrophilic end. The hydrophilic group is polar and is attracted by water while the hydrophobic group is non-polar and is mainly a long -chained hydrocarbon and is absorbed by oil.

If an emulsifier contains charged groups, absorption results in the generation of charged fine droplets which repulses each other [3-5, 17]. Surfactants are classified in three main categories of anionic, cationic and non-ionic activation materials [3-5]. Selection of surfactant to form an emulsion has a special formulation which depends on the balance of hydrophilic-lipophilic groups. Hydrophilic–Lipophilic Balance (HLB) is a parameter which has a specific value for each surfactant and a special surfactant which has a given HLB must be used to develop an emulsion solution [9, 19-20]. In some cases, lipophilic surfactants and in some other cases hydrophilic surfactants are used to develop an emulsion solution, and sometimes combinations of them are used for which the HLB is between those materials [21-23].

Emulsion stability is strongly influenced by temperature, pH, salinity and several other parameters that have been studied by some researchers with different methods [24-32].

Oil droplets in water are stabilized by a monolayer of surfactant and/or co-surfactant molecules enveloped around these droplets [33]. One of the methods of evaluating the stability of emulsions is via distribution of droplets size of dispersed phase within the continuous phase. Microscopy techniques have been used in analysis of colloidal suspensions, particles, and aggregated sediments to examine the characteristics of particles [34]. A number of droplet size distribution methods have been used to characterize of droplets in emulsion [2, 8, 35-38]. One common way to characterize the size distribution of the emulsions is the use of parameters that indicate the dispersion, such as median drop size, Sauter mean diameter, and diameter of the largest stable drop size [8, 32]. Stability of emulsions containing larger drops is lower at equivalent other conditions [39, 32].

The objectives of this study were to determine the droplets size distribution of gas condensates in water to determine emulsion stability. For this purpose, the microscopic images of the gas condensate in water emulsion were obtained by laboratory optical microscope. Effects of salinity, pH and temperature were investigated on the stability of gas condensate in water emulsion using different surfactants.

**EXPERIMENTAL SECTION**

**Materials**

All general chemicals (surfactants) used were purchased from Sigma Aldrich Chemical Company. Distilled water was used for the preparation of all solutions. SDS (purity > %99), Tween 80 (purity > %99), Span 80 (purity > %99) and CTAB (purity > %99) surfactants were used to develop the emulsion of gas condensate donated by the South Pars Gas Company in distilled water. Table 1 shows the formulation of surfactants with their HLB values. The characterization of gas condensate was obtained by Gas chromatography (Vinci, France) and for the determination of boiling point range, the petro test apparatus (made in Germany) was used according to the ASTM D86. The main components of gas condensate were C5-C14. Table 2 shows characterization of the used gas condensate. An optical microscope (Nikon, E400, Japan) equipped with a display was used to observe the droplets of hydrocarbon compounds.

**Emulsions preparation**

In this work, the effects of four kinds of surfactants (SDS, CTAB, Span 80 and Tween 80) with different HLBS on the formation of gas-condensate in water emulsion were studied. For the preparation of emulsions containing 3 vol. % gas condensate in water, 200 ppm of each surfactant in different temperatures (25, 60 °C), pH (3, 5, 7 and 11) and salinities (2, 10 and 26 wt. % NaCl) were used. The emulsion container was 150 mL which had a 100 mL working volume and the mixtures were mixed.
Table 1: Characterization of used surfactants.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formulation</th>
<th>HLB</th>
<th>Type</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Span 80</td>
<td>C_{24}H_{45}O_6</td>
<td>4.3</td>
<td>Non-ionic</td>
<td><img src="image1.png" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>Tween 80</td>
<td>C_{64}H_{125}O_{26}</td>
<td>15</td>
<td>Non-ionic</td>
<td><img src="image2.png" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>CTAB</td>
<td>(C_{10}H_{21})N(CH_3)_3Br</td>
<td>10</td>
<td>Cationic</td>
<td><img src="image3.png" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>SDS</td>
<td>CH_{3}(CH_2)_11OSO_3Na</td>
<td>40</td>
<td>Anionic</td>
<td><img src="image4.png" alt="Molecular Structure" /></td>
</tr>
</tbody>
</table>

Table 2: Characterization of used gas condensate.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15°C (Kg/m³)</td>
<td>741</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>113</td>
</tr>
<tr>
<td>Boiling point range (°C)</td>
<td>52-227</td>
</tr>
<tr>
<td>Mass fraction of N. Paraffins</td>
<td>0.223</td>
</tr>
<tr>
<td>Mass fraction of ISO. Paraffins</td>
<td>0.4115</td>
</tr>
<tr>
<td>Mass fraction of Naphthenes</td>
<td>0.2444</td>
</tr>
<tr>
<td>Mass fraction of Aromatics</td>
<td>0.1174</td>
</tr>
<tr>
<td>Mass fraction of Saturates C15+</td>
<td>0.0026</td>
</tr>
<tr>
<td>Mass fraction of Aromatics C15+</td>
<td>0.001</td>
</tr>
</tbody>
</table>

by a stirrer magnet with a stirrer speed of 1000 rpm. To study the effect of salinity, different weight percents of NaCl in water were used and after adding 3 vol. % gas condensate in saline, different surfactants were added to the solution. Also, to study the effect of pH, HCl and NaOH were used to the adjustment of pH. For this purpose, after preparation of emulsion, HCl and NaOH were added to the solution. The pH value for each solution was controlled by a digital pH meter and adjusted in the values of 3, 5 and 11. Additionally, to investigate the effect of temperature, some emulsions were prepared with different surfactants in two temperatures.

**Determination of emulsion stability**

To evaluate the stability of developed emulsions, the distribution of droplets size for three droplets of different parts of the emulsion was measured by an optical microscope. For this purpose, several pictures were taken from droplets and the average distribution of droplets sizes from all the pictures were reported as...
the distribution of droplets sizes of that emulsion. All the data were reported as mean.

Droplets size distribution

The mean diameter of droplets and the droplets size distribution were determined from the captured images of the optical microscope. The diameters of the recorded oil drops were afterward measured (one by one) by image processing of MATLAB Software.

The microstructure of emulsions was evaluated using an optical microscope equipped with a camera. For this purpose, a few droplets of the homogenized sample were put on sampling glass and the microstructure pictures of samples were observed at magnification ratios of 10, 40 and 100, with this notation that the homogeneity of samples must be verified. Finally, an average diameter was calculated for each emulsion sample. Values of the Sauter mean diameter, \(d_{3,2}\), which is inversely proportional to the specific surface area of droplets, were obtained as follows [2, 8, and 11]:

\[
\frac{\sum n_i d_i^3}{\sum n_i d_i^2}
\]

Where \(n_i\) is the number of droplets with a diameter \(d_i\).

RESULTS AND DISCUSSION

The effect of salinity on stability

Effects of 2, 10 and 26 wt. % of NaCl on the stability of emulsions formed were studied. To do so, some emulsions containing 3 vol. % gas condensate in water were made using different surfactants (including Span 80, CTAB and Tween 80). Figs. 1 and 2 show microscopic images and droplets size distribution of gas condensate in solutions containing 3 vol. % gas condensate and 2 wt. % NaCl. The Sauter mean diameter of each prepared emulsion with 2, 10 and 26 wt. % of NaCl in water is shown in Table 3.

According to the results obtained from emulsions formed in a solution containing 2 wt. % NaCl and 3 vol. % gas condensate in saline, it can be concluded all the emulsions were very stable and combinations of Span 80 and Tween 80 had more stability. The HLB value of the surfactants for stable emulsions is expected to be in the range of 8 to 16, the HLB surfactants used were suitable for this type of emulsion (gas condensate in water). The HLB of the combination of Span 80 and Tween 80 was 10 approximately, which was in the range 8 to 16 and proper for this kind of emulsion. The HLB value of CTAB is also 10 but the emulsion formed with Span 80+Tween 80 was more stable than CTAB. CTAB is a cationic but Span 80 and Tween 80 are non-ionic surfactants. Because of the positive charge on the cationic surfactants, emulsions formed by them are less stable than emulsions formed with non-ionic surfactants. The charge on the surfactant causes instability in emulsions. To study the effect of salt on the stability of these emulsions, the effect of 10 and 26 wt. % NaCl was also studied. The maximum value of salt in water is approximately 26 wt. % for saturated water, so the effect of this percentage of salt was considered. Figs. (3-6) show microscopic images and droplets size distribution of the emulsions formed with these surfactants in solutions containing 10 and 26 wt. % NaCl.

As can be seen in these figures, the increasing of salt (NaCl) in water will increase the emulsion stability using three surfactants. The reason is that an increase in the percentage of salt in the water ionizes the solution and forms micella in the emulsion. This micella cover droplets of gas condensate and prevent their coalescence. Thus, the emulsion stability increases.

The most stable emulsion was formed when a combination of Span 80 and Tween 80 was used. The Sauter mean diameter for this surfactant was less than that for the other surfactants for all salinities. The HLB value of the combination of Span 80 and Tween 80 was approximately 10 which was a very suitable value for the preparation of this kind of emulsions (gas condensate in water). Also, the stability of emulsion formed with non-ionic surfactant was more than that of emulsion formed with cationic ones.

Effect of temperature

To evaluate the effect of temperature on the stability of the emulsion, the effects of four types of surfactants (SDS, Span 80, Tween 80 and CTAB) at two temperatures (25, 60 °C) were studied. All emulsions included 3 vol. % gas condensate in water and some droplets of each emulsion were used to determine droplets size distribution. Figs. (7-a, b, c, and d) show the images of droplet sizes of gas condensates in water using the optical microscope for prepared emulsions at 25 °C with Tween 80, Span 80, CTAB and SDS, respectively, and the droplets size distribution...
Table 3: Sauter mean diameter in the emulsion formed including 3 vol. % gas condensate in water with different surfactants and salinities.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Sauter mean diameter for 2 wt. % NaCl in water</th>
<th>Sauter mean diameter for 10 wt. % NaCl in water</th>
<th>Sauter mean diameter for 26 wt. % NaCl in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tween 80</td>
<td>7.5</td>
<td>6.8</td>
<td>5.7</td>
</tr>
<tr>
<td>Span 80 + Tween 80</td>
<td>5.4</td>
<td>4.7</td>
<td>4.4</td>
</tr>
<tr>
<td>CTAB</td>
<td>8.5</td>
<td>5.8</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Fig. 1: Optical microscope images of 3 vol. % gas-condensate in 2 wt. % saline emulsion formation with 200 ppm of different surfactants at 25°C with a mixing time of 2 h including a) Tween 80 + Span 80, b) Tween 80 and c) CTAB.

Fig. 2: The distribution of droplet sizes of 3 vol. % gas-condensate in 2 wt. % saline emulsion formation with 200 ppm of different surfactants at 25°C with a mixing time of 2 h including a) Span 80 + Tween 80, b) Tween 80 and c) CTAB.
Fig. 3: Optical microscope images of 3 vol. % gas-condensate in 10 wt. % saline emulsion formation with 200 ppm of different surfactants at 25°C with a mixing time of 2 h including a) Tween 80 + Span 80, b) Tween 80 and c) CTAB.

Table 4 displays the type of surfactants used to develop the emulsion and the Sauter mean diameter of gas-condensate droplets in the emulsion. Figs. 9 and 10 also show emulsions formed with these surfactants at 60 °C.

As can be seen in Table 4, the increasing temperature had no effect on the stability of the emulsion formed with anionic and cationic surfactants but when non-ionic surfactant (eg Span 80 or Tween 80) were used, droplets diameter decreased as temperature increased, and the stability of emulsions increased. Also, observing all samples shows that...
Effect of Salinity, pH and Temperature on Stability...

Fig. 5: Optical microscope images of 3 vol. % gas-condensate in 26 wt. % saline emulsion formation with 200 ppm of different surfactants at 25°C with a mixing time of 2 h including a) Tween 80 + Span 80, b) Tween 80 and c) CTAB.

Fig. 6: The distribution of droplet sizes of 3 vol. % gas-condensate in 26 wt. % saline emulsion formation with 200 ppm of different surfactants at 25°C with a mixing time of 2 h including a) Span 80 + Tween 80, b) Tween 80 and c) CTAB.

all the solutions are stable because the Sauter mean diameter of the droplets is very small and among them, the emulsion formed with Tween 80 at 60°C was more stable than the other ones. To evaluate the stability of these emulsions, an amount of them were evaluated one month later, and the average diameter of their droplets did not change, indicating the high stability of these emulsions.

Effect of pH

To evaluate the effect of pH on the stability of emulsion, the effect of four amounts of pH (11, 7, 5 and 3) on emulsions formed with different surfactants (Tween 80, CTAB, SDS and combination of Span 80 and Tween 80) were studied. All emulsions included 3 vol. % of gas condensate in water. The pH value for all emulsions...
**Fig. 7:** Optical microscope images of 3 vol. % gas-condensate in water emulsion formation with 200 ppm of different surfactants at 25°C with a mixing time of 2 hrs including a) Tween 80, b) Span 80, c) CTAB and d) SDS.

**Fig. 8:** The distribution of droplet sizes of 3 vol. % gas-condensate in water emulsion formation with 200 ppm of different surfactants at 25°C with a mixing time of 2 h including a) Tween 80, b) Span 80, c) CTAB and d) SDS.
Table 4: Sauter mean diameter of droplets in the emulsions formed including of 3 vol.% gas condensate in water with different surfactants at 25 and 60 °C.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Sauter mean diameter at 25°C</th>
<th>Sauter mean diameter at 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>12</td>
<td>12.4</td>
</tr>
<tr>
<td>CTAB</td>
<td>12</td>
<td>11.5</td>
</tr>
<tr>
<td>Span 80</td>
<td>17</td>
<td>9.8</td>
</tr>
<tr>
<td>Tween 80</td>
<td>8</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Fig. 9: Optical microscope images of 3 vol. % gas-condensate in water emulsion formation with 200 ppm of different surfactants at 60°C with a mixing time of 2 hrs including a) Tween 80, b) Span 80, c) CTAB and d) SDS.

was about 7 initially, and for change of pH, HCl and NaOH have been used. Figs. 11-18 show the microscopic images and droplets size distribution of gas condensates in the water at 25 °C in different pH. Table 5 displays the type of surfactants used to develop the emulsion and the Sauter mean diameter of gas-condensate droplets in different pH and surfactants.

As shown in these figures, the effect of pH on the four emulsions formed with different surfactants (Both anionic and non-anionic) was considered. The results showed the Sauter mean diameter of droplets at a high amount of pH were bigger than those at pH 7 for all solutions. When non-ionic surfactants were used for the formation of emulsion, the solution was more stable in low pH in comparison with high pH, although in low pH-value the changes in the Sauter mean diameter was small.

But in emulsions formed with cationic and anionic surfactants, the best pH for stability was 7 and at low and high amount of pH, the Sauter mean diameter was increased and emulsion stability decreased. Generally, for all samples, the results showed the addition of NaOH caused gas condensate droplets to grow and stability of emulsion decreased.

CONCLUSIONS

Four types of surfactants (SDS, CTAB and Tween 80 and Span 80), were used for the preparation of emulsions. These surfactants are anionic, cationic and nonionic, respectively. To prepare the emulsion, 3 vol. % gas condensate in water and 200 ppm of each surfactant were used. In this work, the effect of two temperatures (25 and 60 °C) on the formation and stability of emulsions was studied.
To investigate the stability of the emulsion, droplets size distribution was used that was carried out using an optical microscope equipped with a camera. The results indicated that the temperature had no effect on the formation of emulsions using anionic and cationic surfactants but when a non-ionic surfactant (e.g., Span 80 or Tween 80) was used, droplets diameters decreased as temperature increased, and the stability of emulsions increased. The effect of salt (NaCl) on the emulsion stability was also studied. To investigate the effect of salt,
Fig. 12: The distribution of droplet sizes of 3 vol. % gas condensate in water emulsion formation with Tween 80+Span 80 in different pH including a) pH=11, b) pH=7 and c) pH=3.

Fig. 13: Optical microscope images of 3 vol. % gas condensate in water emulsion formation with Tween 80 in different pH including a) pH=11, b) pH=7 and c) pH=3.

2 and 10 and 26 wt. % of NaCl were considered in distilled water. The results indicated two very important points, first all emulsions formed using these surfactants were very stable, and besides increasing the salt increases the stability of the emulsion. The emulsion formed with a combination of Span 80 and Tween 80 also had more stability than other surfactants, indicating that non-ionic surfactants can be more suitable to the form of these emulsions than anionic and cationic surfactants. Additionally, the effect of pH has been studied.
Fig. 14: The distribution of droplet sizes of 3 vol. % gas condensate in water emulsion formation with Tween 80 in different pH including a) pH=11, b) pH=7 and c) pH=3.

Fig. 15: Optical microscope images of 3 vol. % gas condensate in water emulsion formation with SDS in different pH including a) pH=11, b) pH=7, c) pH=5 and d) pH=3.
Fig. 16: The distribution of droplet sizes of 3 vol.% gas condensate in water emulsion formation with SDS in different pH including a) pH=11, b) pH=7, c) pH=5 and d) pH=3.

Fig. 17: Optical microscope images of 3 vol.% gas condensate in water emulsion formation with CTAB in different pH including a) pH=11, b) pH=7, c) pH=5 and d) pH=3.
Table 5: Sauter means diameter of droplets in the emulsions formed including 3 vol. % gas condensate in water with different surfactants and pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Sauter mean diameter for emulsion prepared with Tween 80+Span 80</th>
<th>Sauter mean diameter for emulsion prepared with Tween 80</th>
<th>Sauter mean diameter for emulsion prepared with SDS</th>
<th>Sauter mean diameter for emulsion prepared with CTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>5</td>
<td>8</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
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<td>3</td>
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<td>6</td>
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</tr>
<tr>
<td>11</td>
<td>9</td>
<td>9</td>
<td>22</td>
<td>26</td>
</tr>
</tbody>
</table>

Fig. 18: The distribution of droplet sizes of 3 vol. % gas condensate in water emulsion formation with CTAB in different pH including a) pH=11, b) pH=7, c) pH=5 and d) pH=3.

Four amount of pH (11, 7, 5 and 3) on the formation of the emulsion was considered. Results showed emulsions formed with non-ionic surfactants in low pH were more stable than those in high pH although, with change of pH, Change in droplets size was small. Also, emulsions formed with anionic and cationic surfactants in pH 7 were more stable than another pH. Generally, for all samples, the results showed that the emulsions were less stable at high pH than other ones. These results are useful on emulsification and demulsification of refinery wastewater while their stability is affected by different factors such as temperature, pH and salinity. Therefore, it can be used the results of this work on separation of gas condensate from industrial wastewater for future works where a little amount of gas condensate is dispersed in water as emulsion.

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