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Evaluation of the dynamic interfacial tension between visco-elastic surfactant solutions and oil using porous micromodels

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Abstract

Interfacial tension (IFT) is a crucial parameter in many natural and industrial processes, such as enhanced oil recovery (EOR) and subsurface energy storage. IFT determines how easy the fluids can pass through pore throats and hence will decide how much residual fluids will be left behind. Here, we use a porous glass micromodel to investigate the dynamic IFT between oil and Armovis viscoelastic surfactant (VES) solution based on the concept of drop deformation while passing through a pore throat. Three different concentrations of VES, i.e., 0.5%, 0.75%, 1.25% vol%, prepared using 57K ppm synthetic seawater, were used in this study. The rheology obtained using a rheometer at ambient temperature showed zero shear viscosity of 325 cP, 1101 cP, and 1953 cP for 0.5%, 0.75%, and 1.25% VES respectively with a power-law region between 2 to 50 l/s. The dynamic IFT increases with the shear rate, and then reaches a plateau. The results of IFT were compared with those obtained from the spinning drop method, which shows 97% accuracy for 1.25% VES, whereas the accuracy decreased to 65% for 0.75 VES and 51% for 0.5% VES. The findings indicate that we can reliably estimate the IFT of VES at higher concentrations directly during multiphase flow in porous micromodels without the need to perform separate experiments and wait for a long time to reach equilibrium.
Introduction

Enhanced oil recovery (EOR) is used to maximize hydrocarbon production as primary and secondary methods are not sufficient to produce the economically feasible amount of hydrocarbon. Chemical Enhanced oil recovery (CEOR) is the branch specialized in using chemicals to enhance the recovery such as surfactants and polymers [1]–[3]. Low recovery in primary and secondary methods is due to higher water mobility which leads to fingering and early water recovery and oil trapping in the reservoir pore network. Oil trapping in hydrocarbon reservoirs can be affected by the geometric properties of the rock, fluid properties, and fluid-rock interaction such as wettability [4]. Surfactants are used to lower the interfacial tension (IFT) to facilitate the transportation of the trapped oil. Polymers are used to increase the viscosity of the displacing fluid and provide a mobility control agent to prevent water breakthrough [5]–[8]. Usually, a combination of surfactant-polymer or alkali-surfactant polymer is used in the industry to achieve both IFT reduction and mobility control [9]–[13]. Visco-elastic surfactants have both properties of polymer and surfactant, and they can lower the IFT and increase the viscosity. It showed good potential as a CEOR candidate which can also withstand harsh conditions such as salinity and temperature [14]–[16]. Salinity presents a great challenge especially in the middle east as freshwater is rare and barely sufficient for domestic purposes. It causes chemical precipitation when divalent ions exist [17], [18]. It can also, decrease the viscosity and enhance degradation. It should be studied carefully in the lab before applying the treatment in the field. Using the seawater directly without softening is an advantage and leads to cost reduction.

Laboratory assessment for any chemical to be used in CEOR includes compatibility, stability, phase behavior, rheology, IFT, and recovery [6], [19], [20]. Recovery is typically assessed by core flooding; however, microfluidic has recently been introduced as a means to assess recovery as
well. Core flooding is considered the primary evaluation method for recovery, as it considers the reservoir rock properties and can provide a good representation of reservoir conditions, such as pressure, temperature, initial saturation, and wettability. However, these types of experiments are expensive in terms of time and effort, and the equipment is difficult to handle as the accumulators and core holders are heavy. In addition, the core preparation may take up to two weeks for maturation and aging though the experiment itself may take a few hours [21]–[23]. Microfluidic has more advantages than core-flooding as it can allow visualization of pore-scale processes and facilitate their interpretation. Moreover, it is easy to handle, time-effective, and occupies small lab space [24]–[26]. Even though these devices are generally manufactured from glass, some coating can be applied to represent different lithologies and wettabilities.

Micromodels have been employed to provide a detailed understanding of pore-scale transport phenomena, dispersion, two-phase flow visualization, and dynamic interface changes [27], [28]. Many studies have utilized the concept of drop deformation and its relationship with the viscosity ratio and capillary number [29], [30]. Hudson et al.[31] used that concept to do microfluidic interfacial tensiometry by measuring the drop deformation while its movement through a microchannel fabricated from glass. The drop is circular when passing through the wide channel at a constant speed. This can allow us to calculate the radius of the drop. Deformation can be calculated from minor and major axes when the drop enters the microchannel and accelerates [31], [32]. Brosseau et al.[33] designed a microfluidic setup to investigate the surfactant adsorption kinetics by measuring the interfacial tension at nanoliter drop volumes. They studied the dynamic adsorption by relating the change of IFT from the initial value to the equilibrium value with the deformation parameters and then using the microfluidic IFT to estimate adsorption constants. The results were in good agreement with the values obtained from the pendant drop method [33].
D’Apolito et al. [34] used the same deformation concept as Taylor [29], [30] and used it to measure the IFT by injecting already prepared emulsion in capillary tubes. They analyzed the droplets that were in the simple shear zones which are closer to the capillary wall. Its main novelty is that the drop is formed in the injected emulsion outside the micromodel and does not need special geometry for its formation as used in previous studies.

In this study, we applied Taylor’s deformation theory to measure the IFT between oil and surfactant while passing through pore throats in a typical surfactant flooding. We neither use special geometries to form droplets nor inject already prepared emulsions, rather, we trace the formed emulsion in-situ and use the drop deformation parameters to measure the IFT. Since our chemical is a non-Newtonian viscoelastic surfactant we used the rheological shear scan viscosity for capillary number calculation at different shear rates. IFT from spinning drop is a single stable value and in reality, the fluids in porous media are moving so the instant dynamic value is more needed as the drop does not find a long time to stabilize while flooding. We compared our results with the spinning drop to prove that our method is valid and in the range of the stable IFT value as the changes are only due to the movement in the porous media and not due to errors in the method itself.

**Methodology**

**Materials**

**Glass micromodel**

A glass model was used with 136 µm diameter circular grains with 63 µm spacing (Figure 1). The total length of the pore network is 14 mm, width is 7.27 mm, depth is 0.011 mm, and 65% porosity which gives a total pore volume of 0.72 µL (Figure 1). The photomask was designed by AutoCAD
with high-resolution transparent film masks up to 10 µm and 25400 dpi as explained by Mejia et al. [24]. The glass chip was etched using the hydrofluoric acid etching technique and then fused with a cover glass plate at a 500°C oven as described by Xu et al. [27].

Figure 1. Glass micromodel with the whole network in the top panel and a zoomed-in portion with details in the bottom panel.
Crude oil

Arabian heavy crude with a density of 890 kg/m³ and approximate zero shear viscosity of 170 cp at 25°C as shown in Figure 2. The oil was filtered in two stages, using an 8 µm and then 0.5 µm metal filter to ensure the removal of all solid impurities to prevent line and pore plugging.

Figure 2. Shear scan for crude oil viscosity against shear rate, which shows shear-thinning non-Newtonian behavior.

Brine

Synthetic seawater with 57612 ppm was prepared from laboratory standard salts as shown in Table 1, which was then used in micromodel saturation and surfactant preparation. The brine was filtered using 0.5 µm filter paper.
Table 1. Seawater composition

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>41,041</td>
</tr>
<tr>
<td>CaCl$_2$.2H$_2$O</td>
<td>2,384</td>
</tr>
<tr>
<td>MgCl$_2$.6H$_2$O</td>
<td>17,645</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>6,343</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>165</td>
</tr>
<tr>
<td>TDS</td>
<td>57,612</td>
</tr>
</tbody>
</table>

**Surfactant**

Armovis viscoelastic surfactant (VES) was provided by Nouryon chemical company in a liquid form with 42% active content. The solution was prepared using the prescribed seawater in a beaker with a magnetic stirrer. The required surfactant concentration was added slowly to the top of the vortex, which was then stirred for 2 hours at 90°C to ensure good solubility.

**Rheology**

Anton Paar rheometer (MCR 302) was used with concentric cylinder geometry to study the rheological properties of our VES samples. All the experiments were performed at 25°C temperature for shear scans ranging from 0.01 to 1000 S$^{-1}$. The concept of the device is to measure
the torque resulting from spinning the rod inside the cylinder filled with the fluid under consideration. Afterward, using specific formulas to calculate the shear stress and shear rate from the geometrical parameter with the measured torque and then calculate the viscosity at the required shear rate [35], [36]. The rheology was done at this temperature because our microfluidic device work under ambient conditions.

Figure 3. Concentric cylinder and rod geometry for rheology measurement.
Spinning drop IFT

The interfacial tension was measured using a spinning drop tensiometer (SDT-20190425) provided by Kruss company. All experiments were performed at 25°C, and 4000 RPM rotational speed, and the Young-Laplace model was used. The concept is that the drop will be in balance after deformation stops, so the centrifugal force will equal the surface force. The drop should have less density than the bulk fluid so it will be in the center. The IFT is calculated from the drop dimensions after deformation reaches equilibrium, the rotational speed, and the fluid densities.

Microfluidic

The microfluidic device consisted of a syringe pump, high-speed microscope, pressure sensors, a glass micromodel with its holder, and a base with a light source (Figure 4). The micromodel is first saturated with seawater at a slow flow rate of 1 µL/h till we cover most of the pore volume and then at a high flow rate up to 500 µL/h to drive the air bubbles out of the model. Surfactant solution is injected at 1 µL/h and the recovery performance is analyzed during this flooding process. The performance is investigated in a specific region of interest in the middle of the micromodel.
**Figure 4.** The Microfluidic setup consisted of a Micro syringe pump, Highspeed microscope, glass micromodel with base, pressure transducers, and a computer for control and data recording.

**IFT from microfluidic**

The concept for this method is to use the drop deformation parameters resulting from its movement through the pore throat to calculate the interfacial tension (IFT). The early work of Taylor produced a relationship between the deformation parameter (D) and viscosity ratio between the continuous and the dispersed phase [29], [30]. From the image analyses, we can get the major and minor axis of the drop and its center of mass. The velocity can be calculated by dividing the distance between two positions of the drop center at the throat inlet and outlet by the time duration needed to reach there as in Figure 5. The shear rate can be estimated from the drop velocity and the distance between the drop center and the capillary wall. We have the rheology profile for the continuous and the dispersed phases from which we can get the viscosity value corresponding to the specific calculated shear value. D’Apolito et al.[34] used this concept to measure the IFT in a capillary tube for injected emulsion and suggested that the ratio of drop radius to tube radius be 0.1 for the drop to be in the simple shear zone. To avoid this in our study as the pore throat is already narrow.
and maybe the same size as the drop we injected with a very slow flow rate. The calculation steps are explained in the equations below:

Figure 5. Drop movement through the pore throat.

\[ u = \frac{x_2 - x_1}{t_2 - t_1} \] .......................... (1)

\[ \dot{\gamma} = \frac{u}{d} \] .......................... (2)
\[ D = \frac{a-b}{a+b} \] \hspace{1cm} (3)

\[ D = \frac{19\lambda+16}{16\lambda+16} Ca \] \hspace{1cm} (4)

\[ \lambda = \frac{\mu_d}{\mu_c} \] \hspace{1cm} (5)

\[ Ca = \frac{\dot{\gamma}R\mu_c}{\sigma} \] \hspace{1cm} (6)

\[ \sigma = \frac{\dot{\gamma}R\mu_c 16\lambda+16}{D 19\lambda+16} \] \hspace{1cm} (7)

(u): droplet speed through pore throat (mm/s).

D: drop deformation factor.

d: distance between drop center and capillary wall (mm).

\dot{\gamma}: shear rate (1/s).

X1, X2: horizontal position of drop center (mm).

(t1, t2): time at each position (s).

\lambda: viscosity ratio of dispersed phase to the continuous phase.

Ca: capillary number.

\sigma: Interfacial tension (mN/m).

The D in Eqn (3) is the deformation factor from the geometrical parameters and in Eqn (4) is the deformation factor based on Taylor’s theory. We calculated it from the geometrical parameters which can be estimated from the drop shape image analysis then substitute the value in Taylor’s relation along with the capillary number to get the IFT value.
Results and discussion

Rheology

Three VES concentrations; 0.5 % vol., 0.75% vol. and 1.25% vol. was investigated to observe the effect of shear rate on the fluid viscosity to determine the behavior of the fluid used in this study (Figure 6). The rheological values are important in the IFT calculation formula as we need the exact viscosity value at each local shear rate. It is clear that for 0.5% vol. VES, the no shear average viscosity is 325 cp and it varies slightly until it reaches the power-law region at 1 s\(^{-1}\) shear rate then it decreases down to 8.47 cp at the infinite shear region at 1000 s\(^{-1}\). Increasing the concentration to 0.75 % vol. shows increment in the zero-shear viscosity to almost 1101 cp with infinite shear viscosity of 9.7 cp. Increasing the VES concentration to 1.25% vol. shows the same trend, where the zero-shear value for 1.25% vol. is 1953 cp while the infinite shear viscosity is 11.09 cp. The viscosity is directly proportional to the concentration in both the zero shear and the infinite shear. It is noted that the transition from zero-shear to the power-low region is non-monotonic like typical polymers and that can be attributed to the special characteristic of VES in building gits viscosity. VES builds viscosity due to normal long-tail same as polymers and also due to micelles formation in the presence of salt.
Figure 6. Shear scan for VES at variable concentrations of 0.5% vol., 0.75% vol. and 1.25% vol. Viscosity in cP is shown against shear rate in (1/s)

**IFT spinning drop**

A spinning drop device was used to test the interfacial tension between crude oil and brine. The results were used to validate the value obtained from the new method. Figure 7 shows the IFT for three VES concentrations of 0.5%, 0.75% and 1.25%. Note that the IFT value in all these cases started from a high value and decreased gradually to the equilibrium value due to the time needed for the surfactant to be adsorbed at the interface between oil and brine. The IFT value is directly proportional to concentration, which in our case was 0.096 mN/m for 0.5% VES, 0.118 mN/m for 0.75% VES and 0.152 mN/m for 1.25% VES.
Figure 7. Interfacial tension (mN/m) for 0.5% vol., 0.75% vol. and 1.25% vol. VES against elapsed time (s).

IFT microfluidic

Tracing a droplet from inlet to outlet and applying the prescribed method to estimate the IFT for three VES concentrations provided average values of IFT of 0.04 mN/m, 0.07 mN/m, and 0.155 mN/m for VES concentrations of 0.5% vol., 0.75% vol. and 1.25% vol. respectively as in Figure 8. Figure 9 shows the variations of the IFT with the distance from the micromodel inlet for all concentrations. Many factors can affect the accuracy of the IFT calculation by this method such as the position of the droplet with the solid wall which directly affects the shear rate calculations. In addition, the deformation parameters can affect the results when the drop shape is not perfectly elliptical. The drop is affected by the shear force from its movement and the viscous forces from the bulk fluid. The shear forces tend to deform the droplet while the viscous forces act as resistance...
to deformation, which explains why we get higher deformation in lower shears in low viscosity fluid at 0.5% VES and got lower deformation in higher viscosity fluid at the higher shear rate at 0.75% and 1.25% VES.

The dynamic IFT was noted to be in a directly proportional relationship with the shear rate at low shear and have a maximum value above which it decreased again as in Figure 10. That can be attributed to the reduction of the viscous forces from the VES surrounding fluid upon the oil drop. This will result in increasing the summation of the force vector pointing outward the drop and so increasing the force component tangent to the drop surface. Furthermore, as we can understand from the equation of the IFT the shear rate has complex relationships with the viscosity and the deformation factor. Higher shear means lower deformation, while the viscosity, depends on the instant slope of the curve for the specific fluid. In our case, the relationship shows shear-thinning behavior at different slopes. When the effect of shear in decreasing the viscosity is higher than its effect on increasing the deformation the IFT will increase with the increasing the shear and vice versa. The maximum point will be when the effect is equal to both viscosity and deformation.
Figure 8. Dynamic IFT between the oil droplet and the bulk VES solution at 0.5%, 0.75%, 1.25% vol from inlet to outlet, the labels show IFT, the shear rate at the drop position, and the drop deformation factor (0) for non-deformed drop and (1) for completely deformed drop.

Figure 9. The IFT was calculated from microfluidics for three VES concentrations used in this study.
Figure 11 shows the match between the IFT from spinning drop and the IFT from microfluidics. The IFT from microfluidics showed 97% accuracy for 1.25% VES, which decreased to 65% for 0.75% VES and 51% for 0.5% VES. The results show that this method is more accurate for high IFT values. However, note that the spinning drop method may also have uncertainties at low IFT values. For the spinning drop method, it is difficult to maintain the required drop shape for a long time in very low IFT values as the drop tends to split into smaller drops. Moreover, when the bulk fluid has high viscosity like the VES case, the equilibrium takes a longer time to occur and the drop seems to deform forever until it gets out of the required shape. The variations of the IFT value
as the drop moves from inlet to outlet can be attributed to the difference in drop velocity from place to place. The difference in velocity is mainly because of the fluid diversion due to different oil saturation which makes the flow faster in lower oil saturation regions and slower in higher saturation. The drop deformation response to rapid force change will be slower in high viscosity fluids like our case. Since we are measuring the IFT in the pore throat, we are not giving it enough time to stabilize when the force exerting on it changes. However, in the case of spinning drop measurement, the stabilization time is adequate because the force is fixed at the given rotational speed.

Figure 11. Comparison of the average IFT from microfluidics and spinning drop methods.
Conclusions

VES flooding has been investigated for its performance in Enhanced oil recovery. Rheology, spinning drop IFT and microfluidics IFT has been tested. The drop deformation theory was utilized for IFT calculation inside the porous medium while flooding. Three concentrations of VES were investigated 0.5%, 0.75%, and 1.25% vol. were used. All the experiments were done under ambient conditions and the following conclusions are extracted:

- The zero-shear viscosity increased proportionally with the concentration increment and resulted in values of 325 cp, 1101 cp, and 1953 cp for 0.5%, 0.75%, and 1.25% vol. VES respectively.
- The same IFT trend was noted in both spinning drop and microfluidics, as the concentrations increase the IFT increases.
- The shear rate increase resulted in a dynamic IFT increase that started linearly at the beginning and then reached almost a plateau at the end.
- The IFT from microfluidics showed 97% accuracy for 1.25% VES, whereas accuracy dropped to 65% for 0.75% VES and 51% for 0.5% VES.

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Author Contributions

The manuscript was prepared through the contributions of all authors. All authors have approved the final version of the manuscript.
Conflicts of interest

There are no conflicts of interest to declare.

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Figure 12. For table of contents only