

**THE EFFECT OF PRECIPITANT INHIBITOR ON THE  
MICROEMULSION PHASE BEHAVIOUR CRUDE OIL, ALKALI AND  
SURFACTANT SYSTEM**

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UNIVERSITI TEKNOLOGI PETRONAS  
MAY 2011**

## **CERTIFICATION OF APPROVAL**

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Alkali and Surfactant System**

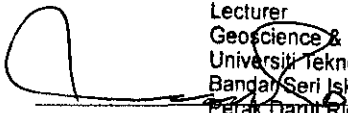
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Tronoh, Perak

May 2011

## **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

A handwritten signature in black ink, appearing to read 'Ri', is written over a horizontal line.

**ABDUL RAHIM BIN AZIZ**

## **Abstract**

Chemical flooding combination involving alkali-surfactant-polymer (ASP) has been recognized as a cost-effective chemical flooding process for light and medium oils. The main challenge in using ASP flooding is the use of hard and high saline brine due to precipitation. Precipitations will result in blocked of pore spaces which will eventually reduce the volume of recoverable crude oil. Furthermore, the reaction to form the precipitations will also decrease the pH of the solutions and reduce the surfactant performance and increase surfactant absorption into the rocks.

In this project, acrylic acid will be introduced into the formulation to prevent the precipitation from occurring. However, this will results in changes to parameters such as salinity, alkali concentration, surfactant concentration and reduce the aqueous phase solubility. Furthermore, as the mentioned parameters changes, it could lead to the changes of phase behaviour of microemulsion. This will later affect the IFT produced by the ASP flooding formulation and ultimately, the amount of recoverable oil.

## **Acknowledgement**

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## **Nomenclature**

AOS – Alpha Olefin Sulfonate

$\text{CaCl}_2 \cdot 2(\text{H}_2\text{O})$  – Calcium Chloride Dihydrate

EOR – Enhanced Oil Recovery

IFT – Interfacial Tension

$\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$  – Magnesium Chloride Hexahydrate

NaCl – Sodium Chloride

PI – Precipitant Inhibitor

## **Chapter1: Introduction**

### **1.1 Introduction**

After the primary and secondary recovery (water injection method), roughly around 65% of oil originally in place is left in petroleum reservoir (refer to *Micelles, Microemulsion and Monolayer Science and Technology*<sup>[1]</sup>). Wagner and Leach, Taber, and Melrose and Brader suggested that capillary forces are responsible for entrapping a large amount of oil in the form of oil ganglia within the porous rock of petroleum reservoirs. In chemical flooding, Stegemeir 1976 stated that mobilizing residual oil in cores can only occur when surfactant solutions reduce the IFT between the residual oil and aqueous phase. Oil and water interfacial tension (IFT) is fairly high (roughly around 20-30 dynes/cm), thus, preventing residual oil to be recovered. Well performing surfactants lower IFT to value of  $10^{-3}$  dynes/cm, which is sufficient to nearly eliminate the capillary forces that originally trapped the residual oil and causing oil mobilization.

K.A. Elraies *et al*<sup>[2]</sup> (2010), the chemical flooding combination involving alkali-surfactant-polymer (ASP) has been recognized as a cost-effective chemical flooding process for light and medium oils. The ASP slug is usually formulated by using the fresh water, alkali, suitable surfactant, and suitable polymers before being injected into the formation. This combination of chemicals can greatly enhanced oil recovery by decreasing interfacial tension, increasing capillary number, and improve mobility ratio (Ping *et al*<sup>[3]</sup> 2009). From Adam K. Flaaten *et al*<sup>[4]</sup> 2008, the surfactant function is to reduce the interfacial tension (IFT) between residual oil and water by forming microemulsion phase while alkali is used to increase the pH of the injection slug (ASP slug) and to generate in-situ surfactant to reduce the IFT. Moreover, as for the polymer, it is used to increase the sweeping efficiencies during the displacement of the oil.

According to Bourrel and Schechter<sup>[5]</sup> 1988, the term microemulsion is used to describe a micelles phase containing surfactant, brine, and oil in thermodynamic equilibrium. Microemulsion is formed due to the nature of surfactant structure (used in chemical flooding); contains both hydrophilic head and hydrophobic tails. The hydrophilic attract water molecules while the hydrophobic attract the oil molecules, allowing the water to dissolve in oil or vice versa. Surfactant reduces the IFT by forming microemulsion to allow the solubilization of oil and water. Thus, allowing the recovery of trapped oil due to capillary forces in reservoir porous rock. In retrospect, microemulsion is highly affected by the salinity of water injected in chemical flooding and other factors such as reservoir temperature.

This project will study the effect of acrylic acid or PI, precipitation inhibitor (products of acrylic acid) on the microemulsion behaviour using high saline water with high hardness concentration. The purpose of the PI is to reduce the effect of the water hardness and salinity on microemulsion performance. This allows the use of any water resource such as reservoir water or seawater as proposed by K.A. Elraies *et al* (2010). In order to achieve the use of hard brine, chemical EOR formulation consists of Alkali-Surfactant-Sodium Acrylate formulation will be tested.

## **1.2 Problem Statement**

In the new formula, acrylic acid is used to prevent the reaction of divalent metal cations with surfactant and alkali by producing precipitant inhibitor (PI) or Sodium acrylate. When surfactant and alkali is added to the chemical slug, it is directly consumed by the divalent metal cations, resulting in an undesired microemulsion. PI or sodium acrylate will be used to reduce the reactions of the metal cations with the added chemicals as mentioned by *K.A. Elraies et al (2010)*. However, this will lead to the change of injected water salinity and alkali concentration which will affect the microemulsion phase behavior.

### **1.3 Objectives and Scope of Study**

The objectives of this research are as below:

1. To study the effect of precipitant inhibitor on microemulsion behavior (optimal salinity, optimal solubilization ratio and type of microemulsion phase).
2. To determine the optimum inhibitor concentration for different water salinities and hardness concentrations.
3. To determine the critical precipitant inhibitor concentration for the desired microemulsion.

The scopes of studies are as follows:

1. Microemulsion Phase Behaviour - Water Salinity Relationship
2. Water Salinity – Precipitant Inhibitor (Acrylic Acid Concentration concentration) Interaction
3. Interfacial Tension – Alkali Concentration Relationship
4. Interfacial Tension – Surfactant Concentration Relationship

## Chapter 2: Literature Review

**2.1 Chemical Flooding (ASP/Micellar flooding):** - In Chemical EOR, there are several types of method which can be implemented. They are Polymer flooding, alkaline flooding, and micellar (ASP) flooding. In this study, ASP flooding will be emphasized.

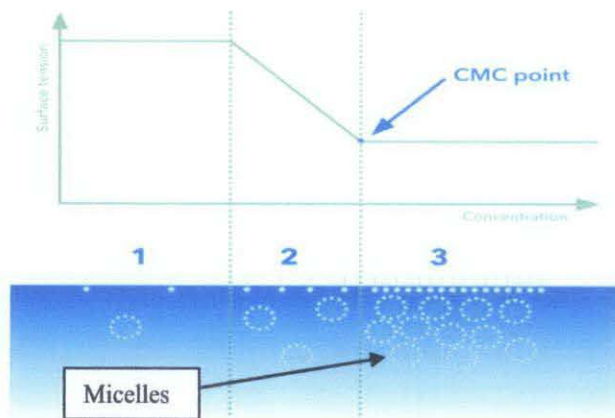
This EOR method uses the injection of a micellar slug into a reservoir. The slug is a solution usually containing a mixture of a surfactant, co-surfactant, alcohol, and brine that acts to release oil from the pores of the reservoir rock. As the micellar solution moves through the oil-bearing formation in the reservoir, it releases much of the oil trapped in the rock by reducing the oil/water IFT. To further enhance production, polymer-thickened water for mobility control is injected behind the micellar slug. A buffer of fresh water is normally injected following the polymer and ahead of the drive water to prevent contamination of the chemical solutions. This method has one of the highest recovery efficiencies of the current EOR methods, but it also one of the most costly to implement. To reduce the cost of this method, K.A. *Elraies et al (2010)* have proposed the use of hard brine (sea/formation water) along with alkali-surfactant-acrylic acid formulation instead of fresh water to reduce cost of fresh water supply and processing especially on offshore oil fields.

**2.2 Microemulsions:** - According to *Bourrel and Schechter 1988*, the term microemulsion is use to describe a micelles phase containing surfactant, brine, and oil in thermodynamic equilibrium. Microemulsion is generally of low viscosity and low water/oil interfacial tension (IFT).

Microemulsion is formed by spontaneous solubilisation of two immiscible fluids (water and oil) with the presence of surfactant in order to reduce IFT of oil/water. Surfactants molecules consists of two parts, hydrophilic (attracts to water) and lipophilic (attract to oil). Refer to figure 1

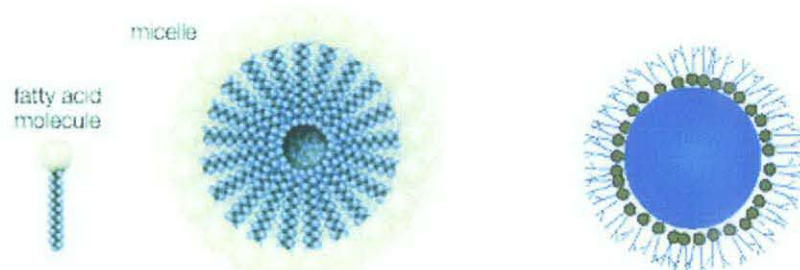


**Figure 1:** surfactant molecule structure <sup>[6]</sup>



**Figure 2:** The formation of micelles based on surfactant concentration. The micelles starts to spontaneously formed after the CMC point of the surfactant concentration <sup>[7]</sup>

The hydrophobic part of surfactant solubilise water while the lipophilic part of solubilise oil. Increasing the concentration of surfactant beyond critical micelle concentration (CMC – minimum concentration of surfactant where micelles are spontaneously formed), surfactants which only congregates at the interface of oil/water start to aggregates forming micelles. Within each micelle, it can contain either dissolved water or oil depending on the orientation of the surfactant molecules structure. Refer to figure 3(a) and 3(b)



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**Figure 3(a):** orientation of surfactant molecules where oil is dissolved in the middle of micelles. <sup>[7]</sup>

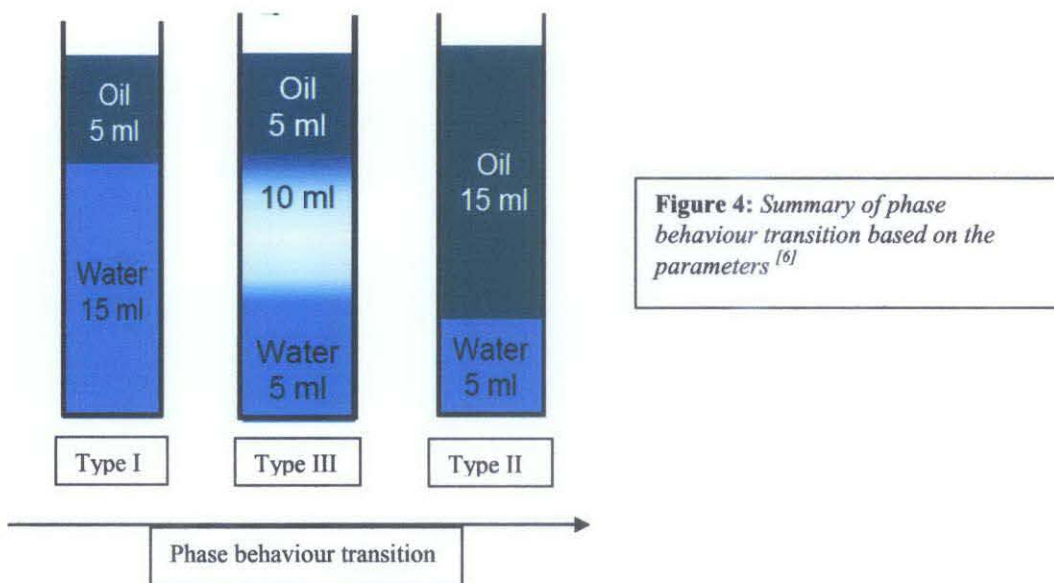
**Figure 3(b):** orientation of surfactant molecules where water is dissolved in the middle of micelles. Also known as reverse micelles <sup>[7]</sup>

As example, when water-soluble surfactant is added to water under proper conditions and above the CMC, surfactants form aggregates known as micelles which solubilise oil. This will result in increment of oil solubility in the aqueous phase which is known as Type I or lower phase microemulsion.

Winsor (1954) has classified different types of microemulsion phases. They are:

1. Type I – Oil in water (o/w) microemulsion or lower phase microemulsion
2. Type II – Water in oil (w/o) microemulsion or upper phase microemulsion
3. Type III – middle phase microemulsion

According to Dinesh O. Shah <sup>[1]</sup>, phase behavior for microemulsion can change by changing one the parameters in figure 4. The changes can be summarized as follows:



**Figure 4:** Summary of phase behaviour transition based on the parameters <sup>[6]</sup>

Parameters:

1. Increasing brine salinity
2. Decreasing temperature
3. Decreasing oil chain length
4. Increasing total surfactant concentration and total volume in a system
5. Increasing surfactant molecular weight
6. Increasing surfactant solution / oil ratio
7. Increasing alkaline concentration
8. Increasing brine/oil ratio



**2.3 Effects of Salinity on Microemulsion:** - Microemulsion phase behaviour is highly affected by the changes of brine salinities. According to *Healy et al<sup>[4]</sup>* (1976), the increasing of salinity of electrolytes in the oil and aqueous surfactant phase cause the transition of microemulsion phase from Type I to Type III and finally Type II.

According to Dinesh O. Shah, the formation of different type of phase behaviour microemulsion is related to the migration of surfactant from the lower phase to middle phase to upper phase with the increase of salinity. This is due to the decrease in water phase solubility with the increase of salinity. In type I microemulsion, the water phase salinity is low compared to the other types of microemulsion. This result in higher solubility of microemulsion in water phase compared to oil phase (lower phase microemulsion). As salinity increases until optimum salinity, the phase behaviour changes from type I into type III. In this phase, microemulsion solubilises equally in both oil and water phase. Thus, creating middle phase microemulsion. The increment of salinity beyond optimum salinity will cause the water phase to be very low in solubility, thus causing the surfactant to migrate to the oil phase (upper phase microemulsion).

Quoting from Handbook of Microemulsion Science and Technology, Chan and Shah concluded that in the formation of the middle phase microemulsion, the repulsive forces between micelles decrease due to the neutralization of surface charge of micelles by counter ions. The reduction in repulsive forces enhanced the aggregation of micelles, as the attractive forces between micelles became predominant. This theory was verified by measuring the surface charge density of the equilibrium oil droplets in the middle phase. IT was observed that surface charge density increased to maximum near the optimal salinity. Salinity beyond this cause the surface charge density to decreased in the three phase region.

According to Adam K. Flaaten et al (2008), salinity higher than the optimal salinity of microemulsion would lower the oil-microemulsion IFT and can trap surfactant in the residual microemulsion in Type II conditions with greater water-microemulsion IFT. This will results in the reduction of oil mobilization. Relating to the previous statement, in type II, surfactant has migrated to the upper phase of the microemulsion (oil phase). Residual oil is originally trapped in rock pore; the surfactant can also be trap in the pore since it is in oil phase. As for salinity lower than optimal salinity, water microemulsion IFT will be lowered while the oil microemulsion IFT will be increased. This will results in surfactants in the lower phase (brine phase).

Optimal salinity can only be gained through experiment and can be defined as salinity of brine which allows oil and water to be equally solubilised in each other. This phase is also known as the middle phase or type III microemulsion. To determined the optimum salinity of the microemulsion, graph of solubility ratio against salinity is plotted (refer to figure 5 a).

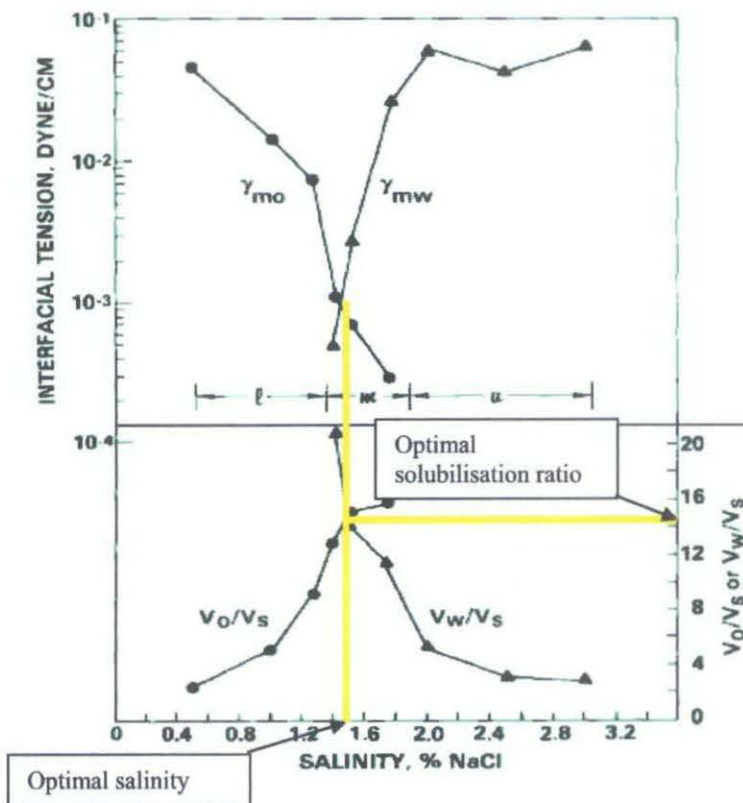


Figure 5(b): the increase of salinity results in decrease of oil microemulsion IFT while increase the water microemulsion IFT<sup>[8]</sup>

Figure 5(a): the increase of salinity will results the increase of solubilisation ratio of oil while decreasing the solubilisation ratio of water<sup>[8]</sup>

*Healy et al. (1976)* stated that volume of oil and water solubilise in microemulsion phase were measured at each increment of salinity, normalized to the total pure surfactant volume. In other word, ratio of oil to surfactant and water to surfactant were represented in solubilisation ratio versus salinity and it shows that Type III occurs at optimal solubilisation ratio and optimal salinity. This statement was made with the assumption that all surfactant participate in the microemulsion phase.

**2.4 Relationship of Salinity to IFT:** - Based on figure 5(b), it is clear that the increase of salinity until optimal salinity decrease the oil microemulsion IFT. As the salinity exceeds optimal salinity, the water microemulsion IFT increases. This is because of the migration of surfactant form lower to middle to upper phase. In type I, surfactant are concentrated in the lower phase (water phase) causing the IFT of oil microemulsion to be higher. As salinity increases, the surfactant migrates to upper phase (oil phase). As result, it shows in the figure 5(b) that as oil microemulsion IFT starts to decrease with the increment of salinity, the water microemulsion IFT are decreasing. From the graph, it is also known that the lowest IFT for both oil and water microemulsion occur at optimal salinity (in type III microemulsion). *Huh (1979)* have established the relationship of optimal solubilisation ratio of the microemulsion and the IFT (Interfacial Tension) as below equation:

$$\gamma = \frac{C}{\sigma^2}$$

Where

$\gamma$  is the Interfacial Tension of Microemulsion

C is the typical IFT of crude oils and surfactants = 0.3 dynes/cm

$\sigma$  is the optimum solubilisation ratio of microemulsion

Based on above equation <sup>[4]</sup>, the microemulsion IFT are inversely proportional to the optimal solubilisation ratio. When the optimal solubilisation ratio is 10 or higher, it will result in the IFT at  $10^{-3}$  dynes/cm which is sufficiently low to mobilize the majority of residual oil under most conditions as stated by *Ping Zhao et al 2008*.

**2.5 Effects of alkaline concentration on microemulsion:** - Adam K. Flateen *et al* 2008

have conducted the experiment to see the effect of alkali concentration towards optimal solubility ratio for both hard and soft water. The results are as shown in figure 6

Alkali - wt%	Surfactant	Co-surfactant	Ratio	Co-solvent	Optimal Solubilization Rate, $\sigma$ (cc/cc)	Eq. Time at $S^*$ (days)	Optimal Salinity, $S^*$ mg/L	Hard or soft brine
	$C_{12}E_{11} - 7PO_4SO_4^-$ (wt%)	$C_{12}E_{11}KOS$ (wt%)	surf: co-surf	SBA (wt%)				
None	0.25	0.25	1:1	0	19	-	58360	Soft
	0.25	0.25	1:1	0	78	14	29740	Hard
$Na_2CO_3$ - 1 wt%	0.25	0.25	1:1	0	19	28	53750	Soft
$Na_2B_4O_7(OH)_4$ - 1 wt%	0.25	0.25	1:1	0	12	21	36000	Hard
	0.25	0.25	1:1	0	19	-	59900	Soft

**Figure 6:** Effects of conventional and novel alkali at 1wt% for both hard and soft brine (source from SPE paper 113469)

From the series of experiment conducted, the alkali concentration of 0.5-1 wt% was determine sufficient to provide suitable pH and satisfy alkali consumption in the core. In this experiment, alkali was found to improve fluidity of microemulsion. Figure 6 compare phase behaviour results with and without alkali with the use of hard and soft brine. When soft brine is used, the optimal salinity remains to a range of 53000 to 60000 ppm. However, the use of hard brine lowers the optimal salinity and solubilisation ratio. From figure 6, it is also clear that the addition of alkali concentration from 0wt% to 1wt% in hard brine reduce the optimal solubilisation ratio to 7cc/cc. However, since both alkali concentrations provide optimal solubilisation ratio above 10cc/cc, it satisfy the resultant IFT at  $10^{-3}$  dyne/cm to allow oil mobilization (as mentioned in chapter 2.3). Based on this result, Adam K. Flateen concluded in his paper that adding alkali does not affect the phase behaviour significantly.

**2.6 Effects of surfactant concentration on microemulsion:** - Adam K Flateen *et al*

2008 has also studied the effect of phase behaviour performance towards the reduction of total surfactant concentration in his SPE paper 113469. The result as shown in figure 7

Total Surfactant (wt%)	Surfactant C <sub>12</sub> E <sub>10</sub> + TP0-SO <sub>4</sub> <sup>-</sup> (wt%)	Co-surfactant C <sub>12</sub> E <sub>10</sub> OS (wt%)	Ratio surf : co-surf	Co-solvent SBA (wt%)	Optimal Solubilization Ratio, $\sigma$ (cc/cc)	Eq. Time at S* (days)	Optimal Salinity, S* (mg/L NaCl)
2	1.5	0.5	3 : 1	1.5	16.5	21	55325
	1.0	1.0	1 : 1	0.5	16	21	75255
	1.25	0.75	5 : 3	0.5	18	21	55750
	0.75	0.25	3 : 1	0.75	15	3	55325
1	0.50	0.50	1 : 1	0.25	16	15	73720
	0.625	0.375	5 : 3	0.25	18	-	55750
0.5	0.25	0.25	1 : 1	0.125	18	3	66030
	0.3125	0.1875	5 : 3	0.125	15	15	47610

**Figure 7:** Effects of surfactant concentration on microemulsion system (source from SPE paper 113469)

From figure 7, the decrease of total surfactant concentration results in decrease of equilibrium time and optimal salinity of the microemulsion. This is due to the fact that lower surfactant concentration maintained performance with more free-flowing interfaces as stated by Adam K Flateen in his SPE paper 113469. Thus, lower total surfactant concentrations are preferred. He also stated the importance to understand that chemical flooding depends on the total mass surfactant in the chemical flood, proportional to the slug size times its concentration, which satisfies surfactant adsorption in the reservoir. Based on the result in figure 7, Adam concluded that performance of the surfactant is desirable regardless of the surfactant concentration. A small concentrated slug should perform as well as a larger diluted slug as long as the total amount of surfactant is the same. In other word, surfactant concentration does not gives much of affect on its performance, but the total amount of surfactant in a system does.

**2.7 Expectation:** The effect of Acrylic Acid towards microemulsion phase behavior will be studied throughout the 2 semester. The study is conducted to determine how sodium acrylate (product of acrylic acid and sodium) will gives impact towards the salinity of the brine use in chemical flooding and ultimately, its affects towards microemulsion phase behavior. Based on the literature review, it is expected to see the changes towards water salinity. Thus, allowing the formation of more desirable microemulsion with the use of high saline or hard brine.

From the literature review, it is known that Type III of microemulsion is highly desirable as it have low IFT for both water/oil microemulsion. Since the IFT of middle phase is very low, the capillary forces can be reduce to promote oil mobilization to achieve chemical EOR ultimate goal; to increase oil recovery. The experiment in the methodology section is design to determine the concentration of alkali, acrylic acid, surfactant and salinity of brine in order to achieve the lowest value of IFT.

During the first half of the project, the focus will be detail literature reviews about the effects of salinity towards microemulsion behavior, the functions of precipitant inhibitors and experiment methodology to be used. During the next half of the project period, lab experimentations on the solubility of chemical slug (acid, alkali, and surfactant) with crude oil will be conducted to observe the microemulsion phase behavior at different acid concentration and water salinity. All data will be collected and some analysis will be performed to evaluate effects of precipitant inhibitor towards microemulsion behavior.

## **CHAPTER 3: METHODOLOGY**

### **3.1 Proposed Activity**

**3.1.1 Apparatus:** Graduated Pipettes 5ml, Tube Rack, Convection Oven, Laboratory Weighing Scale, Beaker, Spinning Drop IFT meter, Refractive Index meter, Density meter

**3.1.2 Materials:** Surfactant (AOS), Acrylate Acid, Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ ), Angsi crude oil, distilled water, Sodium Chloride, Magnesium Chloride Hydrate, Calcium Chloride Hydrate

### **3.1.3 Experiment Method:**

In performing this experiment, it consists of 2 parts. Part 1 is to determine the critical surfactant and alkali concentration based on the IFT results. In this experiment, series of surfactant concentration along with series of alkali concentration will be used on 92,332ppm brine and oil samples. This is to determine the optimum concentration for both alkali and surfactant before proceeding towards part 2 of the experiments.

In part 2 of the experiments, base on the critical alkali and surfactant concentration obtained in part 1, different Acrylic Acid concentration will be used to study the phase behaviour using different salinities. The methodology of this part of experiment will be the same as Adam K. Flateen *et al* as stated at SPE paper 113469. From this experiment, the study of Acrylic Acid concentration towards salinities of brines will be analyzed.

Before proceeds to the main part of the experiments, different brine salinities will be prepared for the phase behaviour studies. The brine salinities are 0, 16,073, 28,783, 54,202, 79,622, 92,332, 105,041, 130,460ppm. The mentioned brine consists of 400ppm of Calcium ion and 500ppm of Magnesium ion to imitate the properties of hard water. In preparing the brine salinity, 1ppm is equivalent to 1mg of salt per litre of distilled water. From here, the weight of the sodium chloride, magnesium chloride and calcium chloride can be determined.

*\*Table 1-5 in appendices shows the information needed for the below experiment and data needed from the experiments.*

#### Brine Preparation (for 1 Litre)

1. To prepare 16,073ppm of brine, pour 1000 ml of distilled water in a beaker.
2. Place 10.422 grams of sodium chloride, 4.184 grams of magnesium chloride hydrate and 1.467 grams calcium chloride hydrate inside the beaker filled with 1000ml of distilled water. *(refer to appendix A example of salt mass calculation)*
3. Stirred the beaker slowly and gradually heat up the mixture to accelerate salts dissolves in the distilled water. Ensure during heating, the temperature does not exceed or reach boiling temperature to avoid evaporation.
4. After all salts have been dissolves, allow the brine to cool down.
5. Repeat the steps and change the mass of the sodium chloride to 23.132, 48.551, 73.971, 86.6802, 99.3899, 124.809 grams while the mass of the magnesium chloride hydrate and calcium chloride hydrate remain constant. This will create series of brine with salinity of 28,783, 54,202, 79,622, 92,332, 105,041, and 130,460ppm



### Determining the critical concentration of alkali and surfactant

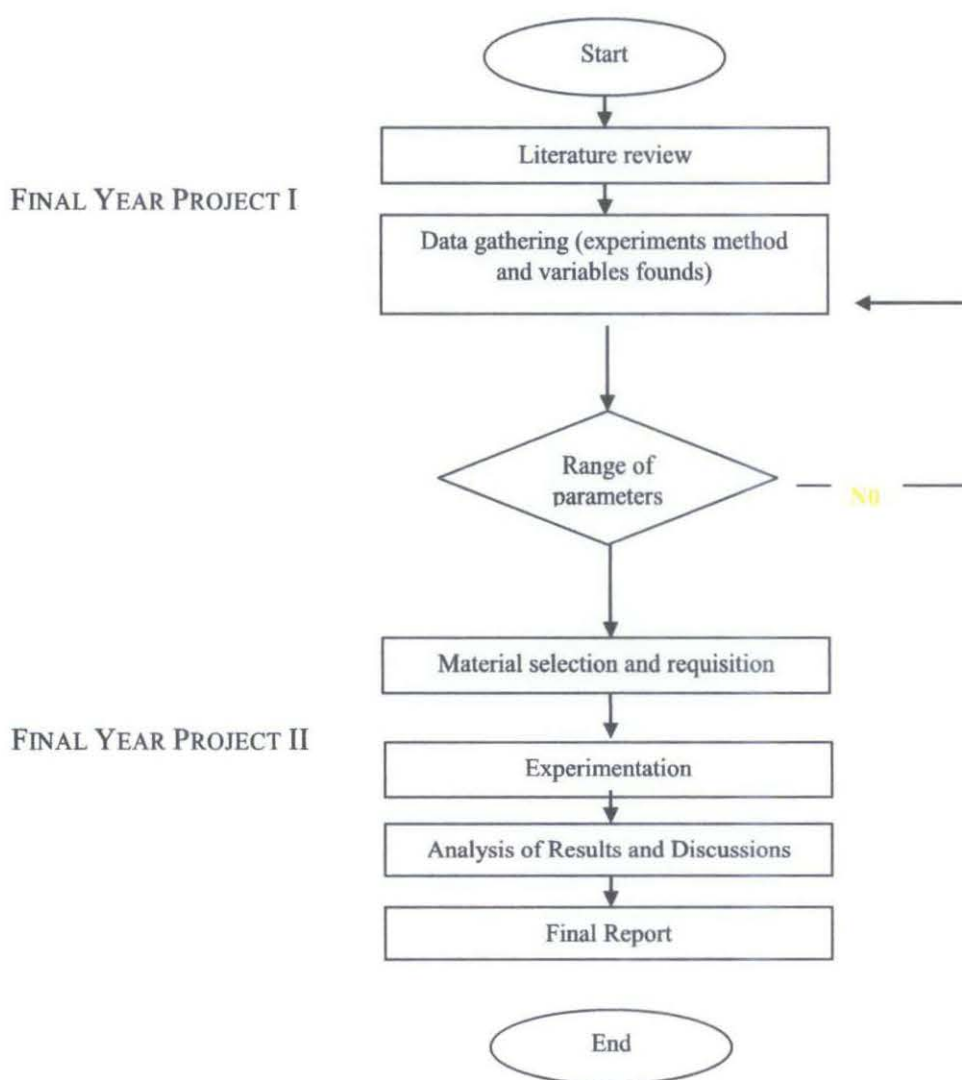
1. Aqueous solutions (Brine of 92,332 ppm salinity) are mixed with different  $\text{Na}_2\text{CO}_3$  concentrations; 0.2 wt%, 0.4 wt%, 0.6 wt%, 0.8 wt% and 1.0 wt% are prepared.
2. For each concentration of alkali used and crude oil, the density and refraction index are taken using the Density meter and Refractive Index meter at temperature of 30°C.
3. Angsi Crude Oil is heated at to prevent it from solidify inside the lab temperature.
4. 2 ml of each sample are injected inside a glass tube and inserted inside the Spinning Drop IFT meter. The temperature of the machine is set at 30°C.
5. The density and Refractive Index of the fluids used are keyed in inside the computer for measurement.
6. Run the Spinning Drop IFT meter at 1000 rpm and inject a drop of oil inside the glass tube. Wait for 15 minutes before continuing the experiment to ensure the fluid temperature have reached 30°C.
7. Adjust the rotation speed (roughly around 3000 rpm) of the glass tube until the droplet of oil reach stabilization.
8. Captured the droplet profile by using the Spinning Drop IFT meter and run the calculation for the IFT of the oil droplet.
9. IFT value is plotted against the alkali concentration and the optimum concentration is indentified.
10. The experiment is repeated by changing the alkali concentration to surfactant concentration of 0.2, 0.4, 0.6, 0.8 and 1 wt%.
11. From both graph, the optimum concentration of alkali and surfactant will be determined.

### Effect salinity and acrylic acid concentration towards microemulsion behaviour

1. 2 ml brine of 0, 16,073, 28,783, 54,202, 79,622, 105,041, 130,460ppm consist of 0 wt% of acrylic acid, and concentration of alkali and surfactant determined in earlier are placed in 7 separates modified pipettes.
2. 2 ml of crude oil are placed in each pipettes and the opening of the pipettes are sealed in.
3. The pipettes are inverted 12 times to allow the mixing of oil and aqueous phase.
4. Pipettes are then incubated at 80°C in a convection oven for 6 days
5. Observations are made each day and at the end of day 6, the new volume of crude oil and aqueous phase are noted in Table 1 provided in the appendices section.
6. The ratio of oil volume over volume of surfactant and ratio of water phase volume over volume of surfactant. (this is known as solubilisation ratio)
7. Graph of solubilisation ratio versus brine salinity is plotted. Repeat the steps by changing the sodium acrylate concentration to 0.6 and 1 wt%.

### 3.2 Key Milestone

Students play the role of investigator or researcher by performing literature review of the given topic. Assistance and supervision from assigned supervisor is essential in ensuring the project speed is within schedule. Moreover, their guidance in ensuring the given project is within the right path is very crucial in completing this project. The flow chart below explains the needs of steps taken to accomplish this project.



**Figure 8:** Flow of work throughout the 2 semester

### 3.3 Gantt chart

No.	Activities /Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Lab Work	■	■	■	■	■	■	■							
2	Progress Report Submission								■						
3	Lab Work cont....									■	■				
4	Pre EDX											■			
5	Draft Report Submission												■		
6	Dissertation Submission													■	
7	Technical Paper Submission													■	
8	Oral Presentation														■
9	Project Dissertation Submission														■

**Figure 9:** *Estimation of the project movement*

## **CHAPTER 4: RESULTS AND DISCUSSION**

### **4.1 Brine Solutions Analysis**

In preparing the brine solution, the salinity of the brine is set as follows with hardness of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  of 400 and 500 ppm respectively as a constant. Below are the salinity use and the composition of cations involved:

Salinity (ppm)	Composition
0 (distilled water)	$\text{Na}^+ = 0\text{ppm}$ , $\text{Mg}^{2+} = 0\text{ppm}$ , $\text{Ca}^{2+} = 0\text{ppm}$
16073	$\text{Na}^+ = 4100\text{ppm}$ , $\text{Mg}^{2+} = 500\text{ppm}$ , $\text{Ca}^{2+} = 400\text{ppm}$
28783	$\text{Na}^+ = 9100\text{ppm}$ , $\text{Mg}^{2+} = 500\text{ppm}$ , $\text{Ca}^{2+} = 400\text{ppm}$
54202	$\text{Na}^+ = 19100\text{ppm}$ , $\text{Mg}^{2+} = 500\text{ppm}$ , $\text{Ca}^{2+} = 400\text{ppm}$
79622	$\text{Na}^+ = 29100\text{ppm}$ , $\text{Mg}^{2+} = 500\text{ppm}$ , $\text{Ca}^{2+} = 400\text{ppm}$
92332 (used for IFT measurement only)	$\text{Na}^+ = 34100\text{ppm}$ , $\text{Mg}^{2+} = 500\text{ppm}$ , $\text{Ca}^{2+} = 400\text{ppm}$
105041	$\text{Na}^+ = 39100\text{ppm}$ , $\text{Mg}^{2+} = 500\text{ppm}$ , $\text{Ca}^{2+} = 400\text{ppm}$
130460	$\text{Na}^+ = 49100\text{ppm}$ , $\text{Mg}^{2+} = 500\text{ppm}$ , $\text{Ca}^{2+} = 400\text{ppm}$

**Table 6:** Shows the salinity and compositions of brine.

Based from the table above, only salinity of 92332ppm (highlighted in blue) will be used in the experiment to determine the optimum concentration of alkali and surfactant while the rest will be used for phase behaviour test.

The prepared brine used for phase behaviour is mixed with alkali, surfactant and acrylic acid concentration of 0, 0.6, and 1.0wt%. The solutions before mixing with oil are as follow.

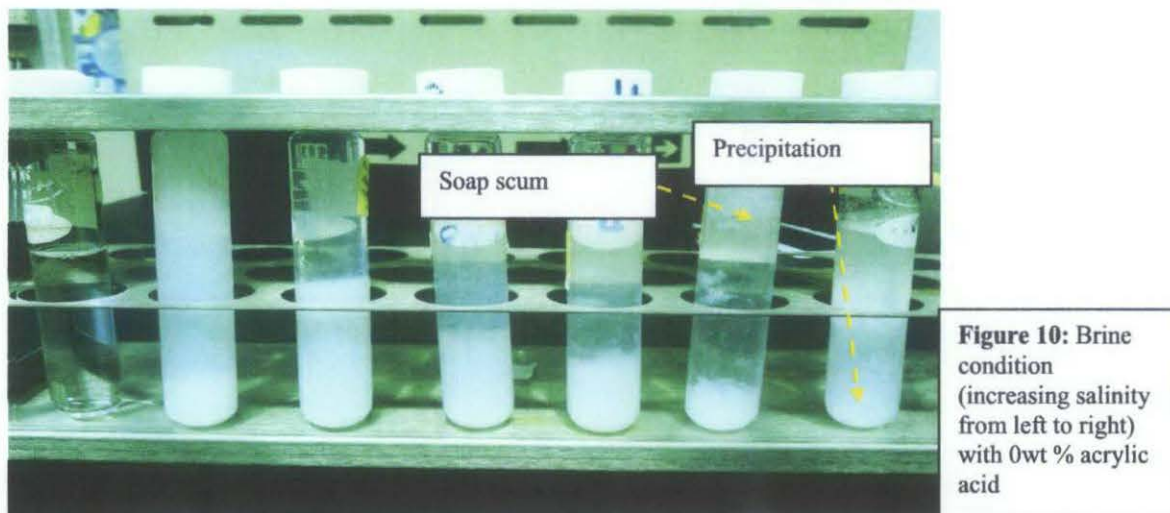


Figure 10 shows the condition of brine solution at 0wt% concentration of acrylic acid. From observation, as the salinity increases from left to right, we can see the formation of “soap scum”. Soap scum is an informal term for the white solid that results from the addition of soap to hard water. Moreover, white precipitation is also formed at the bottom of each glass (begins at 2<sup>nd</sup> glass from left or salinity of 16073 ppm). This is due to the reaction of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions react with Na<sub>2</sub>CO<sub>3</sub> to form almost insoluble salt (very low solubility in water) called Calcium and Magnesium Carbonate. Below equation shows the reaction of alkali and divalent cations (Ca<sup>2+</sup>) in the brine.



Based from above equation, we can conclude that the soluble ions and alkali inside the brine have been reduced as they were converted into the form of precipitation (CaCO<sub>3</sub> and MgCO<sub>3</sub>). As a result, the hardness of the ions inside the brine will be reduced. Moreover, this will also cause decrease of salinity as divalent cations solubilizes in brine but exist in form of CaCO<sub>3</sub> and MgCO<sub>3</sub> (precipitation). As a result, water solubility will increase.

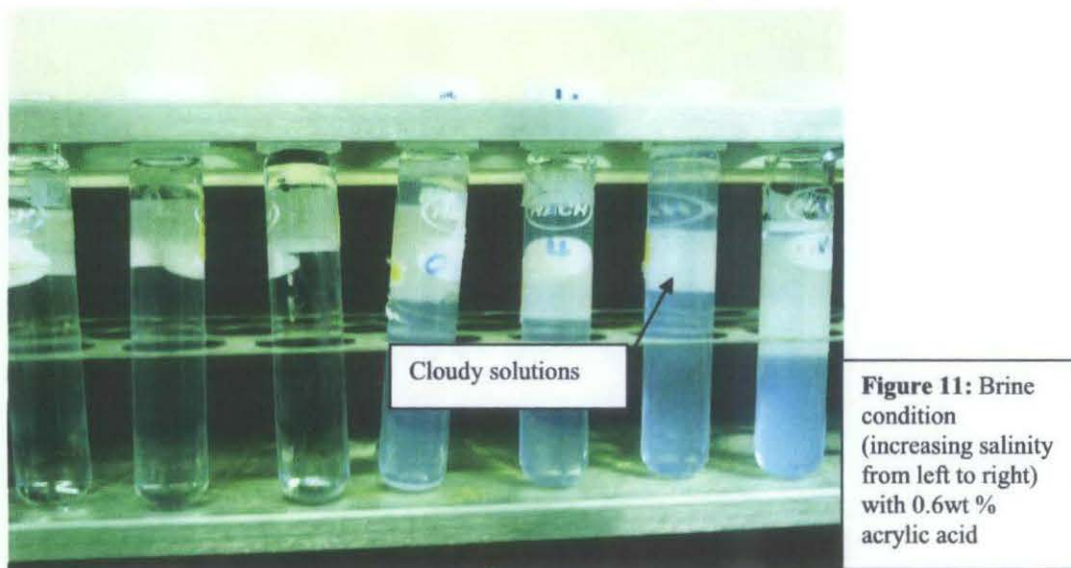


Figure 11 shows the condition of brine solution at 0.6wt% concentration of acrylic acid. From observation, there are no precipitations formed and the solutions are a little bit cloudy. This is due to the actions of PI deactivating the active growth site of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. However, the PI formed is not enough to prevent the reaction 100%. As a results, the mentioned ions the reaction of divalent metal cations with alkali have been reduced. In addition, there is no “soap scum” formed in these brine solutions. Since there are no precipitations formed, we can assume all ions, salts, alkali, acid, and surfactants dissolved in the brine solution. This will results in the reduction of aqueous solution solubility. As a result, brine salinity should be higher if compared to brine solution without the presence of acid.



**Figure 12:** Brine condition (increasing salinity from left to right) with 1 wt % acrylic acid

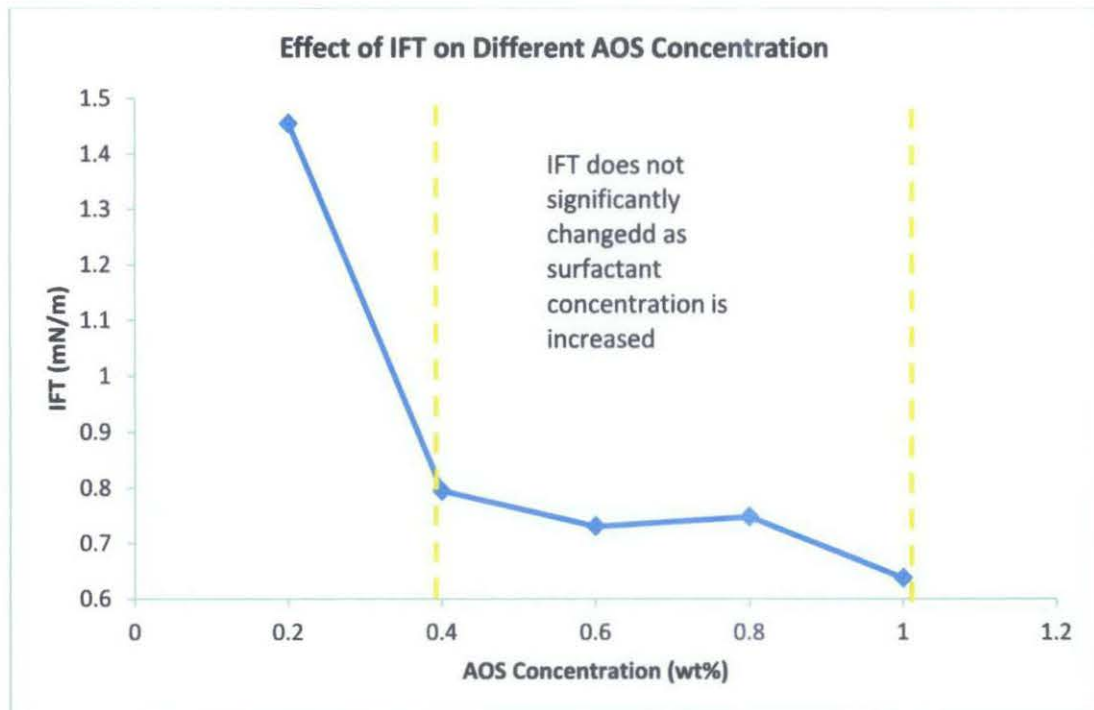
Figure 12 shows the condition of brine solution at 1wt% concentration of acrylic acid. From observation, there are no precipitations formed and the solutions are very clear. From here, it can be assumed that the PI formed has almost completely stopped the reaction of divalent metal cations with alkali. As a result, no precipitation was formed and clear aqueous solution has been obtained. In addition, there is no “soap scum” formed in these brine solutions.

Comparing the presence of acid concentration, 1wt% acid concentration has lower solubility compared to 0.6%. This is because, in 0.6% acid, we can see partially cloudy solutions; this shows the reaction of cations and alkali still occurring. As a result, a very small portion of divalent cations no longer solubilize in brine solutions due to the reactions with alkali, thus, reducing the brine solution salinity by a very small portions. As a result, acid concentration of 1wt% has slightly higher salinity compared to brine solution with 0.6% acid concentration.



## 4.2 Optimum alkali and surfactant concentration Analysis

In determining the optimum concentration of alkali and surfactant to be used, the concentration will be based on the IFT analysis. In this experiment, series of surfactant concentration (0, 0.2, 0.4, 0.6, 0.8, 1.0wt %) are mixed with prepared brine with salinity of 92332 ppm. The procedure for IFT measurement is as mentioned in methodology chapter. The results of the surfactant concentration affects towards IFT are as shown in figure 13.

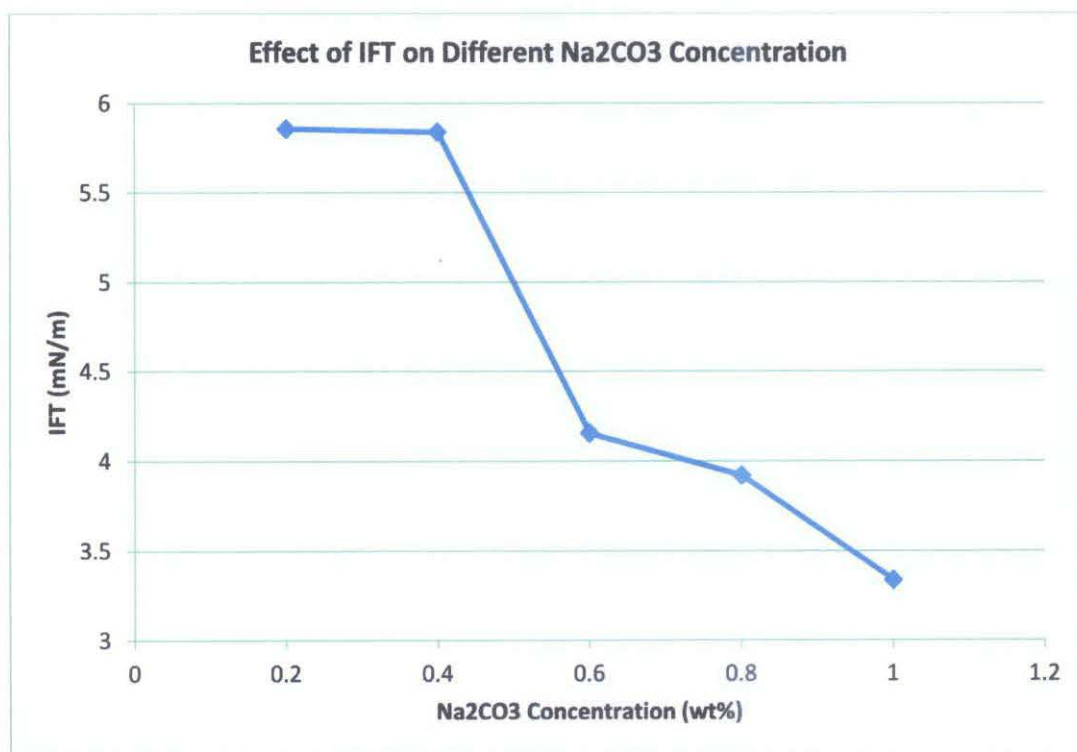


**Figure 13:** Effect of IFT on different AOS concentration

From figure 13, we can see that as the concentration of surfactant increase (0.2 to 0.4wt %), the IFT decrease significantly. However, as the concentration is increased up until 1wt %, the IFT value does not change significantly and seems to have stabilizes at average value of 0.71mN/m. The reduction of IFT is caused by the formation of microemulsion in the oil, surfactant and brine system. However, as the surfactant concentration exceeds the critical micellar concentration (CMC), the surfactant formed micelles instead of reducing the surface tension.

Above graph shows that at the surfactant concentration between 0.4 to 1.0wt %, the IFT starts to stabilize. From here, we can deduce the CMC lies between the surfactant concentrations of 0.4 to 0.6wt %. However, to be on the safe side, the concentration of surfactant decided to be used for phase behaviour test will be chosen at slightly higher than the CMC. The surfactant concentration used is chosen at 0.6wt %.

As for determination of alkali concentration,  $\text{Na}_2\text{CO}_3$  concentration of (0, 0.2, 0.4, 0.6, 0.8, and 1.0wt %) are mixed with brine salinity of 92332 ppm. The procedure for IFT measurement is as mentioned in methodology chapter. The results of the alkali concentration affects towards IFT are as shown in figure 14.



**Figure 14:** Effect of IFT on different alkali concentration

From figure 14, we can see that the increase of alkali concentration decrease the IFT. This is because alkali ( $\text{Na}_2\text{CO}_3$ ) reacts with naphthenic acid inside the crude oil to produce in situ surfactant. As alkali concentration increases, the surfactant generation also increases, resulting in the decrease of IFT between oil and aqueous phase. However, at concentration of 0.2 to 0.4 wt%, they are no significant change. At this concentration, the concentration of alkali is not sufficient to reacts with acids inside the oil. This is because divalent metal cations react with the alkali to produce precipitants. As a result, no in situ surfactants were produced in significant volume to reduce the IFT.

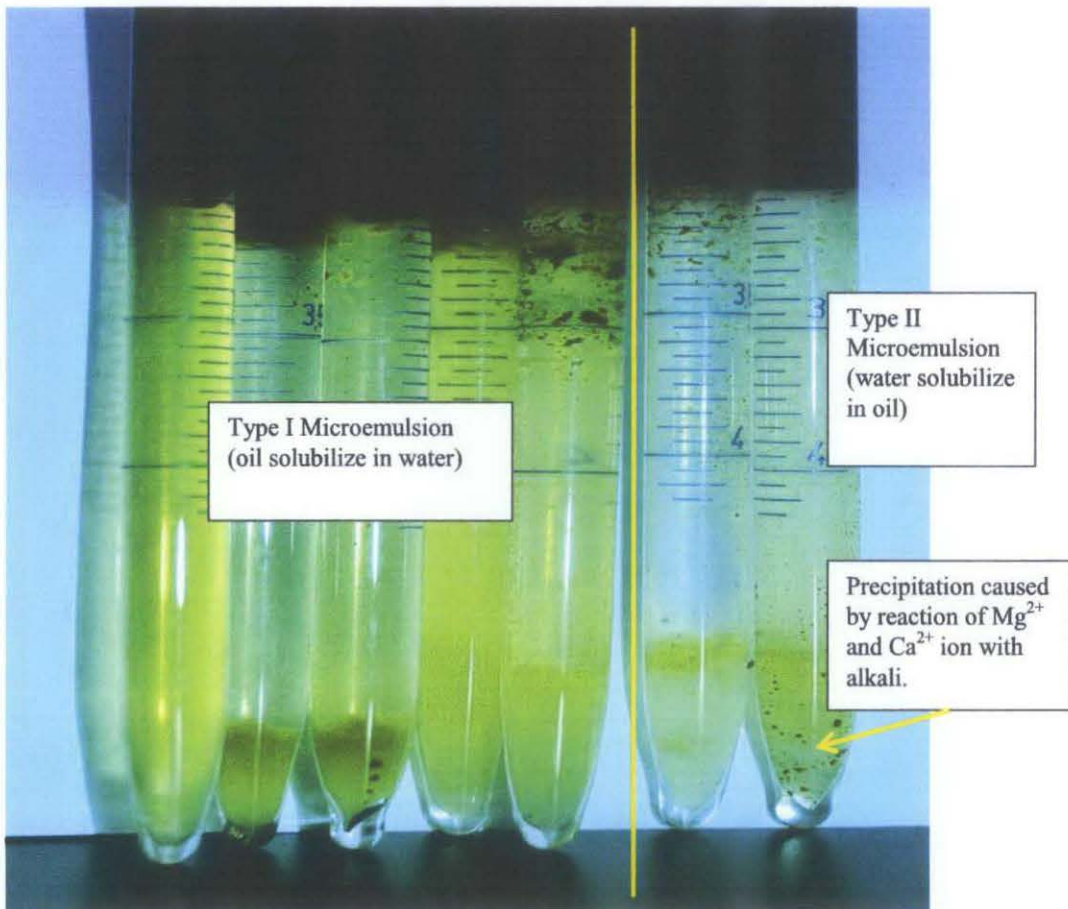
Based from the IFT graph above, it is clear that alkali concentration of 1wt % will cause the oil/brine system to have the lowest IFT for the tested alkali concentration. As a result, alkali concentration of 1wt % is chosen for phase behaviour test.

By comparison, surfactants have better effects towards IFT reduction compare to alkali. This is because alkali reacts with acid inside crude oil to produce surfactant in small amount. As a result, same concentration of acid will result in higher IFT compared to same concentration of surfactant.

### 4.3 Phase Behaviour Analysis

#### **Brine solution (Na<sub>2</sub>CO<sub>3</sub> 1wt%, AOS 0.6wt %, and acrylic acid 0wt %)**

In the phase behaviour test, alkali, brine, surfactant, and oil systems have been tested with acrylic acid concentration of 0, 0.5, and 1wt %. Figure 15 below shows the condition of oil and aqueous system at acid concentration of 0wt %.

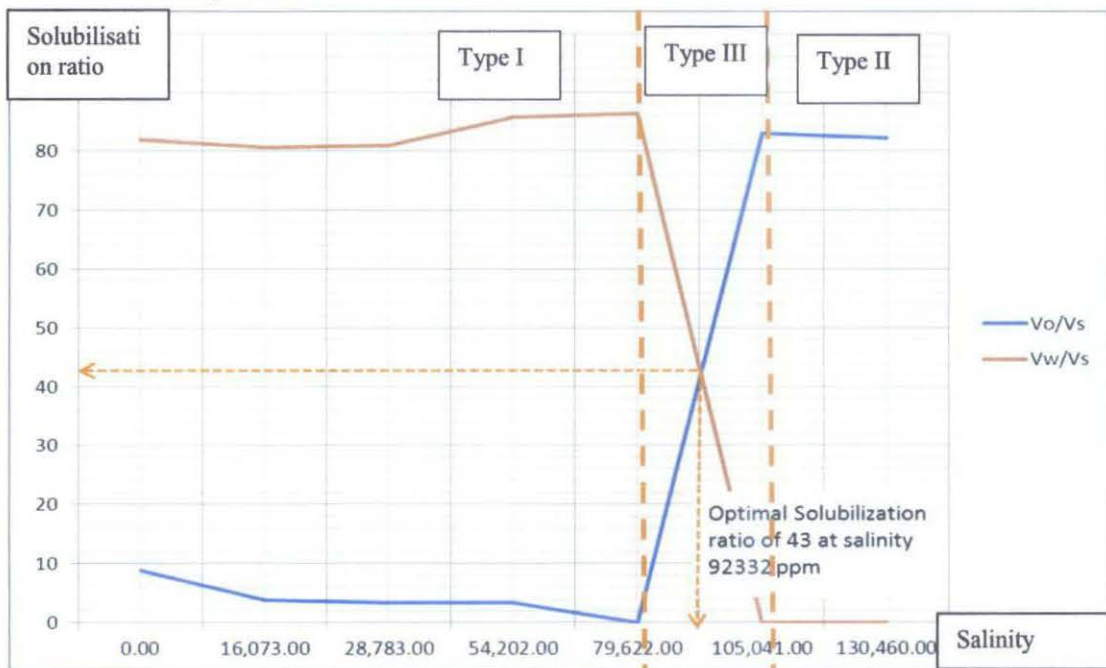


**Figure 15:** Brine salinity from left to right (0, 16073, 28783, 54202, 79622, 105041, and 130460 ppm) microemulsion behaviour

Precipitation (reaction product of divalent metal cation with alkali) starts to occur at salinity of 16073 ppm. Such precipitation is not good for chemical EOR formulation as it will block pore spaces. At salinity of 105041 ppm and 130460ppm, the microemulsion of the oil and brine system is at type II microemulsion. At salinity of 0 ppm to 79622ppm, the microemulsion is observed to be at type I microemulsion. At the last 2 salinity, it is assumed that there are no oil solubilizes in the aqueous phase.

In addition, it is also assumed that all surfactant have migrated to the oil phase as stated by Dinesh O. Shah. The oil ring seen in the precipitation is due to the oil molecules trapped between the precipitations particles.

As discussed in brine analysis, since we did not use acrylic acid to formed PI, alkali reacts with divalent metal cation ( $Mg^{2+}$  and  $Ca^{2+}$  ion) to produce precipitations. As a result of this, fewer ions is solubilize inside the aqueous solution since they have change into insoluble solid. This results in the reduction of brine salinity and increased in brine solubility. This can be proven as transition of type I to type II begins at high salinity of 105041ppm. Figure 16 shows the change of brine and oil volume in microemulsion phase.



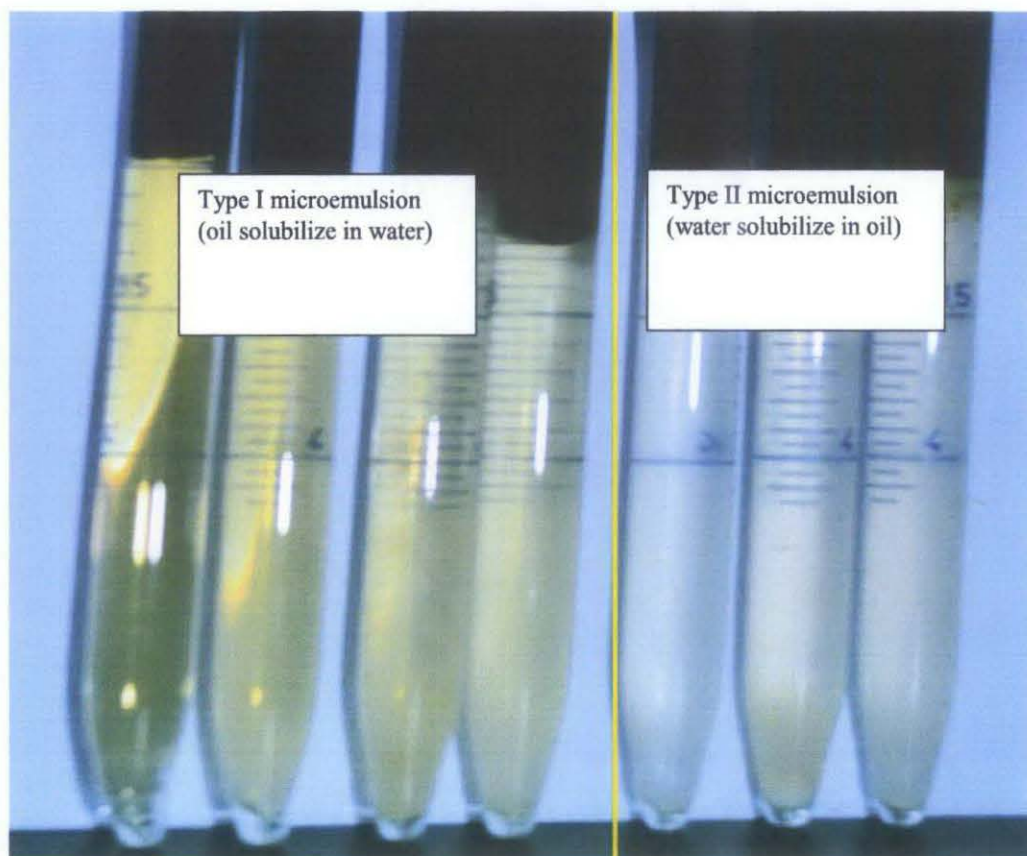
**Figure 16:** Phase behaviour diagram for acrylic acid concentration 0wt %

From the solubilization ratio versus salinity graph, the optimum salinity occurs at 92332 ppm with optimum solubilization ratio of 43. At this intersection point, aqueous phase and oil phase solubilize equally in the surfactants (type III microemulsion). In addition, at this point, the IFT of the microemulsion is at the lowest.

The absence of acid in the brine solution allows the microemulsion type III to form at much high salinity (higher than conventional sea water with salinity of 35000 ppm). In addition, from the graph, type I microemulsion (oil in water) occur much longer until it reaches salinity of 79622 ppm.

**Brine solution ( $\text{Na}_2\text{CO}_3$  1wt%, AOS 0.6wt %, and acrylic acid 0.6wt %)**

Figure 8 below shows the condition of oil and aqueous system at acid concentration of 0.6wt %.



**Figure 17:** Brine salinity from left to right (0, 16073, 28783, 54202, 79622, 105041, and 130460 ppm) microemulsion behaviour

In this aqueous solution formulation, there are no precipitations occurs except for slightly cloudy aqueous solution. However, there are less volume of oil solubilize in the early salinity of the brine (compared to acid concentration of 0wt %).

This can be justified as the solubility of brine (aqueous solution) has been reduced due to the present of high volume of salts or high saline brine. By introducing acid, the  $Mg^{2+}$  and  $Ca^{2+}$  ion active site have been deactivated to prevent reaction with alkali. However, the mentioned ions are still solubilizes in the brine, thus decreasing the solubility of the brine and maintaining the high salinity.

Since this formulation does not present any precipitation besides from the slightly cloudy aqueous solution, it will be good for chemical EOR formulation as it does not clog up the pore spaces.

Figure 18 shows the change of brine and oil volume in microemulsion phase.

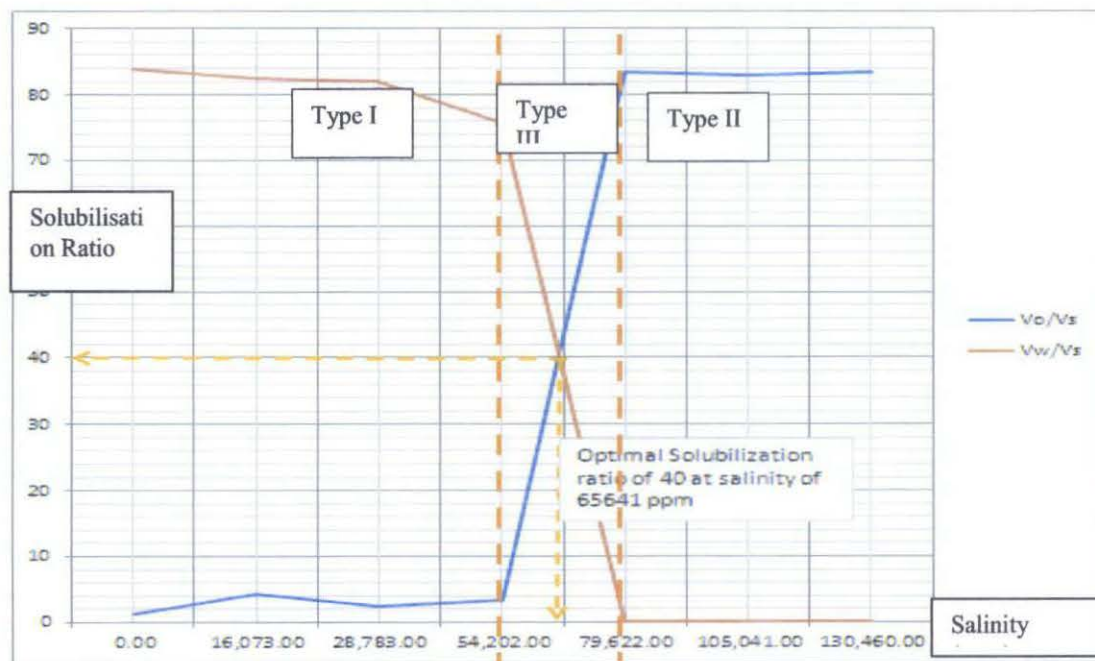
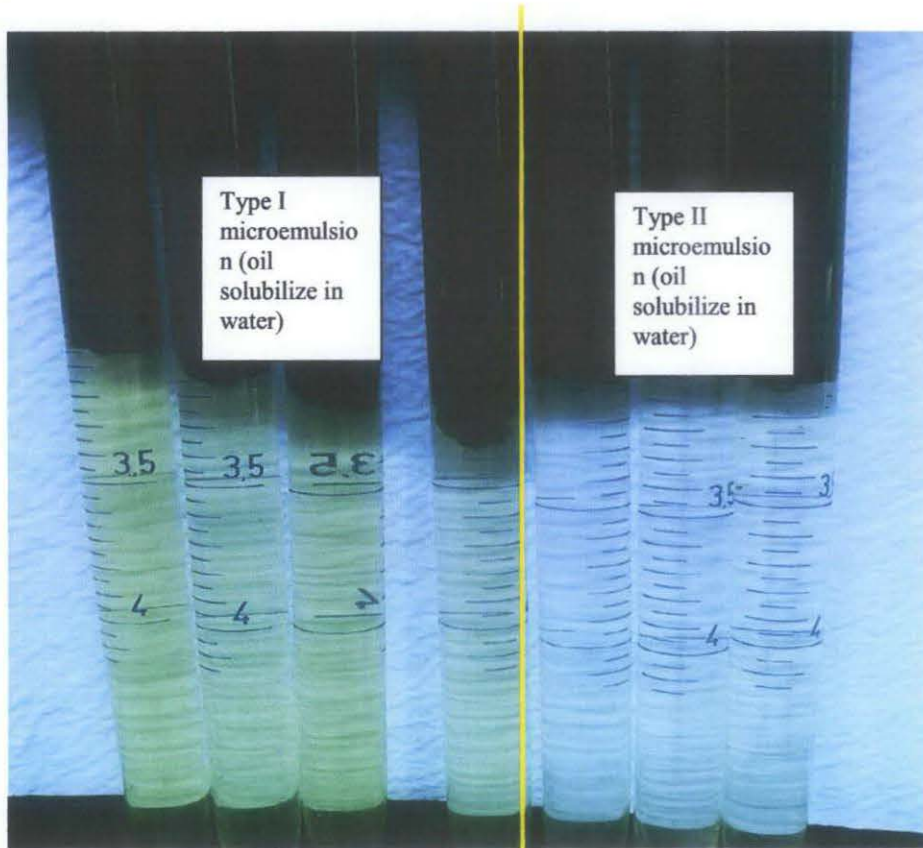


Figure 18: Phase behaviour diagram for acrylic acid concentration 0.6wt %

From the solubilization ratio versus salinity graph, the optimum salinity occurs at 65641 ppm with optimum solubilization ratio of 40. At this intersection point, aqueous phase and oil phase solubilize equally in the surfactants (type III microemulsion). In addition, at this point, the IFT of the microemulsion is at the lowest. Since the presence of acid causes the brine solubility to decrease and salinity to increase, type I microemulsion ended at much lower salinity (54202 ppm) while type II microemulsion begins at 79622ppm. This transition is caused by the migration of surfactant to the upper phase with increase of salinity or decrease of brine solubility. As a result, transition of type I, III to II occurs at much lower salinity compared to solution without acid.

**Brine solution (Na<sub>2</sub>CO<sub>3</sub> 1wt%, AOS 0.6wt %, and acrylic acid 1.0wt %)**

Figure 10 below shows the condition of oil and aqueous system at acid concentration of 1.0wt %.



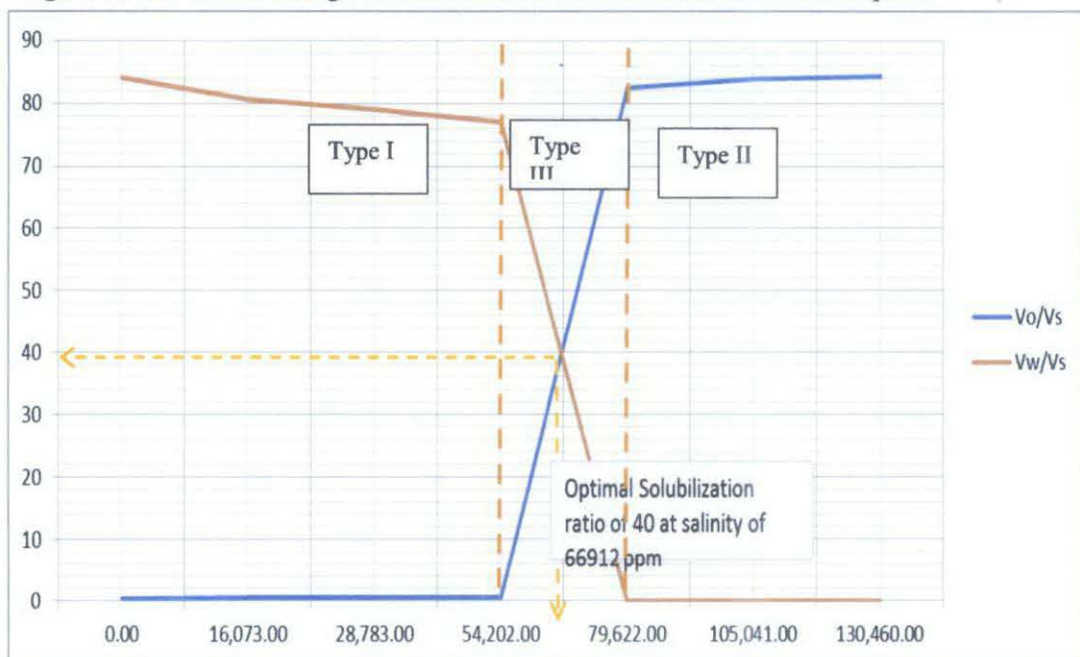
**Figure 19:** Brine salinity from left to right (0, 16073, 28783, 54202, 79622, 105041, and 130460 ppm) microemulsion behaviour



In this aqueous solution formulation, there are no precipitations occurs. However, there are very small volume of oil solubilize in the early salinity of the brine (compared to acid concentration of 0wt %). This can be justified as the solubility of brine (aqueous solution) has been reduced due to the present of high volume of salts or high saline brine. By introducing acid, the  $Mg^{2+}$  and  $Ca^{2+}$  ion active site have been deactivated to prevent reaction with alkali. However, the mentioned ions are still solubilizes in the brine, thus decreasing the solubility of the brine and maintaining the high salinity.

Since this formulation does not present any precipitation besides from the slightly cloudy aqueous solution, it will be good for chemical EOR formulation as it does not clog up the pore spaces.

Figure 20 shows the change of brine and oil volume in microemulsion phase.



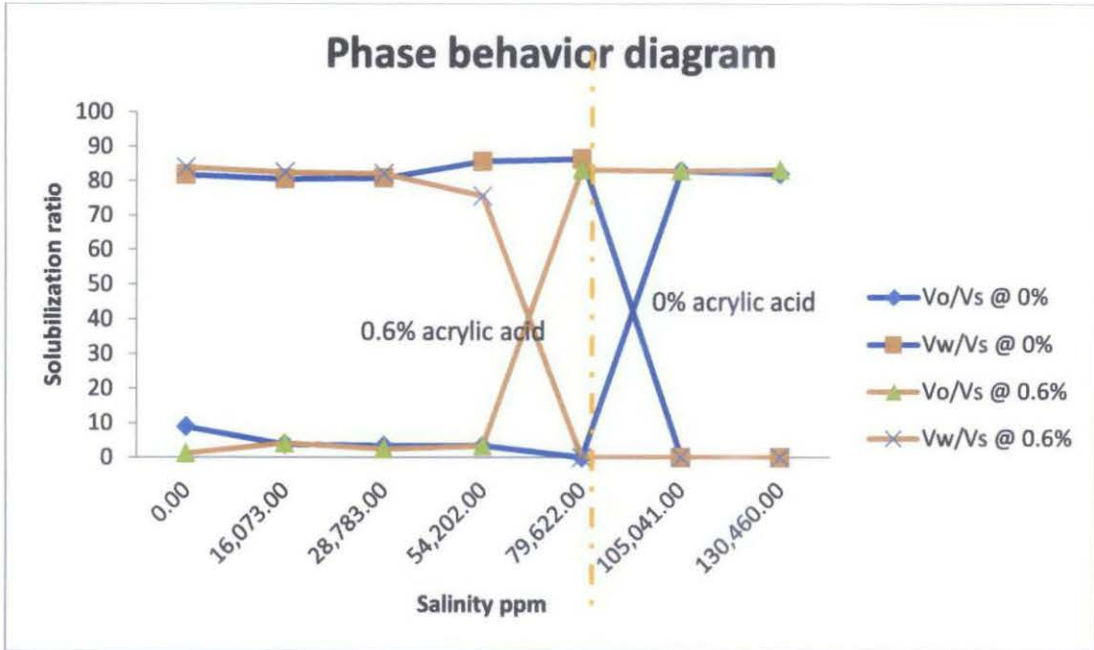
**Figure 20:** Phase behaviour diagram for acrylic acid concentration 1wt %

From the solubilization ratio versus salinity graph, the optimum salinity occurs at 66912 ppm with optimum solubilization ratio of 40. At this intersection point, aqueous phase and oil phase solubilize equally in the surfactants (type III microemulsion). In addition, at this point, the IFT of the microemulsion is at the lowest. Since the presence of acid causes the brine solubility to decrease and salinity to increase, type I microemulsion ended at much lower salinity (54202 ppm) while type II microemulsion begins at 79622ppm. This transition is caused by the migration of surfactant to the upper phase with increase of salinity or decrease of brine solubility. As a result, transition of type I, III to II occurs at much lower salinity compared to solution without acid.

#### 4.4 Solution Comparison Analysis

**Comparison between presence/absence of acrylic acid in brine solutions towards microemulsion phase behaviour.**

For comparison, solution with 0 and 0.6wt % of acid will be used. In this section, the effect of acid in alkali, surfactant, brine and oil system will be discussed.



**Figure 21:** Comparison of phase behaviour diagram with/without presence of acrylic acid

From the combination of both phase diagram of acid concentration 0% (blue line) and 0.6% (red line), it is clear that presence of acid reduces the optimal salinity to a value of 26691ppm. In theory, hard brine has lower optimal salinity compared to fresh water. This is due to the solubility of the aqueous solution. The larger the solubilize salts or total dissolves mass, the lower the solubility will be. Relating to the graph in figure 21, since acid prevent the production of precipitants (reactions of divalent metal cations with alkali),  $Mg^{2+}$  and  $Ca^{2+}$  ion still solubilize inside the aqueous solutions. This results in the migration of surfactants to the oil phase to be at much lower salinity as solubility of brine is very low.

As for solutions without acid,  $Mg^{2+}$  and  $Ca^{2+}$  ion reacts with alkali to form precipitants while the surfactants will reacts with the mentioned ions to formed magnesium or calcium stearate, As a result, less salts, alkali, and surfactants concentration are solubilizes (as they have formed solid precipitants through reactions) in the brine causing the solubility of brine to increase as solubility of brine is higher compared to the previous solution. This results in the migration of surfactants to the oil phase to be at much higher salinity.

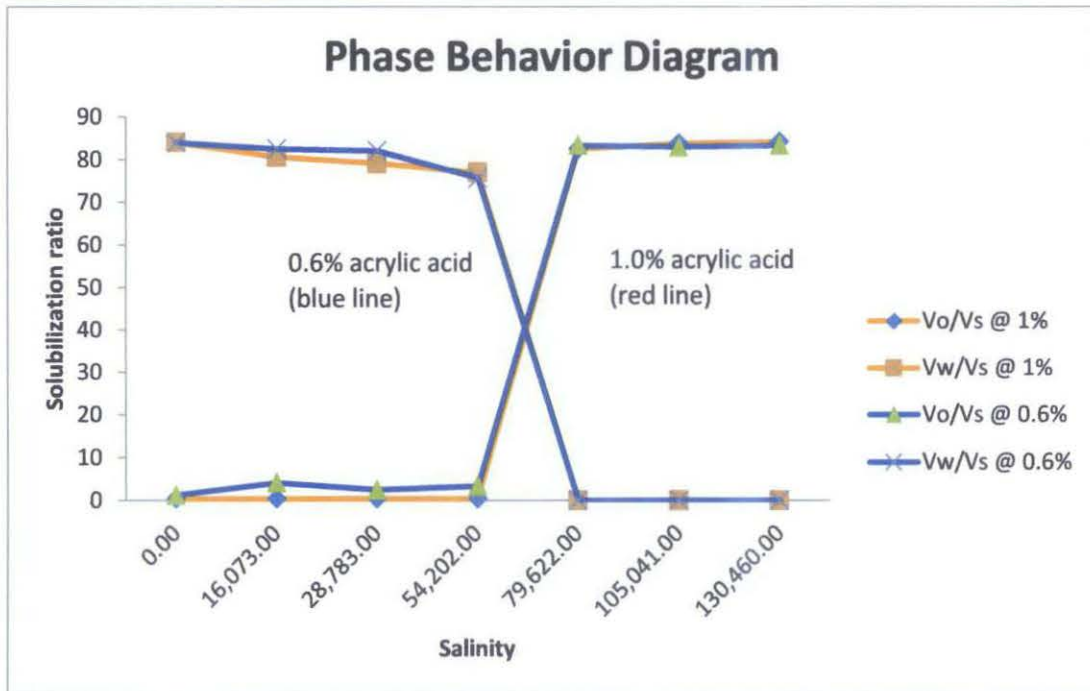
From previous discussion, this explain the occurrence where presence of acid causes the type III microemulsion to occur at much lower salinity compared to solutions without acid.

As for optimal solubilization ratio, solution without acid seems to provide slightly higher compared to solution with acid by value of 3. Optimal Solubilization ratio is vital as it is inversely proportional to the square root of IFT as presented by Healy *et al.* In other word, the higher the optimal solubilization ratio, the lower the IFT will be. However, since the absence of acid causes severe precipitations, it is highly advised to use the acid in the solution for hard brine. Furthermore, the optimal solubilization ratio does not change tremendously with presence of acid. As a result, IFT of the microemulsion will not result in much difference.

In addition, in 0% acid concentration, alkali will completely reacts with divalent cations to produces precipitations. Alkali is vital in producing in-situ surfactant by reactions with naphthenic acid in crude oil. The increase in total surfactant volume in the system causes the transition of microemulsion from type I, III, and to II. As a result, we can see that in 0% acid concentration, almost all alkali have been consumed by the divalent cations, thus reducing the total surfactant volume compared to solutions with 0.6% acid. This will cause the transition of type I to type II microemulsion occur at much lower salinity for solution with 0.6wt % acid compared to 0wt % acid concentration. This can be seen at salinity 79622ppm (dotted orange line); where 0% acid lays in the type I microemulsion region while 0.6wt % acid lies in the type II microemulsion region.

**Comparison between acrylic acid concentration in brine solutions towards microemulsion phase behaviour.**

For comparison, solution with 0.6 and 1.0wt % of acid will be used. In this section, the effect of acid concentration in alkali, surfactant, brine and oil system will be discussed.



**Figure 22:** Comparison of phase behaviour diagram for 0.5 and 1wt % acrylic acid

From the combination of both phase diagram of acid concentration 0.6% (blue line) and 1.0% (red line), it is clear that increase in acrylic acid concentration increases the optimal salinity to a value of 1271ppm. Higher concentration of acid will results in decrease of alkali concentration to form surfactants. This can be explained through chemical equation below:



As a result, at 1% acrylic acid concentration (acid concentration equal to alkali concentration, alkali will be consumed to produce sodium acrylate (PI), thus, reducing the total surfactant volume in the system by reducing in situ surfactant production (reaction of alkali and naphthenic acid inside the crude oil) compared to 0.6% acid concentration. Relating to the early theory, as total surfactant volume increases, the microemulsion will change from type I, III and II. Since 0.6% acid have larger total surfactant volume in the system (as acid concentration is lower than alkali), this solution will change into upper phase microemulsion at lower salinity compared to solution of 1wt % acid (lesser total surfactant volume by comparison). This theory is supported by the data as the optimal solubility for 0.6% acid concentration (the middle phase or type III microemulsion) occurs at lower salinity compared to 1.0% acid concentration. As for solubilization ratio, the increase of acid concentration does not seem to have significant changes towards optimal solubilization ratio of both solutions. We can conclude that additional acid concentration does not drastically change the solubility of the aqueous phase.

## **CHAPTER 5: CONCLUSION**

Presence of acid in the chemical EOR formulation significantly helps to improve the problems of severe precipitations which have become the main problem in hard brine formulation. Even though the presence of acid decreases the optimal salinity of the microemulsion, the value is still at salinity higher than normal sea water (around 35000 ppm). As for the optimum solubilization ratio, the presence of acid does not significantly change compared to solution with 0 acid concentrations. As a result, the IFT would not differ drastically. However, higher concentration of acrylic acid is not recommended as it will consume higher concentration of alkali. Alkali is important in increasing the pH of solutions for lesser surfactant absorption and producing in-situ surfactant for better IFT reduction.

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**APPENDICES**

**Table 1:** *Measurement for 1 litres of brine preparation*

Salinity (ppm)	Mass of Sodium Chloride (gram)	Mass of Magnesium Chloride hydrate (gram)	Mass of Calcium Chloride hydrate (gram)
0.00	0	0	0
16,073.00	10.422	4.18	1.467
28,783.00	23.132	4.18	1.467
54,202.00	48.551	4.18	1.467
79,622.00	73.971	4.18	1.467
92,332.00	86.680	4.18	1.467
105,041.00	99.390	4.18	1.467
130,460.00	124.809	4.18	1.467

**Table 2:** *Part 1 of the methodology, to determine the critical surfactant and alkali concentration based on the IFT produced.*

Brine Salinity (ppm)	Surfactant concentration (wt %)	Alkali concentration (wt %)
92,332	0	0
	0.2	0.2
	0.4	0.4
	0.6	0.6
	0.8	0.8

**Table 3:** *Example of table to record the IFT of the microemulsion formed (0 wt% surfactant with series of alkali concentration; and 0 wt% alkali with series of surfactant concentration).*

Surfactant concentration (wt %)	Alkali concentration (wt %)	Measured IFT (dyne/cm)
0	0	
	0.2	
	0.4	
	0.6	
	0.8	
	1.0	

Alkali concentration (wt %)	Surfactant concentration (wt %)	Measured IFT (dyne/cm)
0	0	
	0.2	
	0.4	
	0.6	
	0.8	
	1.0	

**Table 4:** Part 3 of the methodology, to determine the effect of microemulsion phase behaviour for optimum alkali and surfactant concentration with varies of Acrylic acid and brine concentration and salinity.

Surfactant Concentration (wt %)	Alkali concentration (wt %)	Acrylic Acid concentration (wt %)	Brine Salinity (ppm)
Determine in Part 1	Determine in Part 1	0.2 0.6 1.0	0.00
			16,073.00
			28,783.00
			54,202.00
			79,622.00
			105,041.00
			130,460.00

**Table 5:** Observation table for part 2 of the experiment

Volume of oil in microemulsion phase, $V_o$ (ml)	Volume of water in microemulsion phase, $V_w$ (ml)	Volume of surfactant, $V_s$ (ml)	$V_o/V_s$ (oil solubilisation ratio)	$V_w/V_s$ (water solubilisation ratio)

## Appendix A (salt mass calculation for brine preparation)

The brine is prepared based on the  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions. Since the salt is in formed of chloride and chloride hydrate, molecular weight fraction is needed to calculate the amount of salt needed to prepare such brine. In this example, calculation for brine with hardness salinity of 5000 ppm will be shown:

Molecular Weight for NaCl = 58.44 g/mol

Molecular Weight for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  = 203.31 g/mol

Molecular Weight for  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  = 147.02 g/mol

Molecular Weight for Na = 22.98977 g/mol

Molecular Weight for Mg = 24.3050 g/mol

Molecular Weight for Ca = 40.078 g/mol

### Amount of ions weight needed for 5000 ppm brine:

5000 ppm = 5 g (ions) / 1 L (distilled water)

Hardness of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are chosen at 500 and 400 ppm respectively.

500 ppm ( $\text{Mg}^{2+}$ ) + 400 ppm ( $\text{Ca}^{2+}$ ) + 4100 ppm ( $\text{Na}^+$ ) = 5000 ppm

Also equivalent to

$[0.5\text{g} (\text{Mg}^{2+}) + 0.4\text{g} (\text{Ca}^{2+}) + 4.1\text{g} (\text{Na}^+)] / 1\text{ L} = 5\text{g} (\text{ions}) / 1\text{ L} = 5000\text{ ppm}$

### To calculate NaCl needed for above mass:

Mass Na = (MW Na / MW NaCl) \* mass NaCl

Mass NaCl required = Mass Na \* 1/(MW Na / MW NaCl)

$$= 4.1\text{g} * 1 / (22.98977/58.44)$$

$$= 10.422\text{ g}$$

To Calculate MgCl<sub>2</sub>.H<sub>2</sub>O needed for above mass:

$$\text{Mass Mg} = (\text{MW Mg} / \text{MW MgCl}_2\cdot\text{H}_2\text{O}) * \text{mass MgCl}_2\cdot\text{H}_2\text{O}$$

$$\begin{aligned}\text{Mass MgCl}_2\cdot\text{H}_2\text{O required} &= \text{Mass Mg} * 1/ (\text{MW Mg} / \text{MW MgCl}_2\cdot\text{H}_2\text{O}) \\ &= 0.5\text{g} * 1/ (24.3050/203.31) \\ &= 4.18 \text{ g}\end{aligned}$$

To Calculate CaCl<sub>2</sub>.H<sub>2</sub>O needed for above mass:

$$\text{Mass Ca} = (\text{MW Ca} / \text{MW CaCl}_2\cdot\text{H}_2\text{O}) * \text{mass CaCl}_2\cdot\text{H}_2\text{O}$$

$$\begin{aligned}\text{Mass CaCl}_2\cdot\text{H}_2\text{O required} &= \text{Mass Ca} * 1/ (\text{MW Ca} / \text{MW CaCl}_2\cdot\text{H}_2\text{O}) \\ &= 0.4 \text{ g} * 1/ (40.078/147.02) \\ &= 1.467 \text{ g}\end{aligned}$$

-End of calculation-

## Appendix B (Data taken)

### Data for IFT measurement

Sample No.	AOS Weight Percentage (%)	Weight (g)	Density (g/cm <sup>3</sup> )	RI Index	IFT (mN/m)
1	0	0	1.0644	1.3355	9.2936
2	0.2	0.0515	1.0635	1.34932	1.4553
3	0.4	0.1031	1.0639	1.34949	0.7948
4	0.6	0.1546	1.0643	1.34957	0.731
5	0.8	0.2062	1.0646	1.34962	0.7479
6	1	0.2577	1.0648	1.34956	0.6374

Sample No.	Na <sub>2</sub> CO <sub>3</sub> Weight Percentage (%)	Weight (g)	Density (g/cm <sup>3</sup> )	RI Index	IFT (mN/m)
1	0	0	1.0644	1.34952	9.2936
7	0.2	0.0515	1.0659	1.34966	5.8576
8	0.4	0.1031	1.0663	1.34955	5.8394
9	0.6	0.1546	1.0693	1.34986	4.1552
10	0.8	0.2062	1.0702	1.35023	3.919
11	1	0.2577	1.0742	1.35096	3.3366

### Data for phase behaviour

Brine composition		Weight Percentage (%)
Alkali	Na <sub>2</sub> CO <sub>3</sub>	1
Surfactant	AOS	0.6
Acid	Acrylic Acid	0
Brine	Variable	98.4

Brine Hardness (ppm)	
Mg <sup>2+</sup>	500
Ca <sup>2+</sup>	400

Solution Composition	
Brine Solution	50%
Oil	50%

Total Retention Time (Days)
6

Sample	Salinity ppm	Hardness ppm	Total Volume ml	V <sub>o</sub>				V <sub>w</sub>			V <sub>s</sub> %	V <sub>o</sub> /V <sub>s</sub>	V <sub>w</sub> /V <sub>s</sub>
				ml	excess %	solubilize %	ml	excess %	solubilize %				
1	0.00	0.00	3.93	1.72	43.7659033	5.34351145	1.93	0	49.1094148	0.6	8.905852	81.64902	
2	16,073.00	5,000.00	3.91	1.82	46.5473146	2.30179028	1.89	0	48.3375959	0.6	3.836317	80.56266	
3	28,783.00	10,000.00	3.98	1.9	47.7386935	2.01005025	1.93	0	48.4924623	0.6	3.350084	80.82077	
4	54,202.00	20,000.00	3.95	1.87	47.3417722	2.02531646	2.03	0	51.3924051	0.6	3.375527	85.65401	
5	79,622.00	30,000.00	3.84	1.85	48.1770833	0	1.99	0	51.8229167	0.6	0	86.37153	
6	105,041.00	40,000.00	3.98	1.98	0	49.7487437	2	50.25126	0	0.6	82.91457	0	
7	130,460.00	50,000.00	3.94	1.92	0	49.2385787	2.02	51.26904	0	0.6	82.0643	0	

Brine composition		Weight Percentage (%)
Alkali	Na2CO3	1
Surfactant	AOS	0.6
Acid	Acrylic Acid	0.6
Brine	Variable	97.8

Brine Hardness (ppm)	
Mg2+	500
Ca2+	400

Solution Composition	
Brine Solution	50%
Oil	50%

Total Retention Time (Days)	6
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Sample	Salinity ppm	Hardness ppm	Total Volume		Vo		Vw			Vs %	Vo/Vs	Vw/Vs
			ml	ml	ml	excess %	solubilize %	ml	excess %			
1	0.00	0.00	4.03	2	49.6277916	0.74441687	2.03	0	50.3722084	0.6	1.240695	83.95368
2	16,073.00	5,000.00	4	1.9	47.5	2.5	1.98	0	49.5	0.6	4.166667	82.5
3	28,783.00	10,000.00	3.98	1.92	48.241206	1.50753769	1.96	0	49.2462312	0.6	2.512563	82.07705
4	54,202.00	20,000.00	4.01	1.93	48.1296758	1.99501247	1.82	0	45.3865337	0.6	3.325021	75.64422
5	79,622.00	30,000.00	3.98	1.92	0	50	1.98	0	0	0.6	83.33333	0
6	105,041.00	40,000.00	3.98	1.93	0	49.7487437	1.98	49.74874	0	0.6	82.91457	0
7	130,460.00	50,000.00	4	2	0	50	2	50	0	0.6	83.33333	0

Brine composition		Weight Percentage (%)
Alkali	Na2CO3	1
Surfactant	AOS	0.6
Acid	Acrylic Acid	1
Brine	Variable	97.4

Brine Hardness (ppm)	
Mg2+	500
Ca2+	400

Solution Composition	
Brine Solution	50%
Oil	50%

Total Retention Time (Days)	6
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Salinity ppm	Hardness ppm	Total Volume		Vo		Vw			Vs %	Vo/Vs	Vw/Vs
		ml	ml	ml	excess %	solubilize %	ml	excess %			
0.00	0.00	3.99	1.98	49.6240602	0.25062657	2.01	0	50.3759398	0.6	0.417711	83.9599
16,073.00	5,000.00	3.95	1.94	49.1139241	0.25316456	1.91	0	48.3544304	0.6	0.421941	80.59072
28,783.00	10,000.00	3.92	1.91	48.7244898	0.25510204	1.86	0	47.4489796	0.6	0.42517	79.08163
54,202.00	20,000.00	3.96	1.95	49.2424242	0.25252525	1.83	0	46.2121212	0.6	0.420875	77.0202
79,622.00	30,000.00	3.94	1.94	0	49.4923858	2	50.76142	0	0.6	82.48731	0
105,041.00	40,000.00	4	2	0	50.25	2	50	0	0.6	83.75	0
130,460.00	50,000.00	4.02	2.02	0	50.4975124	2	49.75124	0	0.6	84.16252	0

-End of data-