Research Article
Effects of Surfactant Blend Formulation on Crude Oil-Brine Interaction and Wettability: An Experimental Study

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Abstract: Interfacial tension of reservoir fluids and wettability are important parameters in the process of enhanced oil recovery. These two parameters affect the fluid distribution within reservoir formation. The fluids distribution in the reservoir strongly affects the flow behavior and residual oil recovery. Interfacial tension plays an important role due to its relationship between foam surface energy and foam stability. The wettability by contact angle measurement provides a method for determining fluid interaction and is considered as a basic research than practical tool for analysis of reservoir formation. The main objective of this research study is to determine the effects of interfacial tension and wettability on foam surfactant blend formulations, brine and crude oil. Anionic and nonionic surfactant blend were selected. The interfacial tension test was performed at 85°C. Dynamic interfacial tension of blended surfactant formulations with Malaysian crude oil were measured in fixed brine salinity. The interfacial tension values of tested surfactant blends were found lower than the interfacial tension between brine and crude oil. Interracial tension between crude oil and foam forming surfactant was reduced by using different concentration of surfactant blend. Good values were obtained by the measurement of contact angle between solid and three foam surfactant blend formulations. The interfacial tension and contact angle experimental studies revealed that, the blend of Alpha Olefin Sulfonate and Sodium Dodecyl Sulfonate with Octylphenol Ethylene Oxide play an important role in reducing the interfacial tension at crude oil-brine interface. The reduced interfacial tension and more wetting surface effects indicated that, these foam surfactant formulations are of great importance in the process of residual oil recovery.

Keywords: Foam, interfacial tension, surfactants, residual oil recovery, wettability

INTRODUCTION

Interfacial Tension (IFT) is one of the most important physical properties of fluid-fluid interfaces (Arashiro and Demarquette, 1999). Interfacial tension describes the thermodynamic state and structure of an interface (Farajzadeh et al., 2011). IFT is a measurement of the cohesive energy present at an interface (Liu et al., 2005). The residual oil saturation is a function of capillary number. Higher the capillary number, lower the residual oil. To reduce the residual oil saturation by increasing the capillary number is the aim of the process of enhanced oil recovery and this is possible by reducing its interfacial tension. Brine salinity plays an important role on interfacial tension (Bera et al., 2014). Some of the factors such as, wettability, IFT, capillary and viscous forces are considered as important factors in the process of residual oil recovery (Melrose and Bradner, 1974). Therefore residual oil recovery is dependent on these factors that are related with oil/aqueous/formation interface properties (Alotaibi and Nasr-El-Din, 2009). For the residual oil recovery (tertiary oil recovery) process, IFT study between oil-brine interfaces is an important thermo physical property (Dandekar, 2006). Interfacial tension is the first step to determine the prescription for applying the chemical solution.

In foam generating surfactants study, IFT play an important role due to the relationship between surface energy and generated foam stability. Generated foam reduces CO₂ mobility by immobilizing or trapping a large fraction of gas. This trapped gas is diverted in to less permeable oil rich portion of the reservoir and resulting increases in oil recovery. In addition, IFT can be reduced due to presence of surfactants (Bian et al., 2012). Many industries are used surfactant blends because the interfacial properties of surfactant blend are more pronounced than those of individual surfactant. The blend shows a synergistic interaction (Khalil and Asghari, 2006).
For residual oil recovery, wettability plays an important role. Wettability controls the distribution of fluid in the reservoir and affects their movement in the pore spaces. The contact angle technique is valuable because it provides a method for determining surface/fluid interaction, independent of pore throat geometry. Therefore this technique is considered more of a basic research than a practical tool for analysis of porous rock (Stevenson, 2012). Holt and Kristiansen (1990) studied foam flowing in the North Sea reservoir conditions that were either partially or completely oil wetted. They found that, any degree of oil wet character reduced the effectiveness of the flowing foam. Therefore, foam effectiveness is favored by water-wet conditions (Kristiansen and Holt, 1992). IFT and contact angle of the fluid/rock system affect the fluid distribution in the formation. This strongly affects the flow behavior and hydrocarbon recovery (Ma et al., 2013). In the water-wet conditions oil will be in the large pores and remains in the center of pores. Further water will be in the smaller pore spaces that were not invaded by oil. In the mixed-wet conditions oil has displaced water from some of the surfaces but is still in the center of water-wet pores. In oil-wet conditions, the water remains in the center of pores. These three wetting conditions in the pore channels are presented in the Fig. 1.

A good source of trapped oil is left behind after water flooding due to the dominance of capillary forces over viscous forces. To recover the left trapped oil, Chemical Enhanced Oil Recovery (CEOR) is the most common method. The CEOR methods can increase the viscosity of the displacing fluid and the drive water (Guo et al., 2013). Surfactants have been used for lowering the IFT and are used for tertiary oil recovery for more than 35 years mostly in USA in depleted oil reservoirs after water flooding (Bian et al., 2012). In addition, IFT can be reduced due to injection of surfactant (Zhu et al., 1998).

One parameter can be manipulated by chemical flooding is the reduction of formation brine/oil interfacial tension. Several types of surfactants have been used to change the Interfacial Tension (IFT) of brine/crude oil system (Hezave et al., 2013). Petroleum Sulfonate with use of an alcohol co-solvent is the most popular now a days. Because capillary number controlled the amount of residual oil remained after flooding. The crude oil- brine IFT has to be reduced from 20-30mN/m (dynes/cm) to values in the range of (0.01-0.001mN/m) to achieve the low value of residual oil saturation (Gao and Shrama, 2013).

The spread of liquid on solid surface depends on liquid and solid surface properties. One can optimize the performance to achieve the desired wetting conditions by manipulating the liquid and solid surface properties. Foam surfactant can modify the wettability by adsorbing the liquid rock interface. Suffridge et al. (1989) studied foam effectiveness in the Berea sandstone. They resulted that, the foams were more stable in the water-wet cores. Babu et al. (2015) performed studies on interfacial tension and contact angle of synthesized surfactants and polymeric surfactants. They concluded that, both formulations are effective for oil recovery due to water-wet and low interfacial tension. Schramm and Mannhardt (1996) performed experimental study on wettability effect on foam sensitivity. Their result showed that, effective foam can be formed and propagated in the intermediate-wet porous media. This result was compared with water-wet porous media using core flooding and micro visual cells. The steady state foam effectiveness was reduced when water-wetting was reduced. Ko et al. (2014) performed study on foam surfactant flooding characteristics. Dodecyl Alkyl Sulfate (DAS) was used for residual oil recovery after water flooding through core flooding experiments. 26.6% excess oil was recovered through 2wt% of surfactant solution with 3% brine salinity. Further, residual oil recovery was increased using addition of 0.01wt% of co-surfactant solution. Zhu et al. (2009) carried out experimental study on blend of Triton TX-100 and its Oligomer Tyloxapol with Cetyltrimethylammonium Bromide
(CTAB) induced by Hydrolyzed polyacrylamide (HPAM). Ultra low values of IFT were obtained from these surfactant blend formulations.

In the past years, lot of research has been done on reducing IFT during foam generating surfactant injection, but one of the important factor wettability was not focused. Low IFT and favorable wetting conditions (water-wet) are the requirements of the use of foam generating surfactants in the process of residual oil recovery (Romsted, 2014). In this study two anionic and one nonionic surfactant was evaluated. Blend of Anionic/Nonionic surfactant interfacial properties in presence of brine salinity and Malaysian crude oil was measured. Spinning drop tensiometer was used with computer aided image processing and analysis to measure the oil-brine interaction at 85°C. SCA 20 IFT meter was used for measuring wettabity by contact angle method between solid, brine, oil and surfactant blend formulations.

RESEARCH METHODOLOGY

Materials:
Foam surfactants: Alpha Olefin Sulfonate AOS (C14-16), was provided by Stepan Company USA. Sodium Dodecyl Sulfonate (SDS) was purchased from R&M Chemicals UK. Octylphenol ethoxylate surfactant (Triton TX-100) was purchased from Sigma-Aldrich.

Salts for synthetic brine: Sodium Chloride (NaCl) was purchased from Fischer Company U.K, Magnesium chloride (MgCl₂.6H₂O), Potassium chloride (KCL), Sodium bicarbonate (NaHCO₃), Sodium sulphate (Na₂SO₄) and Calcium Chloride (CaCl₂.2H₂O) were purchased from R&M. Chemicals U.K. The synthetic brine composition was prepared in one liter distilled water as Sodium Chloride 23.6g, Magnesium chloride 10.20g, Potassium chloride 0.62g, Sodium bicarbonate 0.225g, Sodium sulphate3.9g and Calcium chloride 1.3g.

Crude Oil: The crude oil was collected from offshore oil field Malaysia. The density of crude oil was measured as 0.7886gm/cc (49.2307lb/ft³) at 96°C and 1400psi by Anton Par density meter. The oil viscosity was measured as 1.591cp at 96°C and 1400psi by HTHP EV-1000 viscometer. The specific gravity of crude oil was calculated as 0.7889 and degree API was 37.7. The specific gravity and degree API was calculated by using following formula:

\[
API^o = \frac{141.5}{\gamma_o} - 131.5 \tag{1}
\]

Specific gravity:

\[
\gamma_o = \frac{\rho_o}{\rho_w} \tag{2}
\]

Crude oil-brine interfacial tension measurements: Interfacial tension was performed by spinning drop tensiometer (Model SVT 20). The purpose of this test was to investigate the effects of foam generating surfactant formulations on IFT performance. This method is based on balance of centrifugal and IFT forces. For each sample, the fluids whose IFT was to be measured were introduced into a capillary tube (Sample cell). The tube was first filled with the foam forming surfactant solution carefully to avoid bubble formation and then closed with Teflon cap having a rubber septum. The tube-cap assembly was inserted into the tensiometer slot and screwed firmly in the place. The tube was initially rotated at 250 rpm for few minutes to increase temperature of solution at 85°C. A drop of crude oil was then injected into the tube (rotating at 250 rpm) through the rubber septum using a long needle syringe. The shape of major oil drop should be three times greater in diameter than minor diameter drop. This is essential for accurate IFT measurements. After that, the rotating speed of capillary tube was steadily increased in order to elongate the oil drop and to give it an elliptical shape. After maintained the elliptical shape of oil drop at static condition, a dimensional profile was extracted and then hold down to initiate IFT measurement. Figure 2 presents SVT 20 spinning drop tensiometer. Time dependent track for accurate IFT measurements was run until 500 readings.

Wettability measurements: Blend of selected foam surfactants were measured using contact angle between the formulation and solid by SCA-20 IFT meter. The test was performed at room temperature (20°C). Before start the measurement, thin sections of Berea sandstone were vacuumed for 24 h in synthetic brine. After that, these thin sections were saturated in Malaysian crude oil for 72 h at 50 °C.

RESULTS AND DISCUSSION

Interfacial tension effect: Before start the interfacial measurement the density and refractive index of foam
Table 1: Density, refractive index, IFT and contact angle values

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Formulation</th>
<th>Density (gm/cm³)</th>
<th>Refractive index</th>
<th>IFT (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Crude Oil</td>
<td>0.73639</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Synthetic Brine</td>
<td>0.97108</td>
<td>1.3274</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>Brine and Crude Oil</td>
<td>-</td>
<td>-</td>
<td>8.99</td>
</tr>
<tr>
<td>MK1</td>
<td>0.2%AOS+0.2%TX100</td>
<td>0.98511</td>
<td>1.3280</td>
<td>0.96</td>
</tr>
<tr>
<td>MK2</td>
<td>0.6%AOS+0.6%TX100</td>
<td>0.98719</td>
<td>1.3279</td>
<td>0.88</td>
</tr>
<tr>
<td>MK3</td>
<td>0.2%SDS+0.2%TX100</td>
<td>0.98770</td>
<td></td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 2: Measurement of wettability by contact angle method

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Formulation</th>
<th>Density (gm/cm³)</th>
<th>Contact angle (Degree)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK1</td>
<td>Brine/oil/Solid</td>
<td>-</td>
<td>107</td>
<td>Intermediate</td>
</tr>
<tr>
<td>MK2</td>
<td>0.2%AOS+0.2%TX100</td>
<td>0.98511</td>
<td>52.0</td>
<td>Water-Wet</td>
</tr>
<tr>
<td>MK3</td>
<td>0.6%AOS+0.6%TX100</td>
<td>0.98719</td>
<td>50.7</td>
<td>Water-Wet</td>
</tr>
<tr>
<td>MK3</td>
<td>0.2%SDS+0.2%TX100</td>
<td>0.98770</td>
<td>70.7</td>
<td>Water-Wet</td>
</tr>
</tbody>
</table>

Fig. 3: Schematic diagram of wettability by using contact angle method

The contact angle between solid and brine was measured as 107°. It is intermediate oil-wet. Three surfactant blend formulations were measured and found water-wet. The low obtained values of contact angle are because of the head group of these blended formulations away from the surface. This is in favor for releasing oil from pore spaces. The values of contact angle between solid and brine, surfactant blend formulation are

TX 100 might be due to high dissimilarity in to two phases at the interface or due to the Gibbs-Marangoni Elasticity effect. As the film stretches under an applied stress, the area was increased and amount of surfactant adsorbed at the two gas/liquid surfaces (Hargreaves, 2003).

Wettability Effect: Density of drop phase was set in the result collection window. Thin section (solid) was set on the stand of IFT meter. The drop of selected foam surfactant formulation was dispersed from needle. After first drop from the syringe dropped on solid, dispense was stopped. Measured drop shape was display on the SCA software. Image of measured drop shape was saved. Figure 3 presents the schematic diagram for the measurement of wettability by contact angle method.

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CONCLUSION

Based on experimental results the following conclusions can be drawn:

- The Combination of different type of surfactants synergistically exhibit better foaming properties than those of an individual component. Dynamic IFT of blended surfactant formulations with Malaysian crude oil were measured in fixed brine salinity. The IFT values of all surfactant blends were found lower than the IFT between brine and crude oil. IFT between crude oil and foam forming surfactant was reduced by using different concentration of surfactant blend. The IFT studies revealed that the blend of 0.6% AOS +0.6%TX-100 and 0.2%SDS+0.2%TX-100 plays an important role in reducing the IFT at oil-brine interface which indicated that, they are of great importance in Enhanced Oil Recovery.

- IFT and contact angle of the fluid/solid system affect the fluid distribution in the formation. This strongly affects the flow behavior and hydrocarbon recovery. The contact angle between solid and brine was measured as 107°. It is intermediate oil wet. Three surfactant blend formulations were measured and found water-wet. Small values of contact angle were an indicative of the strong wettability. These results showed that, the blended surfactant formulations are effective for oil recovery.

ACKNOWLEDGMENT

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NOMENCLATURE

AOS : Alpha Olefin Sulfonate  
CEOR : Chemical Enhanced Oil Recovery  
CTAB : Cetyltrimethylammonium Bromide  
DAS : Dodecyl Alkyl Sulfate  
HPAM : Hydrolyzed Polyacrylamide  
IFT : Interfacial Tension  
mN/m : Mille Newton per Meter  
SDS : Sodium Dodecyl Sulfonate  
TX-100 : Octylphenol ethoxylate surfactant

Conflict of interest: The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES


