# DYNAMIC CONTACT ANGLE MEASUREMENT

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## ABSTRACT

Contact angle measurements are important to determine surface tension between solids and various fluids. In the oil industry, water wet conditions on the rock surface are needed to extract oil. If it is oil wet, the oil company may need to change the rock wettability. The aim of this project is to determine the contact angle of different fluids when they interact with each other and the solid surface. We will determine wettability (water wet or oil wet), analyze how the effect of different brine concentrations on wettability and contact angle measurements using the Dynamic Contact Angle Analyzer (DCA 315).

## INTRODUCTION

Contact angles between fluids are important in capillary tube measurements in oil industry. Contact angle is one of the common ways to measure the wettability of a surface or material. Wetting refers to the study of how a liquid deposited on a solid (or liquid) substrate spreads out or the ability of liquids to form boundary surfaces with solid states. In other words, wettability basically describes the preference of a solid to be in contact with one fluid rather than another. A drop of a preferentially wetting fluid will displace another fluid; at the extreme it will spread over the entire surface. Contrarily, if a non-wetting fluid is dropped onto a surface already covered by the wetting fluid, it will bead up and this minimizes its contact with the solid. If the conditions are neither strongly water wet nor strongly oil-wet, then the balance of forces in the oil/water/solid system will result in a contact angle, θ, between the fluids at the solid surface. Contact angle can be used to estimate wettability. Complete wettability would be evidenced by a zero contact angle, and complete non-wetting would be evidenced by a contact angle of 180°. In the oil industry it is very important to have a water wet condition on the rock face in order to extract oil. Another aspect with which Contact Angle is directly related to is surface tension, which exists when two phases are present. Surface tension is the tendency of a liquid to contract when exposed to gases and this is caused by the attractions among intermolecular forces. These phases can be gas/oil, oil/water, or gas/water. The purpose and aim of this project is to determine the contact angle of different fluids (mineral oil, real oil, surfactant, alkaline, and brine) when they interact between each other and the solid surface. Students will determine the wettability (water wet or oil wet), analyze how different brine concentrations will affect the wettability, and study the effect of the temperature on the dynamic contact angle measurements. This work will use the Cahn Dynamic contact angle machine to measure the contact angle between different fluids. The Cahn Dynamic Contact Angle Analyzer DCA 315 analyzer is an instrument used to measure the surface properties such as surface tension, contact angle and, interfacial tension of solid and liquid samples by using the Wilhelmy technique. It consists of a highly sensitive balance, a moving stage mechanism, and a control station.

Interfacial tension is the force that holds the surface of a particular phase together. Interfacial tension (IFT) is the contractile tendency at the liquid-liquid interface when two immiscible liquids are in contact (Figure 1).

The Interfacial tension between oil, water, and the solid cannot be directly measured. Hence, the tendency of the solid to be wetted by one phase or another is determined by measurements of the fluid IFT value and the contact angle. Injecting water solutions with some added chemicals can affect the rock surface and change the wettability from oil-wet to water-wet. As a result, oil recovery will be increased. Surface tension is the tendency of a liquid surface exposed to gases which caused by the attractions among molecules (Figure 1). It is the force acting in the plane of the surface per unit length of the surface. Surface tension is affected by the reservoir temperature. An increase in the temperature will decrease the interfacial tension.

Wettability is one of the main factors that control the flow of fluids in the oil reservoir. The arrangement of fluids in contact with a solid surface is governed by both the interfacial tension (IFT) of the liquids and the interfacial-free energy between the individual fluids and the solid equation (1):

→ $$\gamma^{sv} = \gamma^{sl} + \gamma^{lv} \cos\theta \qquad (1)$$

Where:

$\theta$ = contact angle between the oil/water/solid interface measured through the water, degrees
$\gamma^{sl}$ = interfacial energy between the liquid and solid, milli-Newtons/m or dynes/cm
$\gamma^{sv}$ = interfacial free energy of the solid surface, milli-Newtons/m or dynes/cm
$\gamma^{lv}$ = interfacial free energy (interfacial tension) of the liquid surface, milli-Newtons/m or dynes/cm

The above is known as the Young equations. The Young equation is easy to comprehend on ideal physical surfaces. it is not only unique, but also a special case of a more general fundamental equation based on complex contact angles. It explains wettability on both ideal and non-ideal surfaces. The novel mathematical form predicts the existence of imaginary contact angles on all non-ideal surfaces, implying two dimensions of wettability and necessitating the experimental determination of real and imaginary contact angles.

Contact angle measurement is needed to study the wettability effect in the capillary tube size which is present in the microscopic displacement efficiency in the reservoir porous media. In the oil industry, it's important to determine the wettability of your reservoir. Wettability or wetting is the process where by a liquid spreads on (wets) a solid substrate in the presence of other immiscible fluids. Wettability can be estimated by determining the contact angle (Figure 2).

Ultimately, in our research we hope to be able to answer the following questions:

- ➢ What can be observed when different fluids come into contact with each other and the solid surface?
- ➢ What is the effect of different brine concentrations on wettability?
- ➢ How can we apply our findings in the real world?

## EXPERIMENTAL WORK

### Equipment and Materials

*Dynamic Contact Angle Machine*

*Figure (4) Shows the CAHN dynamic contact angle analyzer-315 which was used in this research.*

*233 Schaeffer WET-SOL Concentrate Surfactant*

Obtained from Schaeffer Manufacturing Co., St. Louis, MO. Nonionic surfactant with Poly (oxy-1, 2-ethanediyl), alpha- (nonylpenyl)-omega- hydroxyl, Glycol ethers and Polydimethylsiloxane as its chemical components. This surfactant is a pale yellow liquid with a boiling point greater than 100℃, pH value of 7-8, volatility complete in water and a viscosity of 14.678cP/mPas @ 25℃.

*Surface Cleanse/930 Alkaline*

Acquired from International Products Corporation, Burlington, New Jersey. This alkaline is a clear, colorless to light yellow liquid with a boiling point greater than 100 ℃, pH value of 7-8, volatile by volume @ 21 °C and a viscosity of 0.854cP/mPas @ 25℃.

*Ultra Cruz light Mineral Oil*

It was obtained from Santa Cruz Biotechnology, Inc., Dallas, Texas. This mineral oil is a colorless viscous liquid with a boiling point range of 218-800∘C, melting point of -14.99 ℃, insoluble in water and a viscosity of 4.151 cP/mPas @ 25ºC.

*Crude oil*

1. 500T Louisiana Crude Oil

It was obtained from Louisiana. This crude oil is brown to black liquid with a boiling point of 43.7°C, melting point of -60 to -20°C, insoluble in water and 31 SUS at 37.8°C.

2. 200 Solvent Extracted Coastal Pale Crude Oil

It was obtained from Louisiana. This crude oil clear amber liquid with a boiling point of >550°F, insoluble in water and 112 SUS at 37.8°C.

3. 75 Coastal Pale Crude Oil (Naphthenic Oil)

It was obtained from Louisiana. This crude oil clear amber liquid with a boiling point of >550°F, insoluble in water and 112 SUS at 37.8°C. Figure (5)- Displaying the various fluid which were tested during the carrying out of the experimental works. In the photo from left to right: Ultra Cruz light Mineral Oil, Deionized Water, 500T Louisiana Crude Oil, Sodium Chloride grains, Calcium Chloride grains, 233 Schaeffer WET-SOL Concentrate Surfactant, and Surface Cleanse/930 Alkaline.

PROCEDURE

Measure the contact angle of a fluid e.g. water

*Steps:*

1. Remove the chamber cover.
2. Loosen screws to release beaker from the stage
3. Measure diameter of the beaker (6.7cm)
4. Remove the beaker from the stage and pour a known Volume of liquid into the beaker. (e.g. 80ml)
5. Mount the beaker back onto the stage and fasten screws back on
6. Switch on the Dynamic Contact Angle (D.C.A.) Analyzer
7. Open the Cahn Software on the computer "WinDCA"
8. Select "Run" and observe stage rising up.

NB: It is important to put a very high volume of liquid to make sure that the liquid makes contact with the sensors.

*Pre-Test Run:*

- Physically turn on the CAHN DCA-315 machine, allowing the piece of equipment to reach its optimal operating position.
- Launch the WinDCA application from the desktop of the computer being used to gather the data from the DCA-315.
- Select what kind of fluid that is going to be tested, and then proceed to filling up the container of the DCA-315.
- Unbolt the container from the base block of the DCA-315. Fill it up with the desired amount (105 mL) of the fluid to be tested, place it in and fasten it back to the base block.
- Select what test that is going to be ran, whether it be contact angle or surface tension.

*Running the test and Cleanup:*

- With the WinDCA application running, press the second to last button from the left to initialize Data Acquisition.
- Allow the system to do a complete run on the sample and allow the machine to return to its original position.
- The system will then generate a graph for the sample test run and the results can be compared to the actual value for either the contact angle or surface tension of the fluid in question.
- Withdraw the sample from the cylinder, only discard of the sample if it was mixed with some other substance, otherwise return the sample to its' original container.
- Manually turn off the machine and shut down the WinDCA application on the computer.

## RESULTS AND DISCUSSION

Experiments were conducted with the DCA315 and the results are shown below. Both surface tension and contact angle measurements were noted for better accuracy. The sets of values for surface tension and contact angles were examined as a way of supplementing each other. The results were recorded with the expectation of having definitive values for both surface tension and contact angles.
When analyzing contact angles, the surface tension values are paramount to the investigation as they will aid to stipulate the wettability of the different mixtures as well. Tables 1 through 6 shows the experiments results.
The first set of values obtained were the surface tension values of the individual fluids. The difference between the measured values and the actual values can be due to experimental error. As seen in Table 1, it is clear that the solution with the greatest or largest surface tension is Calcium Chloride solution. Since a high surface tension value would indicate a large contact angle, Calcium Chloride solution on its own would have the biggest contact angle as it has a surface tension measured value of 33.162mN/m. While the value is not exactly the same as the researched result, the same conclusion can be reached. This also means that of all the liquids examined, calcium chloride solution has the least wettability as compared to Alkaline, which has the lowest surface tension, therefore has higher wettability (as you can see in figure 7).
The contact angle values of the fluids are recorded individually. Each sample has two values associated with it, one value for the advancing contact angle and another for the receding contact angle. When examining the figures, we can see that the liquid with the highest advancing and receding contact angles is Mineral oil, with values of 73.10 and 72.17 respectively. The smallest observed contact angles are for Surfactant oil, with values of 39.93 and 40.16, advancing and receding angles respectively. Based on these findings, when it comes to wettability, surfactant has the most desirable characteristics (as you can see in figure 8).

## CONCLUSION

The aim or objective of this project was to determine the contact angles of different fluids when they interact with each other and the solid surface. Ultimately, this promote or abet Enhanced Oil Recovery (EOR), making oil extraction not only much easier, but also faster. Essentially, it important to note that the fluid mixture or combination that produces the highest surface tension induces the most favorable conditions for oil extraction. In resolution:

- When different fluids come into contact with each other and the solid surface, contact angle is established. Two angles are measured, namely the Receding Contact Angle, and the Advancing Contact Angle. A cohesive force between the liquid and solid is formed, known to be the Surface Tension. The surface tension of the different fluids can also be measured using the DCA 315. Thereafter, the surface tension can be used to derive as well as verify the contact angle.
- The different brine concentrations had an effect on the surface tensions of the fluids. This, in turn, affected the wettability of the mixtures. A greater or more extensive surface tension will result to less wettability and therefore a large contact angle. Whereas a decrease in surface tension will produce higher wettability and smaller contact angle.

- Oil extraction or oil recovery comes with many challenges. Implementing the idea of influencing or controlling fluid contact angles to affect wettability will go a long way to make the oil extraction process much easier. The expectation is that a lower contact angle will produce the most favorable conditions for oil extraction. Based on experimentations, surfactant is desirable as it maintains a high surface tension even when mixed with different brine concentrations. This means that when combined with other fluids, in particular oil fluids, Surfactant reduces wettability and increases the Contact Angle. This would therefore make it extraction of a fluid more uninhibited. In the real world, adding surfactant to an oil well may very well improve the extraction process.
- This research project proved to be quite affluent. It however was not easier and a few challenges were faced during the given research period. The CAHN DCA-315 machine is a fairly old machine, we were, however, able to retrieve some older manuals which we pieced together in order to rehash the functionality of the machine.
- One of the challenges faced was finding parts to replace the missing components of the machine. This proved to be quite a hurdle, which we conquered by improvising in order to make progress. Instead of using the Wilhemy Technique, which requires a Wilhemy plate, we simply took measurements using the rod method.
- Another challenge we faced was the length of time it took the machine to acquire results. Upon studying the mechanism of how the DCA-315 machine measures values, we realized that the time taken by the machine depends on the sample size or volume of the fluid sample. We resolved to increase the volume of our sample from 120ml to 105ml. This of course shortened the amount of time taken for a complete run from about 50-60minutes to a range of 10-20 minutes depending on the viscosity of the fluid. The thicker the fluid, the longer the cycle took.
- An important attribute to note is the high sensitivity of the DCA 315 machine. The surface on which the machine is on cannot be moved or agitated as this will cause the machine to show a very large error message. This is presumed to be because any movement during a run would distort the results. Some of the fluids used in this research project such as crude oil and surfactant proved to be difficult to clean using just water and soap. Instead, we used acetone to clean the machine components.

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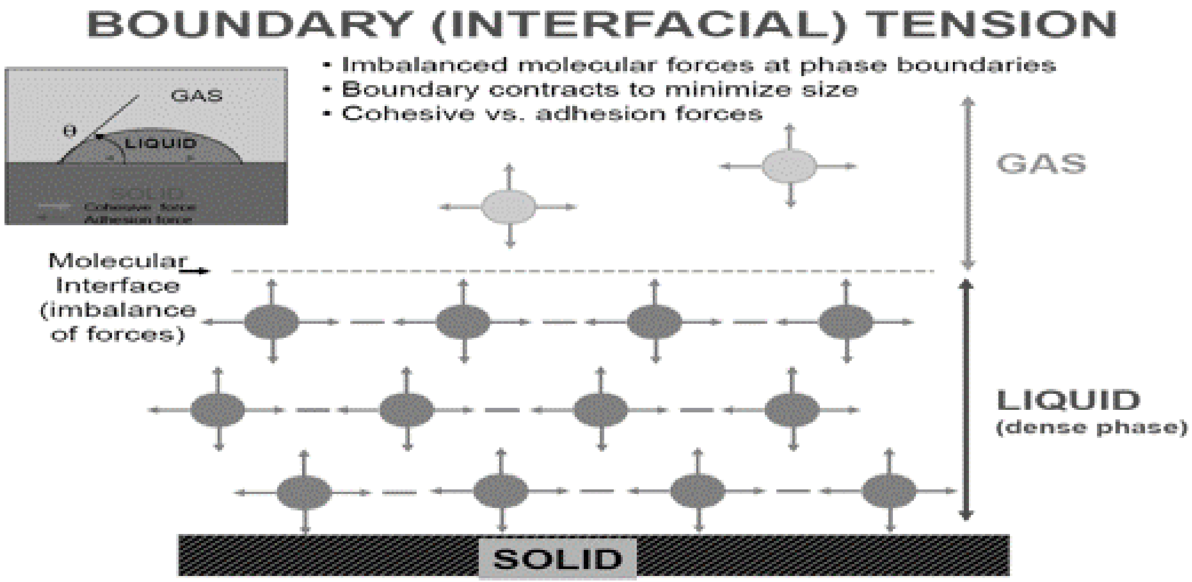


***Figure (1)-*** Displaying the intermolecular relationship between different phases namely liquid and gas. The inset photo displays the measure of the contact angle between a liquid, gas and solid phase and also the direction of the different forces namely cohesive and adhesive forces.

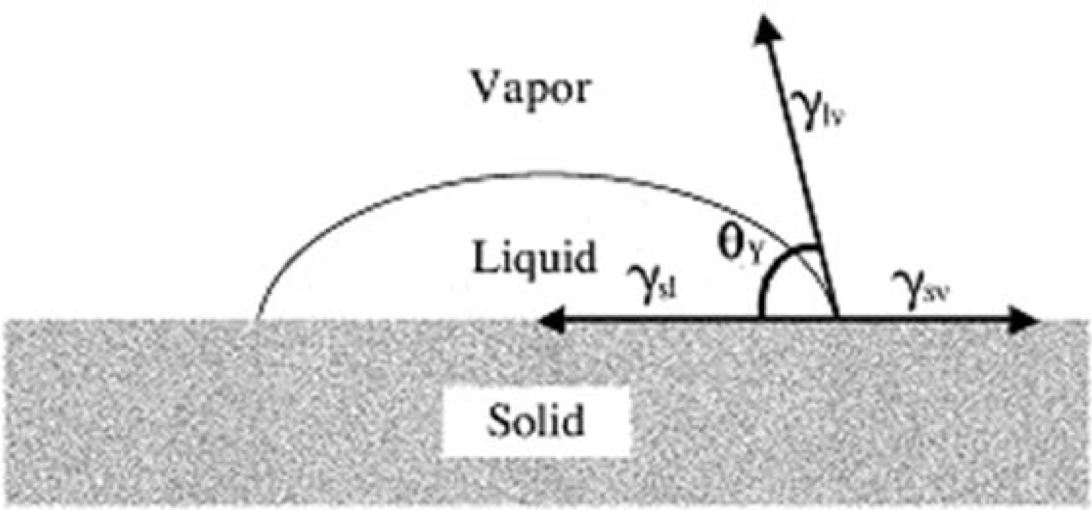


***Figure (2)-*** Displaying the external contact angle between three phases (solid, liquid and gaseous respectively) and also showing the different angles of contacts for instance between the gas and solid, solid and liquid, and gas and liquid respectively.

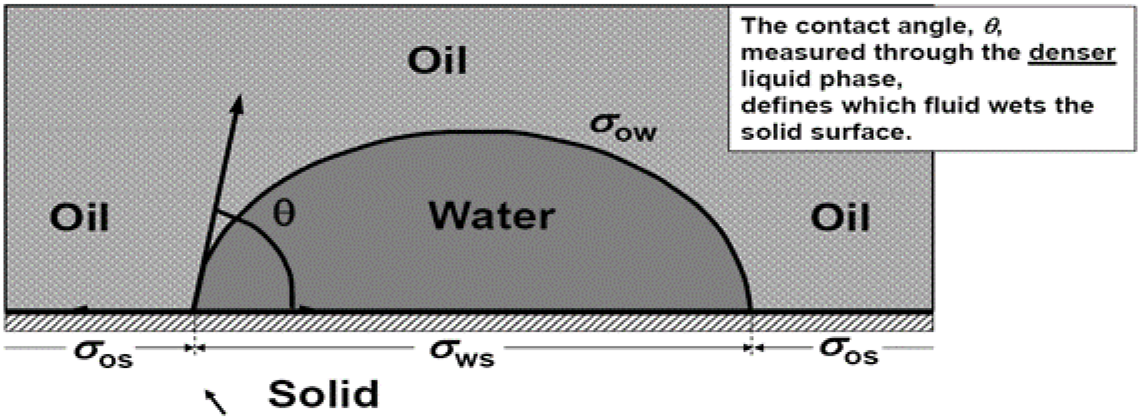


***Figure (3)*-** Displaying the contact angle of the three media (gas, solid, and liquid) and further incorporating the concept of the interfacial energy(σ) between the phases. σos denotes the interfacial energy between the oil and solid, σws denotes the interfacial energy between the water and solid, and σow = interfacial energy (interfacial tension) between the oil and water.

*Figure (4).* CAHN Dynamic Contact Angle Analyzer-315

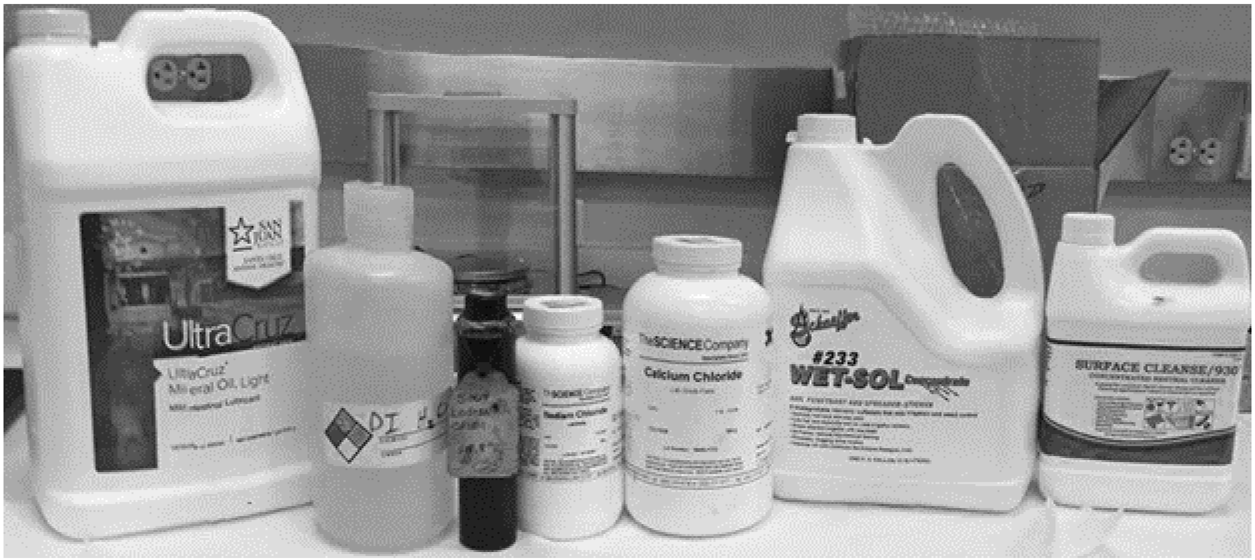


***Figure (5)-*** Displaying the various fluid which were tested during the carrying out of the experimental works. In the photo from left to right: Ultra Cruz light Mineral Oil, Deionized Water, 500T Louisiana Crude Oil, Sodium Chloride grains, Calcium Chloride grains, 233 Schaeffer WET-SOL Concentrate Surfactant, and Surface Cleanse/930 Alkaline.

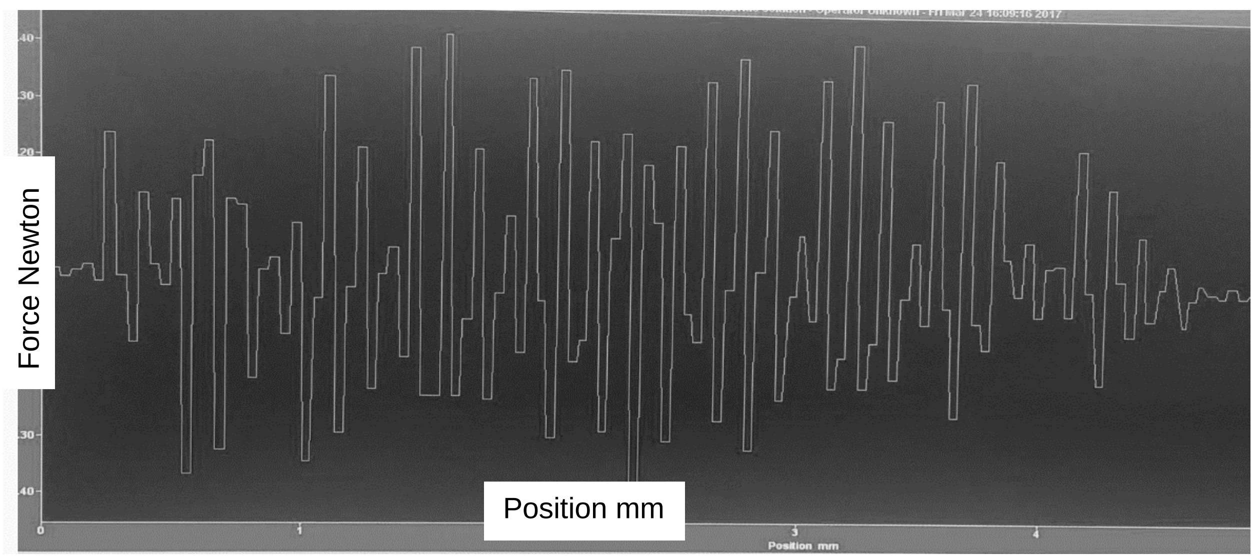


***Figure (6)-*** Displaying the results of a test while it is being carried out on the DCA 315, the x-axis displays the distance away from the neutral(starting) position of the machine and the y-axis illustrates the measure of the force exerted onto the metal rod while submerged in the fluid.

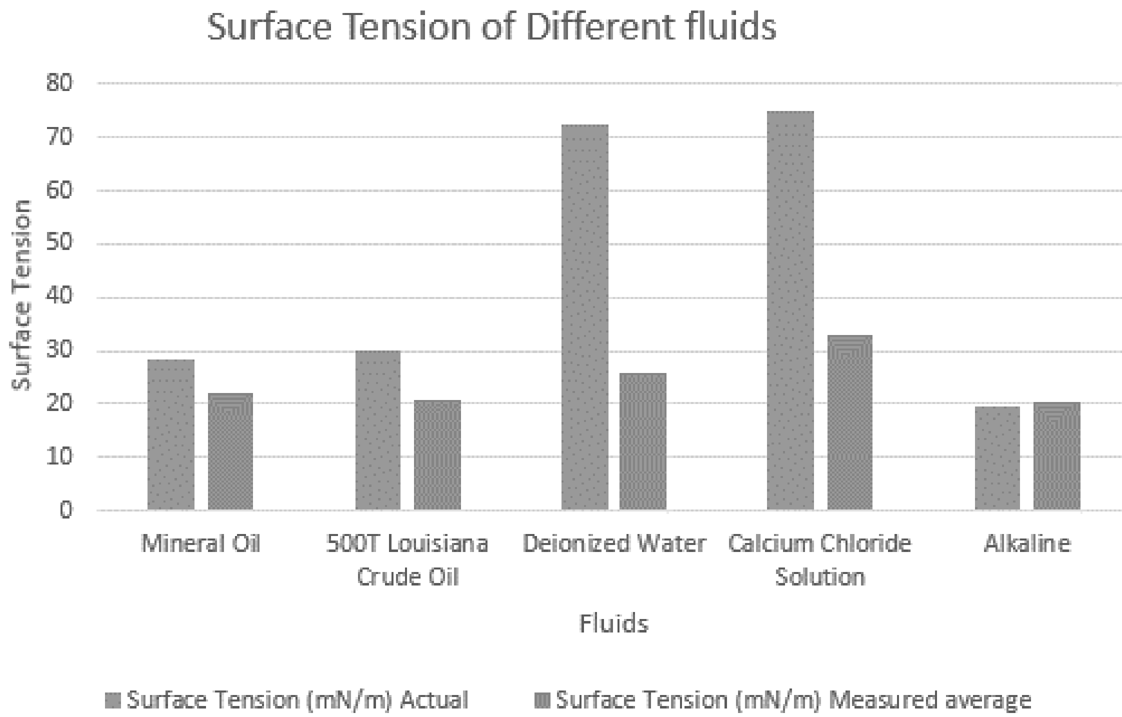


***Figure (7)-*** Shows the surface tension values of the fluid samples. Each fluid has two associated bars; one expresses the actual surface tension gathered from relevant sources and the next is a weighted average of test values obtained from experiments using the DCA 315.

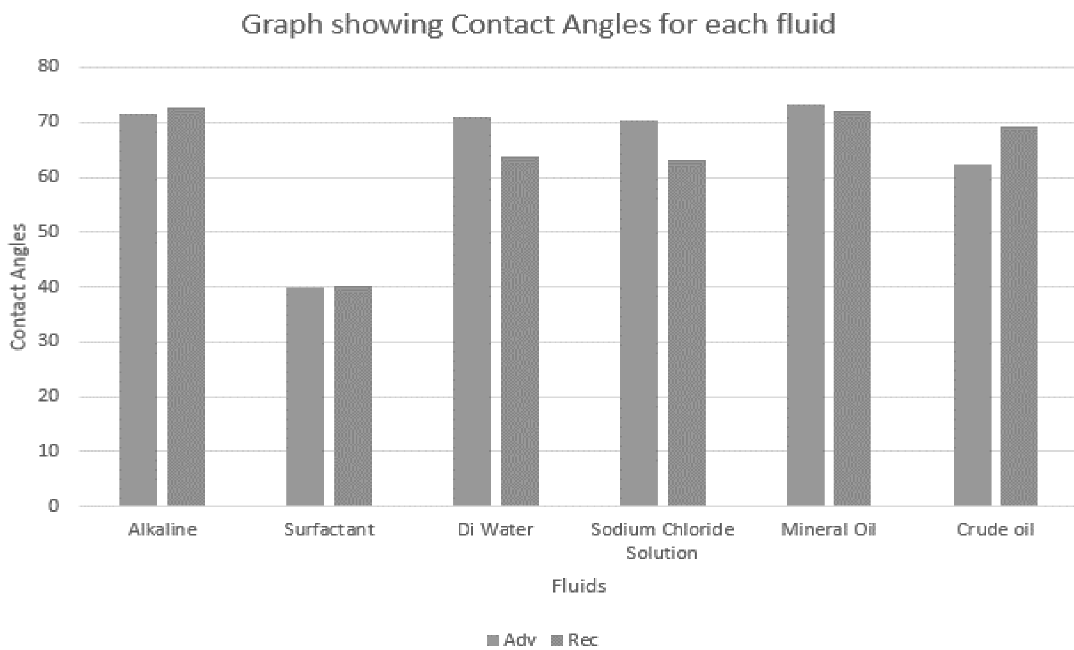


***Figure (8)-*** Shows the individual contact angle values of the samples tested. Each fluid has two associated bars; one depicts the advancing contact angle as the metal rod first enters the fluid and the next is a receding contact angle as the metal rod retracts from the fluid. This data was obtained carrying out experiments using the DCA 315.

***Table 1.*** Displaying Measured Average Surface Tension of the Various Samples vs the Actual Researched Surface Tension of the Fluids

| **Sample** | **Surface Tension (mN/m)** | |
|---|---|---|
| | **Actual** | **Measured average** |
| Mineral Oil | 28.584 | 22.288 |
| 500T Louisiana Crude Oil | 30 | 21.019 |
| Deionized Water | 72.60 | 25.745 |
| Calcium Chloride Solution | 75 | 33.162 |
| Alkaline | 19.4347 | 20.328 |

***Table 2.*** Displaying the individual Contact Angles of the test fluids. Each sample has two values associated with it, one value for the advancing contact angle and another for the receding contact angle.

| **Sample** | **Contact Angles/** | |
|---|---|---|
| | **Advancing** | **Receding** |
| Alkaline | 71.59 | 72.51 |
| Surfactant | 39.93 | 40.16 |
| Di Water | 70.82 | 63.73 |
| Sodium Chloride Solution | 70.43 | 63.13 |
| Mineral Oil | 73.10 | 72.17 |
| Crude oil | 62.19 | 69.12 |

***Table 3.*** Displaying the various Contact Angles of the test fluids when mixed with Alkaline. Each sample has two values associated with it, one value for the advancing contact angle and another for the receding contact angle. The surface tension of these new mixtures are also recorded in this table for further analysis.

| **Samples** | **Contact Angles** | | **Surface Tension/mNm** |
|---|---|---|---|
| | **Advancing** | **Receding** | |
| Surfactant | 106.72 | 103.66 | 93.8353 |
| Deionized water | 72.46 | 73.33 | 20.3743 |
| Sodium Chloride Solution | 57.74 | 39.55 | 21.9710 |
| Mineral Oil | 71.23 | 72.07 | 22.9215 |
| Crude Oil | 74.03 | 75.17 | 19.8421 |

***Table 4.*** Displaying the various Contact Angles of the test fluids when mixed with surfactant. Each sample has two values associated with it, one value for the advancing contact angle and another for the receding contact angle. The surface tension of these new mixtures are also recorded in this table for further analysis.

| **Samples** | **Contact Angles** | | **Surface Tension/mNm** |
|---|---|---|---|
| | **Advancing** | **Receding** | |
| Deionized Water | 73.42 | 72.19 | 22.3222 |
| Mineral Oil | 75.74 | 73.71 | 21.5300 |
| Crude Oil | 75.23 | 75.55 | 17.8006 |

***Table 5***. Displaying the various Contact Angles of the test fluids when mixed with deionized water. Each sample has two values associated with it, one value for the advancing contact angle and another for the receding contact angle. The surface tension of these new mixtures are also recorded in this table for further analysis.

| **Samples** | **Contact Angles** | | **Surface Tension/mNm** |
|---|---|---|---|
| | **Adv.** | **Rec** | |
| Mineral Oil | 71.81 | 71.86 | 21.8602 |
| Crude Oil | 72.63 | 73.02 | 21.1079 |

***Table 6***. Displaying the various Contact Angles of the test fluids when mixed with Sodium Chloride solution. Each sample has two values associated with it, one value for the advancing contact angle and another for the receding contact angle. The surface tension of these new mixtures are also recorded in this table for further analysis.

| **Samples** | **Contact Angles** | | **Surface Tension/mNm** |
|---|---|---|---|
| | **Advancing** | **Receding** | |
| Surfactant | 75.96 | 76.40 | 17.6118 |
| Deionized Water | 68.63 | 66.73 | 28.4669 |
| Mineral Oil | 71.89 | 71.56 | 22.6047 |
| Crude Oil | 73.78 | 74.94 | 19.4519 |