

**EFFECT OF LIVE-CRUDE-OIL, GOR,
AND HPHT ON OPTIMAL SALINITY OF
EOR SURFACTANT FORMULATION**

BY

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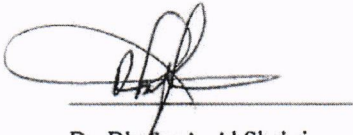
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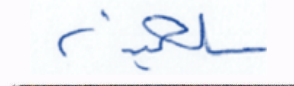
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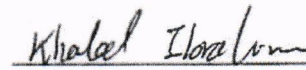


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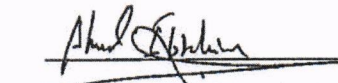
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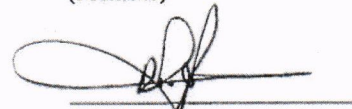
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To my lovely family and friends who supported me throughout my degree journey.

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LIST OF ABBREVIATIONS

ME	:	Microemulsion
GOR	:	Gas-Oil-Ratio
WOR	:	Water-Oil-Ratio
EACN	:	Equivalent Alkane Carbon Number
HLD	:	Hydrophilic-Lipophilic-Deviation
SR	:	Solubilization Ratio
PB	:	Phase Behavior
IFT	:	Interfacial Tension
EOR	:	Enhanced Oil Recovery
HPHT	:	High-Pressure-High-Temperature
TAN	:	Total Acid Number

ABSTRACT

Full Name : Murad Hajiyeu

Thesis Title : Effect of Live-Crude-Oil, GOR, and HPHT on the Optimal Salinity of EOR Surfactant Formulation

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Commercial chemical-enhanced oil recovery (CEOR) has been in enhancing demand due to the descending recovery from primary and secondary recovery techniques in mature oil fields. Achieving ultra-low interfacial tension (IFT) between the residual crude oil and injected water is the ultimate goal of using surfactant injection for EOR. Equilibrium phase behavior tests of the surfactant/oil/water system are used to define suitable formulation compositions to develop microemulsion types that fulfill ultra-low IFT conditions. Although the influence of pressure and live oil on the microemulsion phase behavior has been investigated for a long time, limited data is available in the literature at high pressure and high temperature (HPHT) conditions. Hence, a lack of consideration of such conditions might have misleading results, which can highly affect recovery performance. In addition, the reported optimum salinity to achieve ultralow IFT changes when gas is present in the crude oil. As the gas-oil ratio (GOR) in the same reservoir can vary from one location to another due to pressure changes, it is important to evaluate the combined effect of pressure and GOR on the surfactant/brine/crude oil system during surfactant flooding.

This thesis investigates the combined effect of pressure and gas/oil ratios (GOR) on the optimum parameters of surfactant flooding. The novel approach to study the effect of varying GOR is explained at different levels of pressure for a crude oil sample. The experimental investigation was conducted through salinity screening experiments at atmospheric pressure, and HPHT phase behavior using suitable surfactant and live oil containing methane in its composition.

The results from HT salinity screening determined suitable surfactant formulations showing Type III microemulsion that can be used in HPHT Phase Behavior. The results

from HPHT Phase Behavior experiments with optimum formulations and live oil demonstrated that pressurizing the surfactant system increases water solubilization ratio and decreases oil solubilization ratio; hence, more water is solubilized with the surfactant. Additionally, the presence of methane contributed to better microemulsion generation, which indicates lower interfacial tension between water and oil than in the case of dead crude oil. Moreover, the optimum solubilization ratios increased and optimal salinity decreased with increasing GOR.

The obtained results will benefit the petroleum industry with enhanced reservoir management, better forecasting, and improved recovery efficiency, resulting in increased hydrocarbon production. Such optimizations of production processes may benefit the industry with significant cost savings.

ملخص الرسالة

الاسم الكامل: مراد حاجييف

عنوان الرسالة: تأثير الزيت الخام الحي ونسبة الغاز والنفط والضغط العالي ودرجة الحرارة المرتفعة على الملوحة المثلى لتكرية الاستخلاص المعزز للنفط السطحي

التخصص: هندسة البترول

تاريخ الدرجة العلمية: مايو 2023

يتزايد الطلب على استخراج النفط المعزز بالمواد الكيميائية التجارية بسبب انخفاض الإنتاج من طرق الاستخراج الأولية والثانوية في حقول النفط الناضجة. إن تحقيق توتر بيني منخفض للغاية بين النفط الخام المتبقي والمياه المحقونة هو الهدف النهائي لاستخدام غمر الفاعل بالسطح لتحسين استخلاص الزيت. تُستخدم اختبارات سلوك طور التوازن لنظام الفاعل بالسطح / الزيت / الماء لتحديد تركيبات الصياغة المناسبة - المستحلبات الدقيقة التي تقي بطروف التوتر السطحي المنخفضة للغاية. على الرغم من أن تأثير الضغط والزيت الحي على سلوك طور المستحلب الدقيق قد تم التحقق منه لفترة طويلة، إلا أن البيانات المحدودة متوفرة في الأدبيات حول ظروف الضغط المرتفع ودرجات الحرارة المرتفعة. ومن ثم، فإن عدم مراعاة مثل هذه الظروف قد يكون له نتائج مضللة يمكن أن تلحق الضرر بأداء الإنتاج. بالإضافة إلى ذلك، تم الإبلاغ عن الملوحة المثلى لتحقيق تغييرات التوتر السطحي منخفضة للغاية عند وجود الغاز في النفط الخام. نظرًا لأن نسبة الغاز إلى الزيت في نفس الخزان يمكن أن تختلف من موقع إلى آخر بسبب تغيرات الضغط، فمن المهم تقييم التأثير المشترك للضغط ونسبة الغاز إلى الزيت على نظام الفاعل بالسطح / المحلول الملحي / الزيت الخام أثناء الفيضان السطحي.

تبحث هذه الرسالة في التأثير المشترك للضغط ونسب الغاز / الزيت على المعلمات المثلى لغمر الفاعل بالسطح. يتم شرح النهج الجديد لدراسة تأثير تغيير نسبة الغاز إلى الزيت عند مستويات مختلفة من الضغط لعينة من النفط الخام. أجريت الدراسة التجريبية من خلال تجارب غرلة الملوحة تحت الضغط الجوي، وسلوك طور الضغط العالي ودرجة الحرارة العالية باستخدام خافض للتوتر السطحي وزيت حي يحتوي على ميثان في تركيبته.

حددت نتائج فحص الملوحة بدرجة حرارة عالية تركيبات مناسبة للخافض للتوتر السطحي تُظهر مستحلبًا دقيقًا من النوع الثالث يمكن استخدامه في سلوك طور الضغط العالي ودرجات الحرارة المرتفعة. أظهرت نتائج تجارب سلوك المرحلة ذات الضغط العالي ودرجة الحرارة العالية مع الصيغ المثلى والزيت الحي أن الضغط على نظام الفاعل بالسطح يزيد من نسبة الذوبان في الماء ويقلل من نسبة الذوبان في الزيت؛ وبالتالي، يتم إذابة المزيد من الماء مع الفاعل بالسطح. بالإضافة إلى ذلك، ساهم وجود الميثان داخل النفط الخام في توليد مستحلب دقيق أفضل، مما يشير إلى انخفاض معدل الانتقال بين الزيت والماء مقارنةً بالنفط الخام الميت. علاوة على ذلك، زادت نسبة الذوبان المثلى وانخفضت الملوحة المثلى مع زيادة نسبة الغاز إلى الزيت.

ستفيد النتائج التي تم الحصول عليها من التحقيق في التأثير المشترك لنسبة الغاز والنفط وظروف الضغط العالي ودرجة الحرارة المرتفعة في المكنم صناعة البترول من خلال إدارة المكنم المحسنة والتنبؤ الأفضل وكفاءة الإنتاج المحسنة، مما يؤدي إلى زيادة إنتاج الهيدروكربون. قد تفيد هذه التحسينات لعمليات الإنتاج الصناعة مع توفير كبير في التكاليف.

CHAPTER 1

INTRODUCTION

Oil has been extracted from subsurface formations under three different recovery processes: primary natural depletion, secondary recovery, and tertiary recovery. The average production from the reservoir using its natural depletion depends on the initial condition and type of recovery mechanisms. Recovery factor by primary depletion can be as low as 5% in volumetric reservoirs and can be up to 60% in the case of reservoirs supported by strong water aquifers [1-2]. Secondary recovery aims to displace the residual oil from the primary recovery and sustain the pressure of reservoir by either water or gas injection. Due to the complex formation or fluid properties, the secondary recovery may leave high residual oil due to low sweep and displacement efficiency. Only a third of the original oil in place might be extracted by secondary recovery [3].

Additional improvements in oil production might be done after waterflooding using different EOR techniques (**Figure 1**). EOR is the oil recovery mechanism that is carried out by injecting of chemicals, gases along with energy of high temperatures into the subsurface to produce the residual heavy oil. The choice of the EOR technique is directly proportional to total estimation of rock and fluid properties and economy. The EOR methods can be categorized into 3 main techniques that include: thermal recovery, chemical flooding and miscible displacement. These methods alter the forces of the fluid

that hold it inside the porous space of the reservoir rock to unlock trapped oil [4]. Chemical EOR is one of the main techniques utilized to enhance recovery of oil by reducing the forces in the capillary and freeing the trapped oil in the reservoir. The forces in the capillary are a function of the IFT between the crude oil and the brine. The capillary number combines both the IFT forces and viscous drag force. As the capillary number ameliorates, the displacement efficiency increases, hence the overall recovery is improved [5]. Most of the chemical enhanced oil recovery techniques tend to decrease the IFT to increase the capillary number [6-7]. CEOR can reduce the interfacial tension to very low levels lower than 10^{-3} mN/m compared to high IFT values for brine/crude oil in case of water flooding. Ultralow IFT increases the capillary number enough to displace the crude oil trapped in the pore spaces and significantly reduces the residual oil saturation (ROS) [7–10].

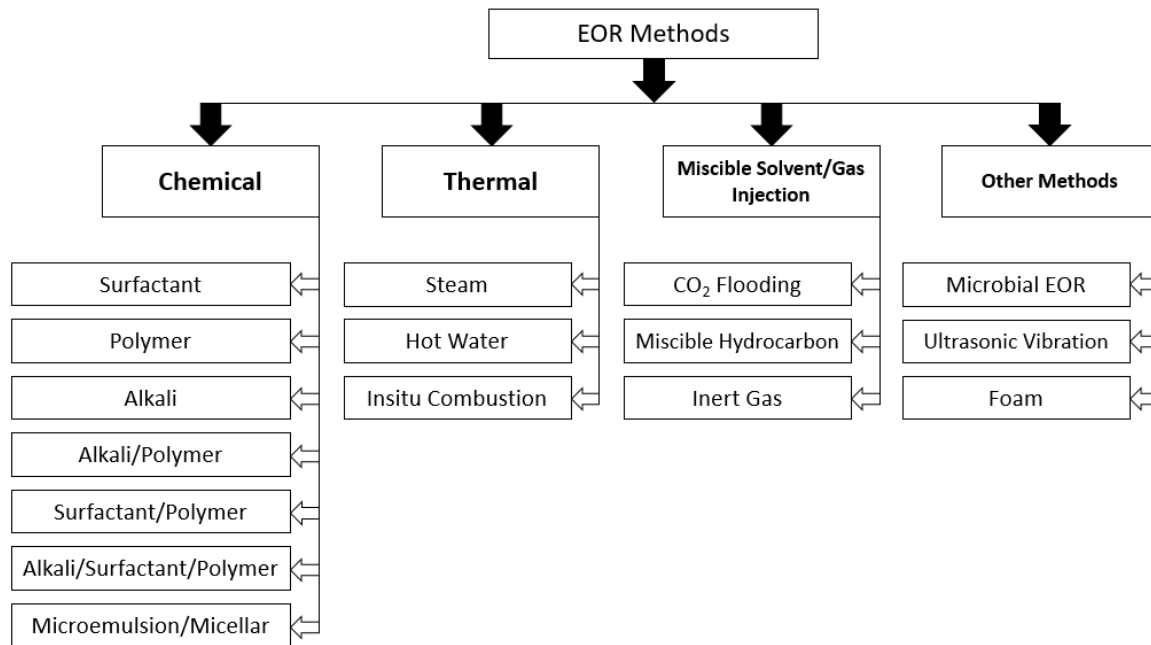


Figure 1: Categorization of the primary EOR techniques [11].

Usually, alkaline is used as the displacing fluid in polymer flooding together with surfactants (**Figure 2**). Reduction in the mobility ratio and/or a rise in capillary number are

the mechanisms behind this process. When it comes to lowering the mobility ratio, water soluble polymers like polyacrylamides have shown to be effective. In order to decrease the interfacial tension between the oil and water, surfactants would be introduced to the displacing solution. Natural surfactants are created in the reservoir when alkaline substances like hydroxide react with the acidic components of crude oil. These compounds help to decrease the IFT between the water and oil.

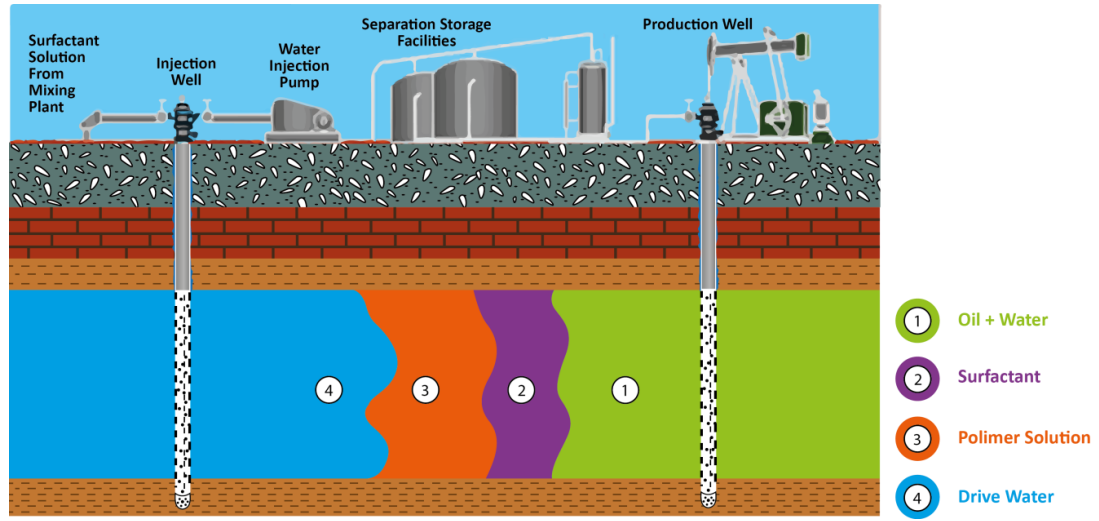


Figure 2: Surfactant-Polymer (SP) flooding.

1.1 Capillary Number

A dimensionless number stands for the capillary and viscous forces ratio of the reservoir is recognized as the capillary number, N_C (Eq. 1.1). The capillary number is a significant contributor to the displacement efficiency of non-wetting phase in the reservoir.

$$N_C = \frac{v\mu_w}{\sigma_{ow} \cos \theta} \quad (1.1)$$

where v is the water velocity, μ_w is the displacing fluid viscosity (water), σ_{ow} is the IFT between aqueous and hydrocarbon phases, and θ is the contact angle. According to Eq.1,

it is apparent that the IFT between aqueous and hydrocarbon is reversely proportional to the capillary number. Hence, with decreasing interfacial tension between aqueous and oleic phases, the capillary number will increase and decrease the forces in the capillary which implies to a reduced residual oil saturation [12].

Another important parameter that should be considered while recovering crude oil from the rock in the reservoir, is the wettability of this rock. It is easier to flood a rock that is water-wet with water to recover more oil rather than from an oil-wet rock. In the case of water-wet rock, the remaining oil is located in the center of the pores and can be easily mobilized, whereas water is adsorbed by the formation and does not interrupt displacement of the crude oil. Therefore, it is logical to state that wettability as well as capillary number affects the capillary desaturation curve (CDC). Joekar [13] determined the effect of alteration of contact angle on the amount of the remaining oil in the subsurface at varying contact angle. With enhancing contact angle, the saturation of the remaining oil decreases at the same capillary number as shown in **Figure 3**.

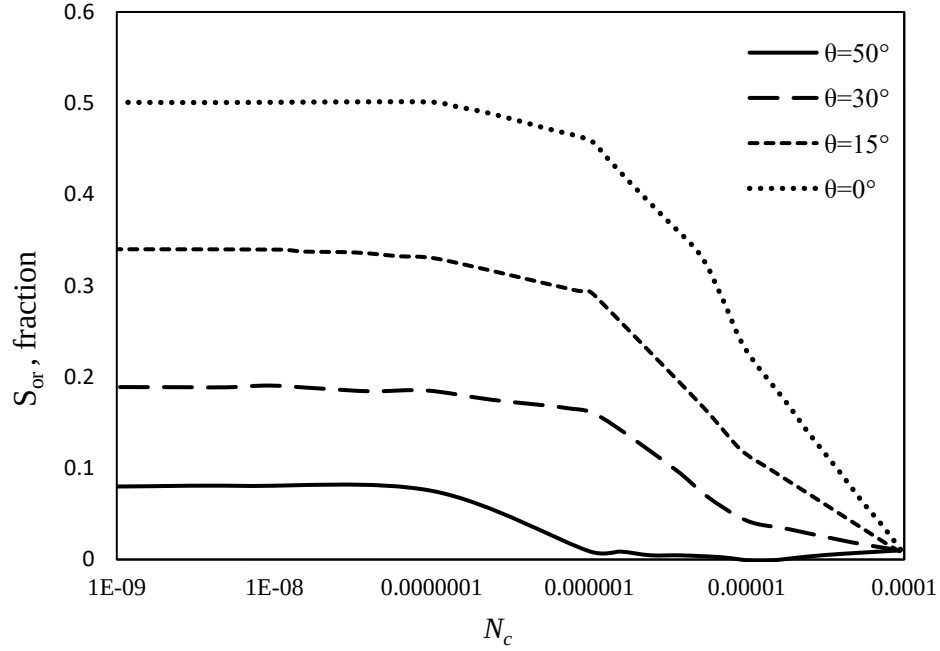


Figure 3: Effect of contact angle on the residual saturation [17]

1.2 Surfactant Flooding

The most common method to achieve ultralow IFT is surfactant flooding which is a very common and efficient in recovering the residual oil after water flooding process [14]. A surfactant owns both hydrophilic and hydrophobic groups (amphiphilic compounds) which allow the surfactant to get congregated at oil-water phases interface and subsequently change the IFT [15]. Depending on the hydrophilic head charge, surfactants could be categorized into four types (**Figure 4**); (a) non-ionic surfactants without any charge (ethoxylated alcohol, phenol, or amide); (b) cationic surfactants containing positive charge (ethoxylated alkyl amine, cetyl trimethyl ammonium bromide); (c) anionic surfactants containing negative charge (carboxylates, sulfates, sulfonates); and (d) Zwitterionic surfactants containing both positive and negative charges (carboxybetaine, sulfobetaine, hydroxysulfobetaine). Among all four types, anionic surfactants represent the common type used for cEOR in carbonate reservoirs. Moreover, while the chief privilege of using

surfactants in sandstone rocks is to reduce IFT, in carbonate rocks they also may alter the rock wettability. As most of the carbonates are oil wet initially, surfactants help to change the wettability towards more water wet apart from the reduction of IFT [16].

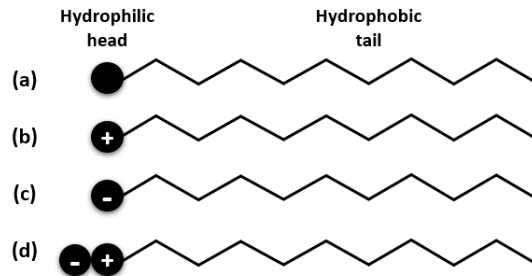


Figure 4: Common Type of surfactant structures [16]

As soon as the reservoir crude oil interacts with the injected suitable surfactant formulation, molecules of surfactants are located at the interfacial area between water and oil where the hydrophobic tail of the surfactant interacts with the residual oil, and the hydrophilic head attaches to the water. Due to this behavior, it forms different types of microemulsion. As a result, the tension significantly decreases at the interface of displaced and displacing fluid [17]. At low IFT, the oil resistance to flow will decrease and the residual oil droplets tend to coalescence then mobilize [18]. The IFT between oil and injected surfactant formulation depends on (1) salinity, (2) temperature, (3) surfactant concentration, (4) surfactant type and purity, (5) nature of the hydrocarbon phase, (6) pressure at a much less degree, (7) alcohol concentration, (9) brine-oil ratio. Optimization of the surfactant formulations to acknowledge all these parameters is very important for the success of surfactant flooding EOR in different scales (**Figure 5**). Different types of microemulsion are formed due to the reaction of water and oil with surfactant with at a surfactant concentrations higher than critical micelle concentration because of the accumulation of molecules of the surfactant amongst themselves [10]. Microemulsion flooding process has been introduced to

overcome the low viscosity issue of a surfactant EOR [10], [19]. The microemulsion systems are characterized by high viscosity (twice the crude oil viscosity) and inducing ultralow IFT, other than overcoming the surfactant adsorption to the rock surface problem [20].

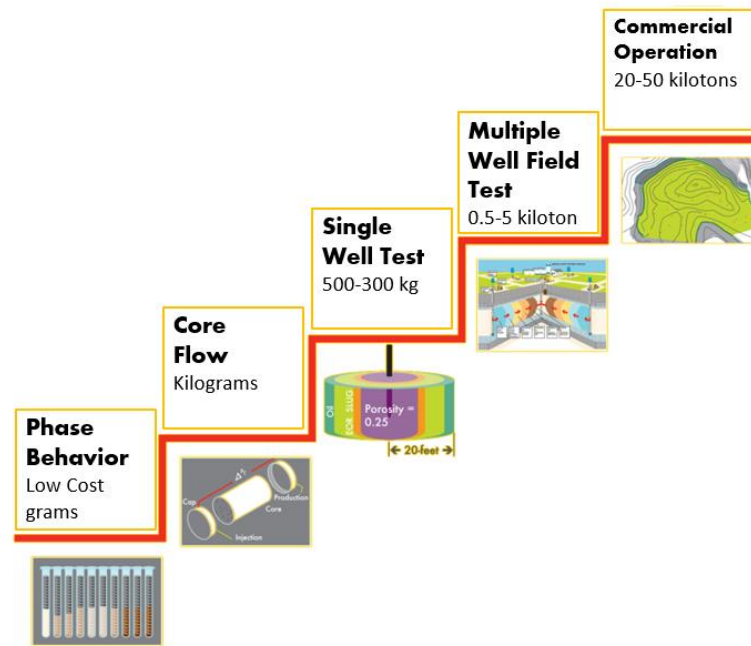


Figure 5: Different stages of Surfactant flooding from lab to field application

Many factors are considered when selecting a surfactant for surfactant flooding such as salinity of the reservoir brine and injection brine, crude oil properties such as equivalent alkane carbon number (EACN, total acid number (TAN), solution gas, reservoir temperature, and reservoir geochemistry (lithology, clays, etc.). In addition, cost, availability, and quality of the chemicals are considered for commercial field applications [21]. Surfactants with longer hydrophobes are recommended for crude oils with higher EACNs [22]. In addition, Live crude oils with high solution gas (>100 scf/stb) exhibit a much different phase behavior compared to dead crude oil. Therefore, surfactant slugs should be designed to effectively interact with the live oil if present [23]. To accelerate and simplify the testing procedure of surfactant slug optimization, usually a surrogate oil is

used in testing different surfactants at ambient pressure and reservoir temperature. In a surrogate oil, a diluent such as toluene or iso-octane is mixed with dead oil at low concentrations to match the EACN and viscosity of live oil and phase behavior.

1.2.1 Phase Behavior Experiments

In crude/surfactant/brine phase behavior experiments, the surfactants are mixed with different salinity brine solutions and oil and stored in pipettes to observe the formation of microemulsions after defining the aqueous solubility limit of the surfactant with respect to salinity. Commonly, co-surfactants and/or co-solvents are added for an ideal behavior of the formed microemulsions. It is practical to store hundreds of samples in ovens at the reservoir temperature and observe them over a period of days or for sometimes up to months until the equilibration of the phase behavior is reached. Equilibrium phase behavior is critical to mimic the behavior in the reservoir and not waiting long enough for equilibrium is perhaps the most common mistake made by experimentalists [21]. It is necessary to note that good hands on physical inspection of phase behavior tubes is a high value qualitative measurement that instruments cannot capture. After identifying a promising formulation with the desired phase behavior (optimal salinity, High solubilization ratios, ultralow IFT, low microemulsion viscosity, etc.) few dilution tests are performed to simulate the dilution of the mixing front ahead of the chemical slug and mixing surfactant slug and polymer drive/chase. Other variations than these dilution tests would be at varying surfactant and oil concentrations. Optimal salinity and solubilization ratio shift as surfactant concentration changes at a given water, especially for SP flooding in hard brine since the change in divalent cations shifts the optimum salinity. Hence, it is

viable to comprehend the effects when surfactant formulation concentration changes due to dilution, adsorption, etc.

1.2.2 Microemulsion Types

Microemulsion is a dispersion of water and oil with a certain quantity of both oil and water that are stabilized by a surfactant. In 1954, Winsor categorized the possible created microemulsion systems into 3 types that include, Type I (oil-in-water microemulsion), Type II (water-in-oil microemulsion), and Type III (bicontinuous) and the distribution of surfactants is different from one type of microemulsion to another (**Figure 6**). In Type I, an oil portion is solubilized in the water by the used surfactant, where the surfactant distributes and the emulsion is called direct microemulsion. In Type II, a portion of dissolved water in the oil by the used surfactant and a reversed emulsion will be formed. In Type III, portions of water and oil are dissolved by the surfactant and form a transition zone between the oil and water phases, and a bicontinuous emulsion is created [6]. The three types are stable and the water and oil never separate from the microemulsion [24-25]. Hirasaki, [26] showed that the optimum microemulsion type for EOR is type III.

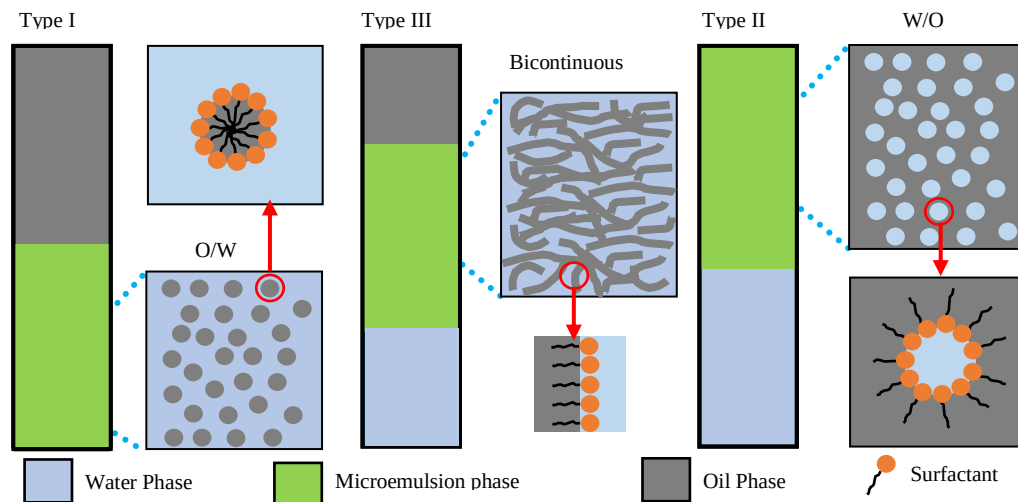


Figure 6: Different types of brine and crude oil microemulsion.

The microemulsion phase behavior alters from Winsor I to Winsor II via Winsor III with changes in content of water, concentration of surfactant, type of cosurfactant, concentration of cosurfactant, temperature, pressure, and salinity. As a rule of thumb, the Winsor Type I microemulsion can be converted to Type III and then Type II by (1) salinity increase, (2) alcohol concentration (propanol, butanol, pentanol, and hexanol) increase, (3) oil chain length reduction, (4) temperature variation, (5) enhancement of overall concentration of surfactant, (6) enhancement of surfactant ratio of solution/oil, (7) enhancement of WOR and (8) surfactant molecular weight increase [11].

With enhanced salinity of water phase, the tendency of anionic surfactants to get solubilized in the water phase reduces. Hence, surfactants are displaced from water and shift microemulsion from Type I to Type II through Type III [1, 6], [9, 27]. As Type III is the preferred structure for EOR, experimental design should be conducted to estimate the optimum aqueous phase salinity.

1.2.3 Solubilization Ratio

Oil and water solubilization are vastly based on the formed microemulsion type. As the microemulsion converted from Type I to Type II via Type III, the oil and water content dissolved in the microemulsion phase alters [28]. The solubilization ratio of water and oil is determined as;

$$SR_i = \left(\frac{V_i}{V_s} \right)_{ME} \quad i = o, w \quad (1.2)$$

where V_s is the surfactant volume in the ME phase and V_i is the constituent I volume in the microemulsion phase. **Figure 7** is showing an example of the change in SR for both oil and water with alterations in water phase salinity. At low salt concentration levels, majority of the molecules of surfactants stay in the water phase, Type I is formed, all the water volume is solubilized and a small oil quantity is solubilized in the microemulsion. With increasing the salt concentration, the surfactant solubility in water will decrease and it tends to move to the oil-water interfaces. While at higher salinity levels, the surfactant molecules preferentially get solubilized in the oil phase. Hence, most of the volume of oil is solubilized in the microemulsion and a small amount of the water is within the microemulsion phase (Type II). At optimum salinity, surfactant reactions with oleic and aqueous phases are the same. A balanced distribution of surfactant in both water and oil phase is observed with equal water and oil solubilization volumes. Moreover, the S^* for the phase behavior is determined at the point where $SR_o = SR_w$.

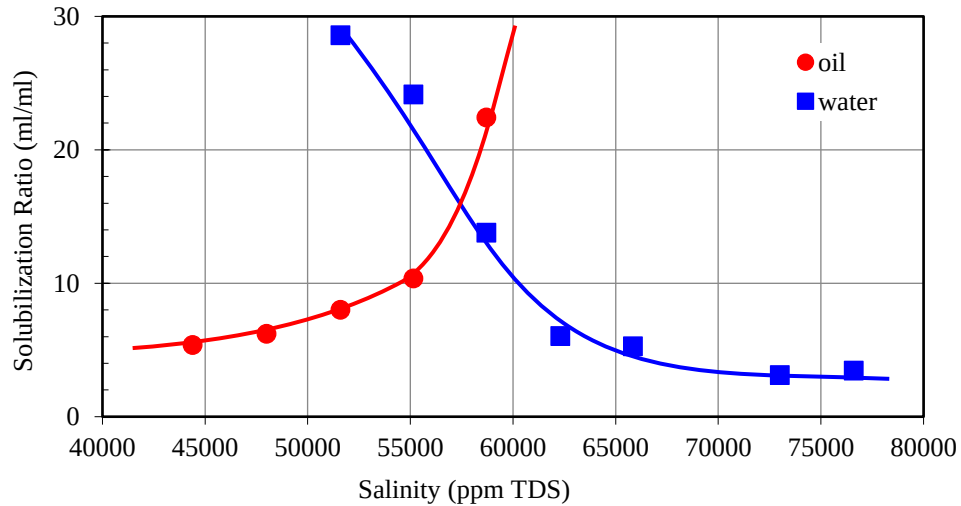


Figure 7: Microemulsion phase behavior of dead crude oil

Type I Microemulsion exists together with almost whole surplus oil at lower salt concentrations. It is demonstrated as depicted on the left part of **Figure 8**. This sort of

microemulsion is referred to as a "lower-phase" microemulsion because its density is larger than that of the oil, placing it under the oleic phase [1]. Also, it is called Winsor Type I in which the radius of the drop of microemulsion will become bigger with increasing salinity, and the oil solubilization will be improved [29]. As the water in oil emulsion is less dense than the pure brine density, it will flow above the brine so it is called an "upper-phase" microemulsion [29]. The structure would be shown as displayed on the right side of **Figure 8**, which is also known as microemulsion Winsor Type II. The microemulsion formed at medium salt concentrations is in balance with both surplus water and oil and is located in the center as seen in **Figure 8**. Almost the total amount of surfactant is in this microemulsion, also known as a "middle-phase" or bicontinuous Winsor Type III microemulsion. Due to its extremely low interfacial tension, and capacity to dissolve excess amounts of both oil and water, this form of microemulsion is excellent in enhanced oil recovery.[1, 9, 28, 30]

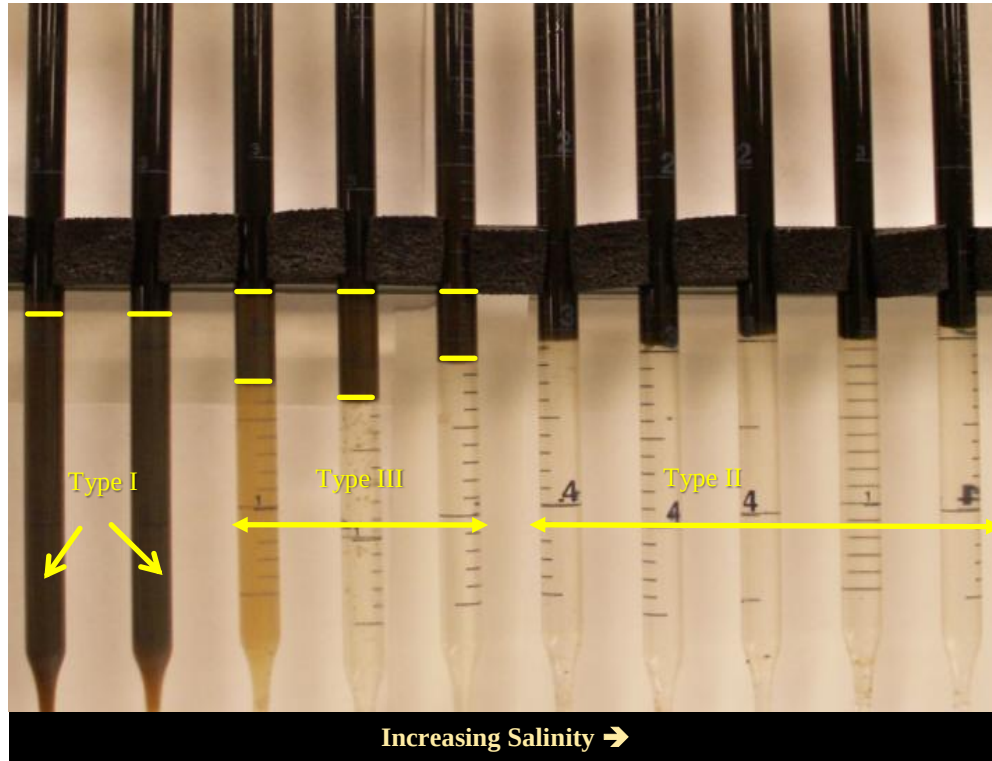


Figure 8: Shift of Microemulsion from type I to III to II

1.2.4 Quasi-Ternary Phase Diagram

During surfactant flooding, the fraction of water and oil, structure, and the salinity, surfactant concentration experience a continuous change while migrates towards production wells. The phase alteration can be demonstrated by the quasi-ternary phase diagram of brine, surfactant and oil. The phase diagram simply depicts the ratios of the brine, additives + surfactant, oil. Phase diagram depends on salinity and changes simultaneously with the alterations in salinity system of microemulsion (**Figure 9**).

Winsor Type I Microemulsion: Demonstrates the microemulsion of the lower salt concentration lower than C_{SEL} (lowest limit of effective salinity), also named as Winsor II (–) phase diagram. There are two coexisting equilibrium phases, and the binodal curve slope is negative. According to the two-phase region's apparent inclination toward the oil,

the affinity between water and the surfactant is much larger than that between the oil and the surfactant. The system contains two phase system that exists together of the lower phase microemulsion(O/W) underlying the excess oil phase.

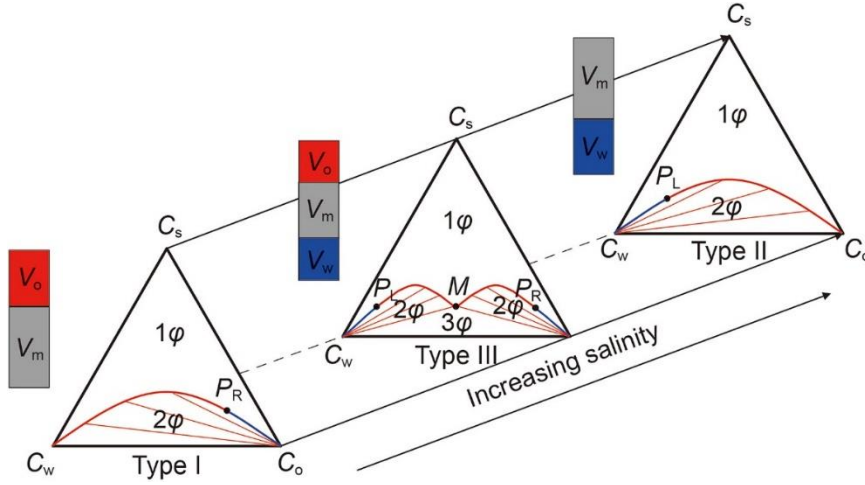


Figure 9: Quasi-ternary phase diagram of microemulsion phase behavior[31].

Winsor Type III Microemulsion: The microemulsion of the mostly suitable for EOR applications salinity system (between C_{SEL} and C_{SEU}) under which the closeness between water and surfactant is similar to that between oil and surfactant, and majority of the surfactant quantity are in the middle phase microemulsion. The system composition falls into the connection triangle having three co-existing equilibrium phases. The excess oil phase and the excess water phase are above and below the microemulsion respectively. With the salinity magnification, the capability of surfactants to solubilize oil enhances and that ability to solubilize water reduces, which causes the relative volume of the excess water phase to increase and the excess oil phase to decrease in volume. The middle phase microemulsion then has a relative amount of oil that rises and a relative quantity of water that falls. After reaching its maximum value, the intermediate phase point, which is made

up of constant points, will descend downward to the oleic phase point from the water phase point.

Winsor Type II Microemulsion: illustrates a microemulsion with two coexisting equilibrium phases that has a salinity larger than the critical salinity C_{SEU} (maximum effective salinity limit). This phase diagram is also called as a Winsor II (+) phase diagram. The binodal curve has a positive slope. The two-phase region's tip appears to be skewed toward the water side, showing a greater closeness between the oil and surfactant than the surfactant and water. The system consists of two coexisting phases, with the top phase microemulsion (O/W) covering the phase with too much water.

1.2.5 Interfacial Tension Vs. Phase Behavior Experiments

Several issues limit the direct measurement of IFT between surfactant formulation and crude oil. Time dependency of equilibration for microemulsions is a major limitation. The equilibration time of microemulsions can range from days to months making the use of a tensiometer impractical for determining IFT. Pendant drop tensiometers have limited range of IFT (10^{-2} to 10^2 mN/m) while spinning drop tensiometers are able to measure IFT in the ultra-low ranges (down to 10^{-4} mN/m) required for chemical EOR microemulsions with lower viscosity oils at moderate temperatures. However, spinning drop tensiometer is limited not recommended to be used at high temperature ($>90^{\circ}\text{C}$), Winsor Type III microemulsions, and heavy oils [21]. Due to these limitations, reliable estimates of IFT are usually made using the Huh equation from solubilization ratios determined from the equilibrium phase behavior [32]. Phase behavior experiments can help to explore a wider range of variables than only IFT measurements which are not feasible under many conditions of practical chemical EOR. In addition, phase behavior experiments can be

performed at reservoir pressure using live crude oil samples in high pressure rated sapphire cells. Spinning drop tensiometers cannot measure live oil IFT, and pendant drop tensiometers cannot measure the ultra-low IFT values required for high performing chemical EOR formulations.

A reliable correlation exists between IFT between the phases at equilibrium and microemulsion system phase behavior. As the phase behavior proceeds in a systematic manner with increasing salinity of brine, a logical result that can be derived is that IFT also would depend on salinity. Solubilization parameters and IFT with increasing salinity (

Figure 10) were reported by [33] in which σ_{om} is the interfacial tension between the microemulsion phase and excess-oil phase, while σ_{mw} is the interfacial tension between the microemulsion phase and the excess-oil phase. As shown in

Figure 10b, σ_{om} decreases significantly as phase behavior progresses from Type I into Type III and toward Type II. Alteration in this direction refers to enhancing salinity increases and solubilization of oil in the microemulsion from the excess phase (

Figure 10a), yielding a microemulsion with low density values. Similarly, σ_{mw} increases as the shift from Type III to Type II takes place and water is displaced from the phase with microemulsion. Also, σ_{mw} enhances as the water volume dissolved by the microemulsion gets reduced.

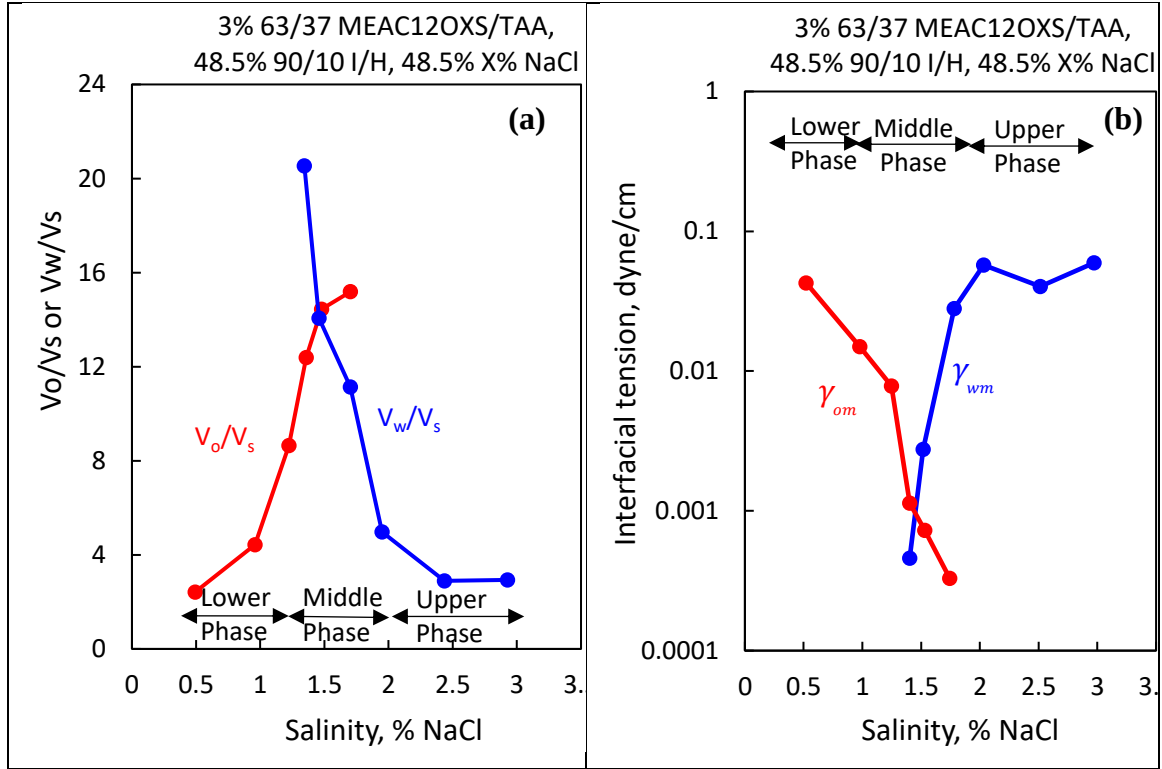


Figure 10: (a) Solubilization parameters and (b) IFT as a function of Salinity [28]

The salinity value at which $\sigma_{om} = \sigma_{mw}$ is called the optimal salinity (S^*) which is very close to the salinity at which $SR_o = SR_w$. It is relatively difficult to measure IFT using the pendant-drop and spinning-drop apparatus when tensions are ultralow. Therefore, the solubilization ratios measured from the relatively easy phase measurements are used to calculate the IFT at S^* . Huh, (1979) obtained a theoretical dependency between the solubilization ratio and IFT in which the IFT (γ) is in the inverse dependence from the square of the solubilization ratio (SR):

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

where C is around 0.3 dynes/cm for characteristic surfactants and crude oils. IFT at optimum salinity is on the range of 10^{-3} dynes/cm or less when the solubilization ratio is

10 or greater, which is considerably low to raise the capillary number to levels sufficient to push most of remaining oil under majority of circumstances. Therefore, an optimum SR of 10 or more is used as a target for microemulsion phase behavior screening [28, 30], [34–37].

This section includes a detailed literature review on the pressure effects and content of live crude on the performance of oil/brine/surfactant phase behavior and microemulsion formation under reservoir conditions.

CHAPTER 2

PROBLEM STATEMENT

From the thorough examination of the literature it can be observed that the majority of the works deduced contradictory to one another results regarding the effects of live-oil, GOR and HPHT on the optimum parameters of the microemulsion phase behavior observed from salinity screening experiments. Moreover, most of the literature did not focus on the phase behavior experiments with live-oil and instead conducted experiments with either dead or synthetic oils as well as the effect of high pressure is not discussed in most of them. Therefore, the primary disadvantage of using non-live oils in phase behavior experiments and observation of salinity scans under atmospheric pressure only is not sufficient to accurately predict the efficiency of surfactant flooding in the reservoir at HPHT conditions in contact with formation waters and the rock. Additionally, in the experiments in such conditions, the obtained optimal salinity could be not similar in the subsurface properties that can eventually damage the production performance. This research focuses on addressing these gaps left in the previous works and make a clear conclusion about pressure influence and live-crude on ME behavior of phases based on the novel approach of investigating the effect of different GOR at various pressure levels.

CHAPTER 3

RESEARCH OBJECTIVES

The objectives of this thesis include Salinity Screening experiments at high temperature and ambient pressure using surfactant formulation and crude oil to determine the optimum surfactant formulation range with approximately equal solubilization ratios of oil and water in the microemulsion phase. Upon determination of the optimum salinity in these experiments, this surfactant formulation range is used at High-Pressure and High-Temperature Phase Behavior experiments with the Live Crude Oil containing methane. To investigate the effect of methane on the Phase Behavior, three Live Oil samples were prepared at the GOR values: 180 scf/stb, 280 scf/stb, and 380 scf/stb. In order to explore the effect of pressure on each of the experiments with various GOR values, the following pressure value range has been utilized in this thesis: 2500 psi – 4000 psi.

CHAPTER 4

LITERATURE REVIEW

A number of different parameters have an effect on solubilization ratios, and thus IFT, including alcohol; temperature, and oil; water/oil ratio (WOR); pressure; polymer presence in the formulation; and structure of surfactant. Studies focused on the impacts of altering a number of these parameters relevant to this project are reviewed in this section. These studies give information to assist in design criteria development for choosing a surfactant solution for a certain reservoir oil.

4.1 Oil Type

Early application of alkaline-surfactant-polymer (ASP) floods has beneficial economic prospects in heavy crude oil reservoirs containing solution gas. ASP flooding would provide mobility control, ultralow values of interfacial tension (IFT) between the displacing and displaced fluids, and pressure support to keep the gas in solution. Mobility control provides both efficient areal sweep efficiency and ultralow values of IFT, reducing the capillary pressure to pressure gradients that can be produced by a waterflood, and solution gas keeps the crude oil viscosity at its minimum. Viscosity of the crude oil system is often matched by diluting oil with pure hydrocarbons to simulate reservoir oil behavior in core floods. Viscosity controls the mobility of the fluids and thus is a good parameter to match; however, diluting crude oil changes the microemulsion behavior of oil [38]. Variations of GOR affect significant changes of the brine/surfactant/oil PB. Therefore, S^*

under only high temperature conditions for a certain surfactant formulation needs to be corrected for the presence of live crude oil with different GOR values in different parts of the reservoir due to pressure changes.

In order to provide a methodical strategy for establishing the relationship between phase behavior and hydrocarbon composition, hydrocarbon/brine/surfactant systems have been analyzed in detail. These examples are helpful in a surfactant selection for a specific system that contains hydrocarbon/brine. Cayias, [39] determined that IFT minima for a series of pure-alkane/0.2%-surfactant/1%-NaCl-brine systems happened at an ACN that was equal to 8. Pure alkane hydrocarbons mixtures also had IFT minima at an EACN of 8. By estimating the EACN of various crude oil systems, this idea for crude oils was established. It has been suggested that only one EACN would be required to describe a specific crude oil.

In the next work [40], a relationship was obtained between S^* and Equivalent Alkane Carbon Number. This theory has been practiced in the development and estimation of oils for tests in the field and for defining the influence of utilizing live crude oil on productivity of surfactant injection performance [41-42]. The notion of Equivalent Alkane Carbon Number is not applicable in all cases. Differences in Alkane Carbon Number with type of alcohol cosolvent, sample overall Water-Oil-Ratio, and composition of crude oil were presented [43]. Reproducibility of lower limit of IFT was investigated by [27]. When S^* was connected with CAN without a straightforward relationship between S^* and the carbon numbers of n-alkylcyclohexanes or n-alkylbenzenes and n-alkanes, significant differences between alkylbenzenes and alkanes were discovered [44].

A three-parameter correlation of the ME PB was developed by [44]. They discovered that three factors (optimal salinity, S^* ; solubilization ratio, V_o/V_s , and molar volume of oil, V_{mo}) advanced the association of the ME PB with the oil type for a variety of circumstances. In order to model live crude oil, three-parameter correlations can help identify related oils. Equivalent oils have the same molar volume, S^* , and SR.

Phase behavior system can be affected by the type of oil and the effect can be substantial.

Figure 11 exhibits solubilization ratios as a function of salinity for two varying crudes and with a certain mixture of surfactant utilized for use in a test at the field [45]. Salinity is expressed as a percentage of Tar Springs brine (TSB), which has a salinity of approximately 10% and high Ca^{++} and Mg^{++} ions concentrations. When using a diesel oil as the oil phase, the behavior was typical. However, using London crude oil led to a non-ideal behavior in which S^* did not exist.

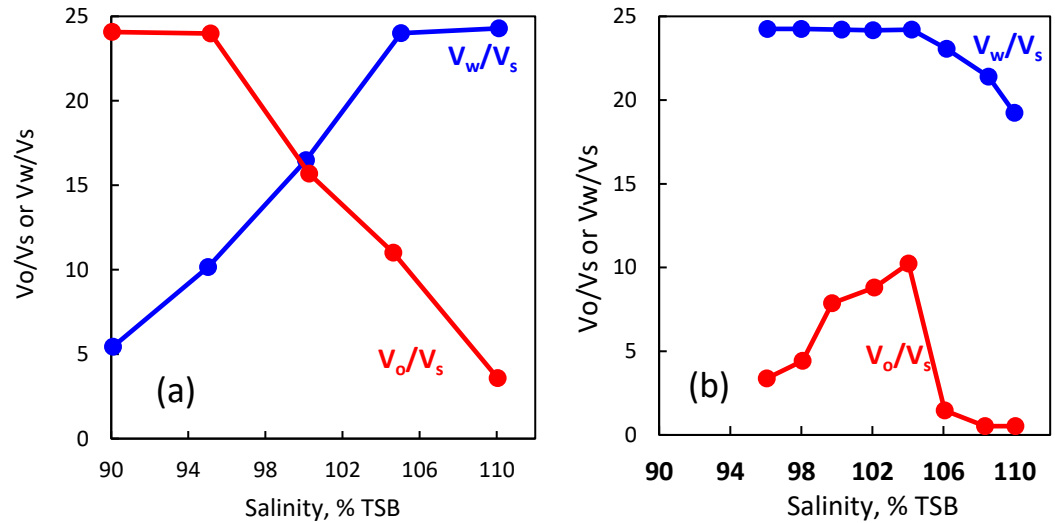


Figure 11: Curves at 78°F for 2% 60/40 blend [45].

Roshanfekar, [46] examined the influence of the methane addition in dead oil at a continuous pressure of 1000 psi and a temperature of 77°F. With addition of methane, the ratio of

solubilization at optimum salinity increased and S^* decreased and the phase behavior shifted towards Type II. Nevertheless, when adding 17.7 wt% of methane to the dead oil at constant pressure optimum salinity decreased and the optimum solubilization ratio increased significantly (**Figure 12**). Knowing the reverse relationship between IFT and solubilization ratio, it could be concluded that the IFT for live oil will be less than the dead oil IFT.

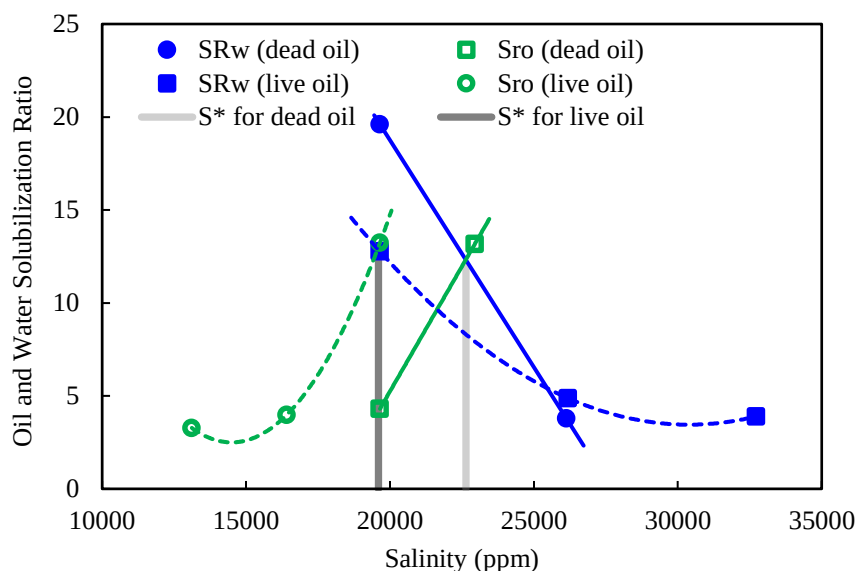


Figure 12: S^* and optimum SRs for dead oil and live oil at 1000 psi [46].

Pinnawala, [46] investigated the development of surfactant formulations that demonstrate stable phase behavior at harsh reservoir conditions such as temperature $> 90^{\circ}\text{C}$, high salinity, high GOR, and the addition of H_2S that can usually be present in most of the carbonate reservoirs. The chemicals that were utilized in this research: alkyl ether carboxylates, alkyl aryl sulfonate (AAS), numerous isomerized olefin sulfonate, and nonionic surfactants with different structures. Tri-ethylene glycol mono-butyl ether (TEGBE) was utilized as a co-solvent. The total acid number of crude oil utilized in this work is $< 0.2 \text{ mg KOH/g oil}$. For estimation of the contribution of H_2S to the live oil system, live oil behavior of phases and stability tests in aqueous phase were performed. Different

types of recombination were used for the preparation of live oil as following: (1) Injection of only methane, (2) Addition of methane and 8 mol% H₂S and (3) Methane injection and 16 mol% H₂S.

The effect of pressure on the live-oil system is also evaluated by increasing it from 4000 psi to 7000 psi and 10000 psi. The surfactant formulation used for live-oil experiments comprised: alkyl ether with high PO and EO carboxylate, IOS with low molecular weight, co-solvent, and nonionic surfactant. The WOR was equal to 2.33, and the optimal salinity, solubilization parameters were equal to 55000 ppm and 6 correspondingly at temperature = 110°C. The results of this work also accord with the prior works on the pressure influence on ME behavior of phases. They reported that with increasing pressure 4000-10000 psi, a negligible effect on optimum salinity was observed while the optimum solubilization ratio surged from 7 to 11 as the pressure increased. Another conclusion is that injection of H₂S into the live oil containing methane decreased S* by 20-30% in both experiments (8 mol% and 16 mol% H₂S). In the case of adding methane only, the optimum solubilization ratio is enhanced with increasing pressure. Moreover, methane alone had a minor effect on S*.

Monette and Nguyen, [48] investigated the impact on microemulsion phase behavior of pressurized methane and ethane/methane at a salinity of 95000 ppm (85000 ppm NaCl and 10000 ppm Na₂CO₃). The surfactant formulation comprised the combination of a carboxylate, internal olefin sulfonate (IOS) and a TGBE co-solvent. Overall concentration of the surfactant in the formulation was 0.5 wt% with an equal ratio of IOS to carboxylate to co-solvent. Density of the crude oil was equal to 0.85 g/cc and a viscosity at 52°C was 7.04 cP. A number of high-pressure phase behavior were performed using high pressure sapphire cells at maximum pressure 350 bar and maximum temperature 150°C. Initially, 6

ml of surfactant formulation was injected in the cell which was followed by the addition of 2 ml of crude oil and finally the gas composition was pumped into the formulation. To explore the influence of the injected gas in the composition, methane was added to the hydrocarbon gas mixture at 900, 1200 and 1500 psig. From the performed salinity scan in the range 85000-105000 ppm, it was observed that during pressure increased from 900 to 1500 psig, transition in the Type III was slight, only the solution with highest salinity 105000 ppm started to shift to Type II range. Nevertheless, substantial enhancement in the overall solubilization ratio was observed, because the microemulsion phase in each cell began to enlarge in volume as a function of increasing pressure. The similar observation was recorded in the injected with methane/ethane system. In this case, the last two cells with respective salinities 100000, 105000 ppm demonstrated shift from Type III to Type II, therefore deducing that changes in S^* occurred. The corresponding water and oil SRs as well as the optimum salinities for pure methane are presented in **Figure 13**. The trends of solubilization parameters are shown both for atmospheric pressure and highest applied pressure 1500 psig.

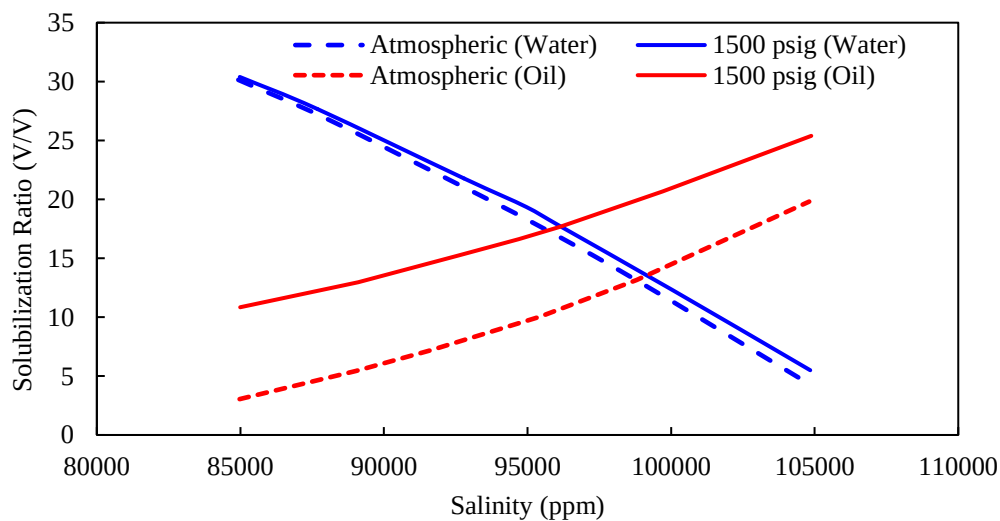


Figure 13: Effect of methane on the solubilization parameter of oil and water[47]

From **Figure 13** it can be observed that S^* is reduced slightly (around 2000 ppm) as the pressure increased. On the other hand, solubilization ratio at S^* increased substantially from around 13 to 18 with increasing pressure from atmospheric to 1500 psig. It means that the volume of microemulsion increased, and this augmentation leads to even larger reduction in the IFT between water and oil phases [47]. In contrast, in the system containing injection of combined methane/ethane in the formulation reduction in S^* was more significant (6000 ppm) as well as the increase in SR at this S^* was higher than in the case with only methane injection.

4.2 Effect of Pressure

Similar to systems containing liquids, the general pressure effect is negligible on phase behavior. The single pressure effect is usually negligible, however, when methane is injected to varying oils so that certain quantity of methane solubilized in the oil, the pressure influence was reported [23], [42]. Nelson, [49] recommended that for crude oils containing gas in the composition (live oil), the potential pressure impact on behavior should be taken into consideration in the process of design. Fotland & Skauge, [50] examined the ultralow IFT in the microemulsion multiphase system with pressure magnification. The HP cell with a maximum capacity of 680 bar was used to investigate the changes in IFT and oil and water SRs at high pressure. The Chemical system that was used during this work consisted of sodium dodecyl sulphate (SDS), sodium chloride, 1-butanol, and cyclohexane. Furthermore, total system composition comprised 41.82% cyclohexane, 42.99% brine (2.75% NaCl in water), 5.04% SDS and 10.15% 1-butanol. 100 cm³ of the solution was prepared, and the high pressure was applied in the cell containing this solution, then it was shaken for several minutes to achieve equilibration of the phases

and record the volumes of phases and measurements executed. The WOR was kept constant in the pressure scan. From the pressure scan it was determined that oil-excess phase is increasing with increasing pressure, meaning that the phase behavior shifts to Winsor type I microemulsion. In other words, the ability of the microemulsion to dissolve oil decreases in such a case. The trends of interfacial tension values of water and oil versus pressure are quite in accordance with the other literature. In this study, it was also concluded that the IFT between ME and oil is rapidly increasing with increase of pressure and the excess oil phase is created at the pressure of 20 bar. In contrast, the IFT of the water interface and microemulsion decreases with pressure. The optimum pressure which is considered as the pressure at which equal volumes of brine and oil are dissolved in ME was also determined. This can be graphically presented in **Figure 14**, the intercept of the two curves represents optimal pressure (250 bar). From this study, it was also concluded that the pressure effect is analogous to the impact done by temperature, that is transition of phase behavior II/III/I. Fotland & Skauge, [50] also reported that enhancing the pressure contributed to the transition in phase behavior toward a Type I and for a particular system, S^* magnified as pressure enhanced.

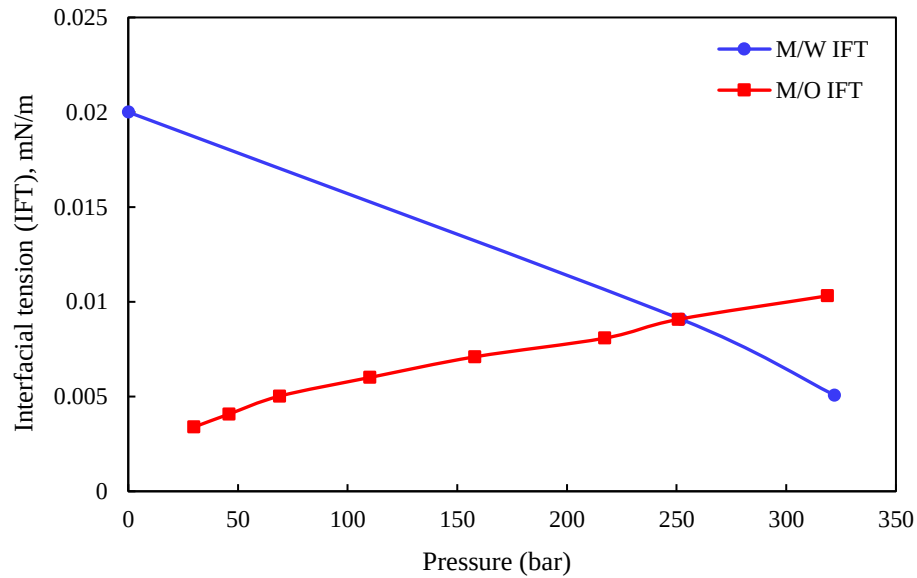


Figure 14: IFT with pressure increase [51]

Austad, [52] observed that for dead oil with increasing pressure in temperature range 60-100°C the water SR in the ME increased and in contrast the solubilization between oil and microemulsion phase remained constant. At high temperature (110°C) no middle phase was observed and the microemulsion of type I was formed. They concluded that with increasing pressure and temperature the system shifts toward type I microemulsion which is in a good agreement with [50] [58]. From the experiments with live oil, the PB depended strongly on the system salinity. For example, at low salinities complex PB was noticed with four different phases, whereas at higher salinities close to Type II microemulsion only one middle phase was observed. Moreover, solubilization ratio of water and oil at higher temperatures, reduced lightly. Roshanfekr, [46] also examined the impact of pressure on the transition of phase behavior and changes in S^* and optimum SR. The experiments with increasing pressure have been conducted with both dead and live oil. Moreover, the effect of increasing pressure from 14.7 psi to 1000 psi on the variation of S^* and optimum solubilization ratio of the dead oil was minor.

[53] investigated the impact of the composition of the oil on phase properties, and sensitiveness of IFT and SRs of the phases to the alterations in pressure and temperature. The composition of the used oil was 25 wt% cyclo-octane, 25 wt% ethyl benzene, and 50 wt% *n*-decane experimented without and with methane. The surfactant formulation consisted of only one surfactant – C12 oxylene sulfonate in 2.20 wt% NaCl brine. The WOR in all experiments was approximately equal to 1. The ranges of temperatures and pressures that were used during all experiments were as follows: 55-120°C and 50-600 bar respectively. For dead oil, the solubilization ratios for water and oil have been defined depending on pressure at different temperatures. For each used temperature, respective optimum pressure was defined. It was determined that with increasing temperature, optimum pressure decreased (**Figure 15**). These results are in good agreement with other results on the context that with increasing pressure, solubilization ratio of water increases, while it's IFT decreases and conversely, solubilization ratio of oil decreased when the interfacial tension between the oil and middle phase increased. It can be concluded from this result that significant alterations in ratios of solubilization of oil and water could be observed at high pressures when the temperature is low with comparison to the case with low pressures and high temperature. Furthermore, enhancing temperature and pressure moves phase behavior moves towards Type I. Additionally, the temperature at which ratios of solubilization of oil and water are equal at constant salinity was augmented with decreasing pressure.

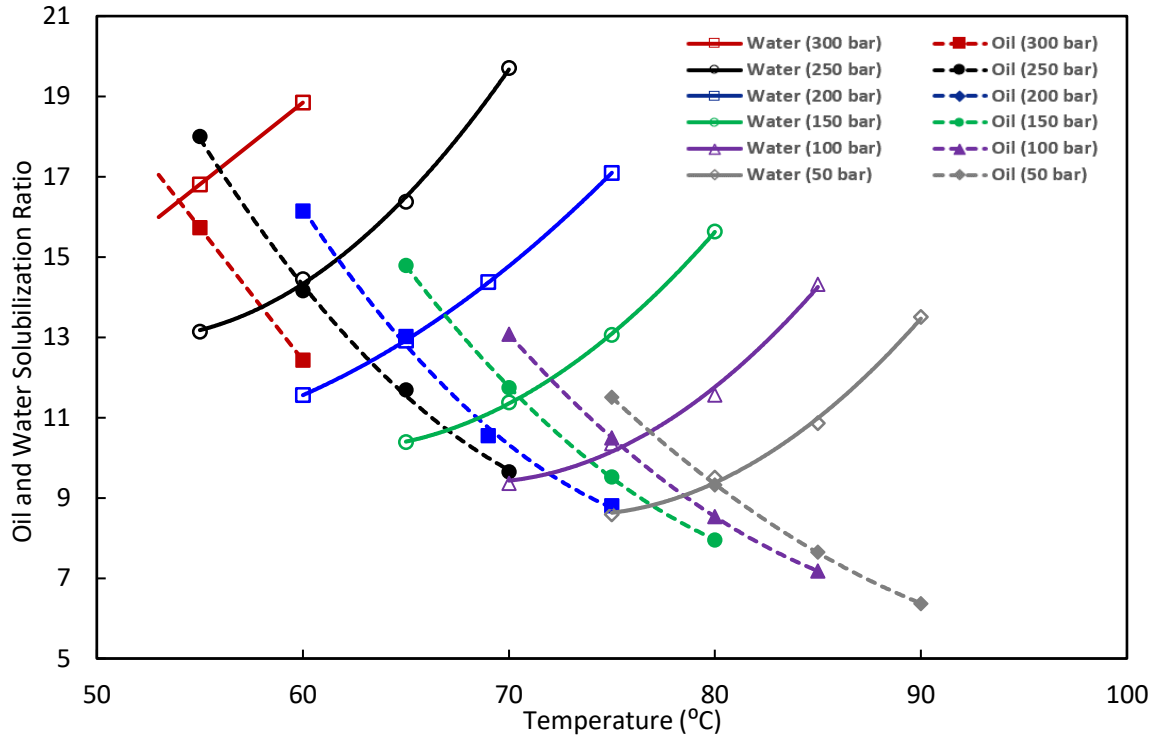


Figure 15: Solubilization ratios for dead oil and water [54].

For comparison with dead oil system, experiments with live oil were conducted at the same salinity. Close to the optimum, the system in this case demonstrated ordinary phase behavior, and the alterations in solubilization ratios of water and oil are showing similarities with changes of these parameters in case of a dead oil system as well as the fact as a function of pressure, the system makes a transition towards Type I state (**Figure 16**). In contrast to the experiments containing dead oil, values of optimal salinity for the live oil have been determined to be larger than for the dead oil at the same quantities of temperature.

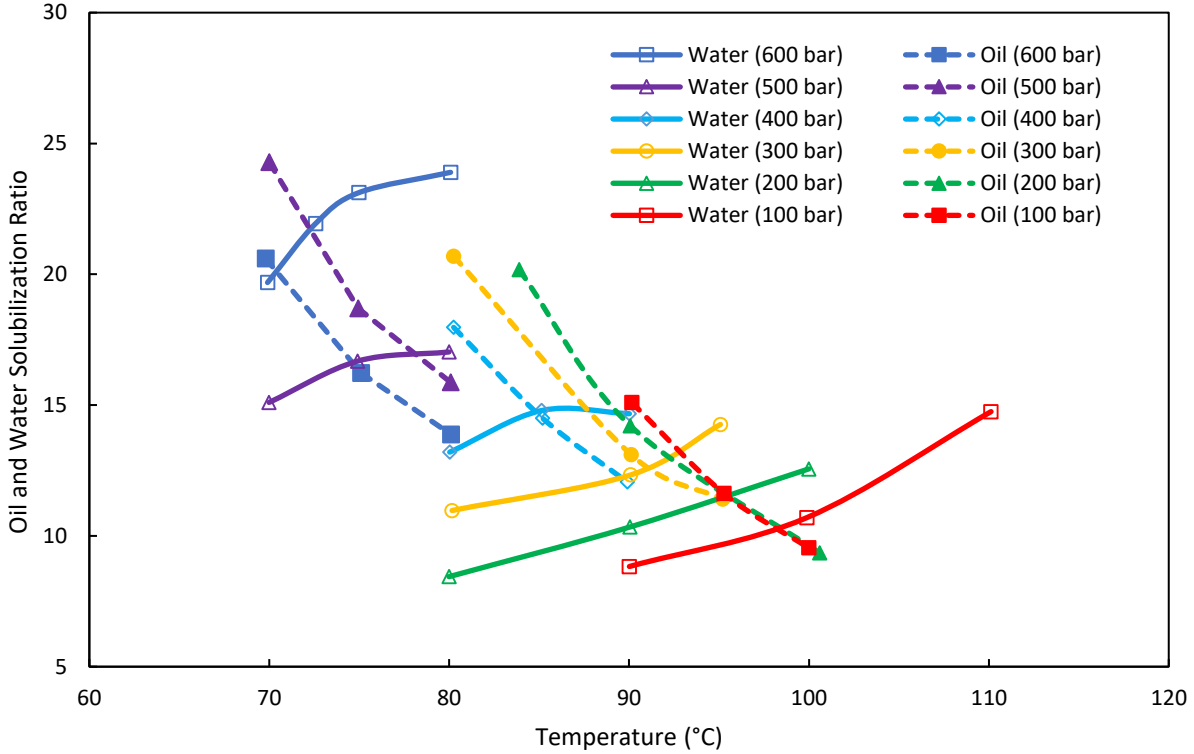


Figure 16: Solubilization ratios for live oil and water [54].

Austad, [54] focuses on the study of the influence of temperature on the PB of the system consisting of alkyl oxylen sulfonate as one component of surfactant system, different types of oil based on the composition and the brine which varied throughout all experiments by its concentration (2.7 wt%, 2.5 wt%, and 3.3 wt% for different types of oil). The average weight of the molecules of the oils was ranging between 84 and 86. A JEFRI PVT window cell was used for observation and execution of the experiments. Water to oil ratio in all experiments depending on pressure and temperature was equal to unity. Interesting note made by the authors was that at the pressure scan at various temperatures no optimum pressure was defined. At the different fixed temperatures, it was observed that microemulsion phase behavior shifts to Type I with increasing pressure, whereas when pressure decreased, system moved to Type II. Additionally, it was defined that with increasing temperature transition from different phases shifted at higher pressures. For

example, if the shift to Type III from Type II microemulsion was happening at pressure range 250-300 bar when temperature was fixed at 60°C, this boundary moved to the point indicating range of pressure 550-600 bar when temperature increased to 100°C (**Figure 17**). When temperature was equal to 120°C the system shifted to type II, because temperature has the reverse impact on phase behavior comparing to pressure, as the augmentation of pressure moves phase behavior to Type I from Type II. Hence, as the system moved to type II, solubilization parameter of water increased. Another reason for increasing of water SR is that water in the ME phase is less compressible than water that exists in excess phase.

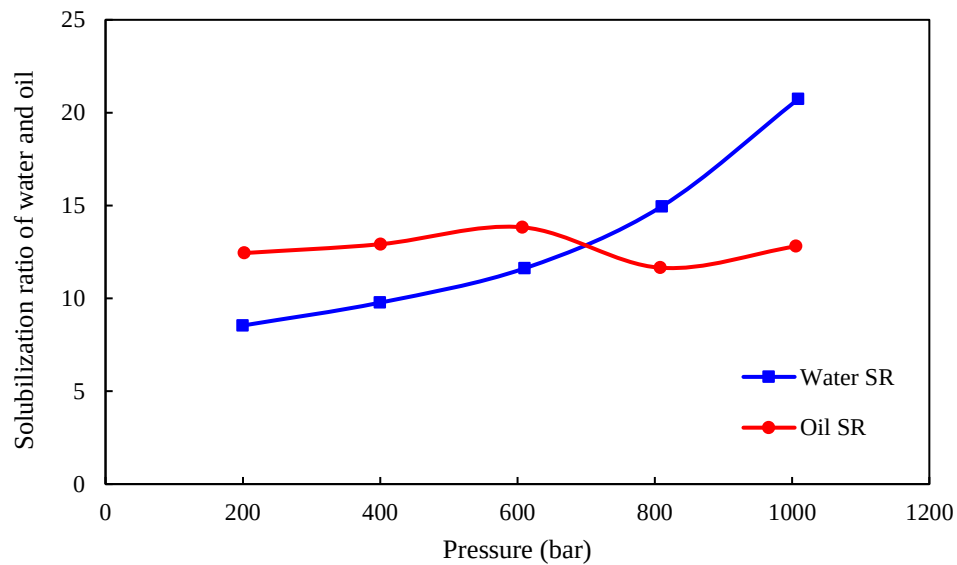


Figure 17: Comparison of water and oil SR [55]

The temperature impact on the PB was found to be responsive both to the oil type and studied temperature range. Therefore, the effect of temperature was studied on the oil without and with addition of 0.5 wt% of isopropanol. It was determined that the oil composition does not possess substantial influence on the trend in phase behavior of a pressure scan, however it is impactful on the phase behavior that is connected with

temperature scan. It was concluded that crude oil showed I/III/II phase transition during temperature increase. Temperature scans at different fixed values of pressure and the alteration of SRs of water and oil with increasing temperature is presented in **Figure 18**. It might be easily observed from the mentioned data, that the SR enhancement of water is more significant than the changes in the solubilization ratio of the oil as a function of pressure. Sassen, [56] discussed the significant pressure influence on the PB of water/oil/nonionic surfactant system. During all experiments water to oil ratio was kept constant. With changing temperature, it was determined that at low temperatures the usual case is the formation of Type I, whereas as the temperature is increased Type II microemulsion is created. In addition, at constant temperature and increasing pressure, phase behavior changes from type II to Type III and from type III to type I microemulsion system. It is explained by the fact that the middle phase of the system that is rich with surfactant moves in accordance with its composition from the side with excess oil phase to the side with excess water phase. Moreover, the water solubility in the phase with microemulsion increased while the solubilization of the oil in the middle phase decreased as a function of pressure.

Kahlweit, [57] investigated the impacts of temperature and pressure on the ME PB and reported that the water solubilization increases while the solubilization of phenyl hexane decreased with increasing pressure. Moreover, at room temperature nonionic amphiphile becomes more soluble in water rather than in oil. However, as the temperature is elevated the amphiphile solubility in oil is increasing. This can be corrected by the way of altering the injected salinity. Furthermore, the temperature as the important parameter affecting microemulsion phase behavior is discussed. In case of majority of anionic surfactants,

elevation of temperature causes transition of phase behavior Type II/III/I. Moreover, increase in temperature, enhances solubilization ratios, however the opposite occurs in case of usage of non-ionic surfactants.

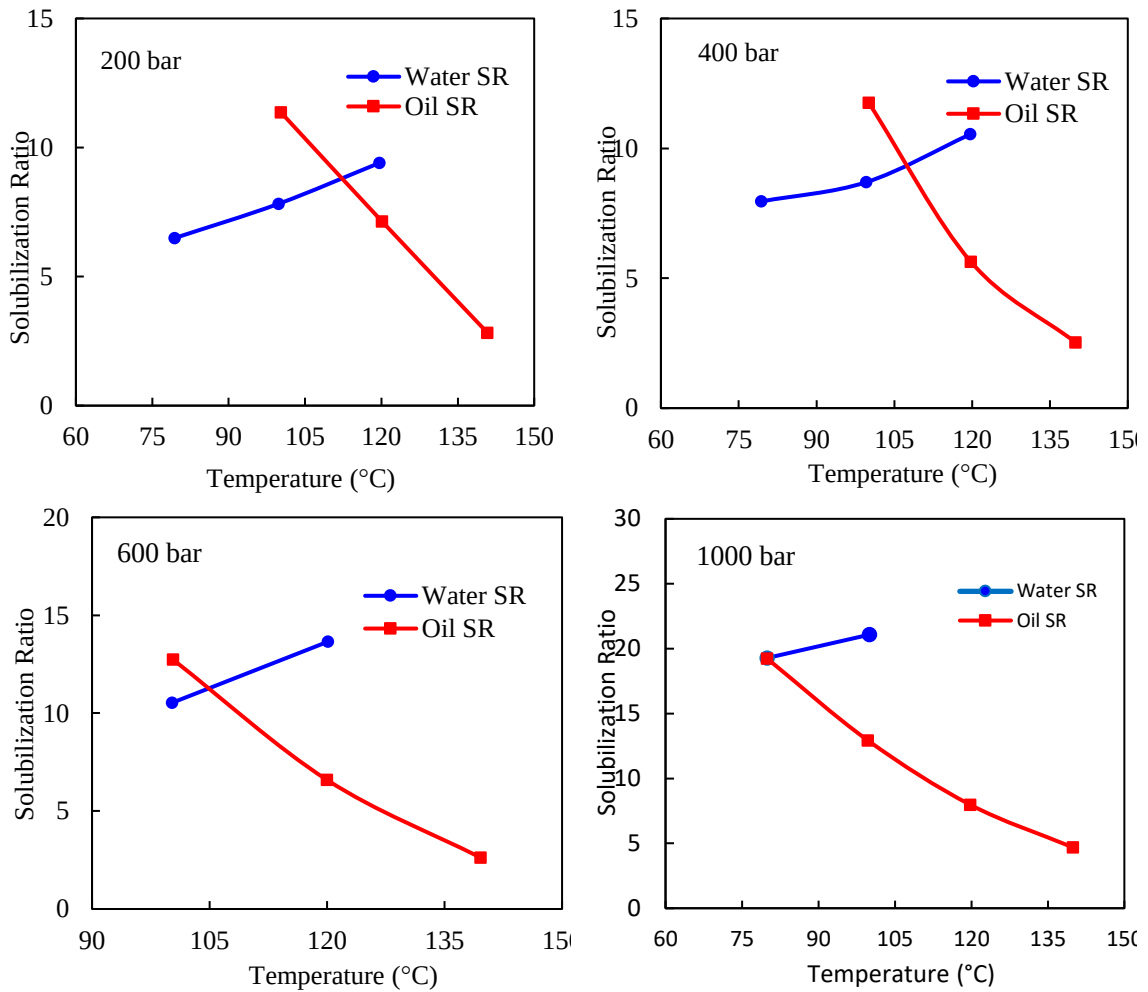


Figure 18: Ratios of solubilization for water and oil [55]

Southwick, [59] noted that the phase behavior with live oil demonstrates larger solubilization ratios and thus lower IFT values. It is concluded that the systems which help to get exceptional production in porous media show IFT values between brine and oil of around 1 millidyne/cm. From the phase behavior done with both dead and live oil it is

stated that live oil gives lower IFT value than dead crude and will be easier to displace in the relevant experiments.

Roshanfekr, [60] tried to shed a light on the understanding the influence done by pressure, salinity and solution gas contained in the oil on the Winsor Type III microemulsion phase behavior. Experiments have been conducted both with dead oil and live oil containing methane. Based on the results of the experiments, it was deduced that at constant temperature and keeping solution gas ratio the same, the optimum SR reduces as a function of pressure and in contrast the S^* enhances as a function of pressure. It was found that the effect of methane addition has the reverse influence on the system with comparison to the application of pressure, because the methane injection to dead oil at the constant pressure and temperature enhanced the optimum SR and reduced the S^* . Another evidence of the reverse impact of pressure and methane was that with pressure enhancement, the system moves towards type I, while the methane addition moves it to type II. While keeping salinity, temperature and solution gas ratio, logarithm of solubilization parameters of oil and water vary linearly as a function of pressure (**Figure 19**). With increasing pressure, the SR of oil enhances while the reverse occurs for the SR of water. At the constant pressure, salinity and GOR, the solubilization parameters linearly depend on the inverse of temperature as well. The SR of oil increases with increase of temperature, whereas the solubilization ratio of water decreases with temperature. The alterations in SR and S^* in case of dead oil were insignificant as a function of pressure in comparison with live oil. The S^* reduced and SR increased substantially with increased pressure when methane was introduced to dead oil. This again proves that the interfacial

tension between water and live oil would be lower in the reservoir than the value of IFT between dead oil and water [59] [51].

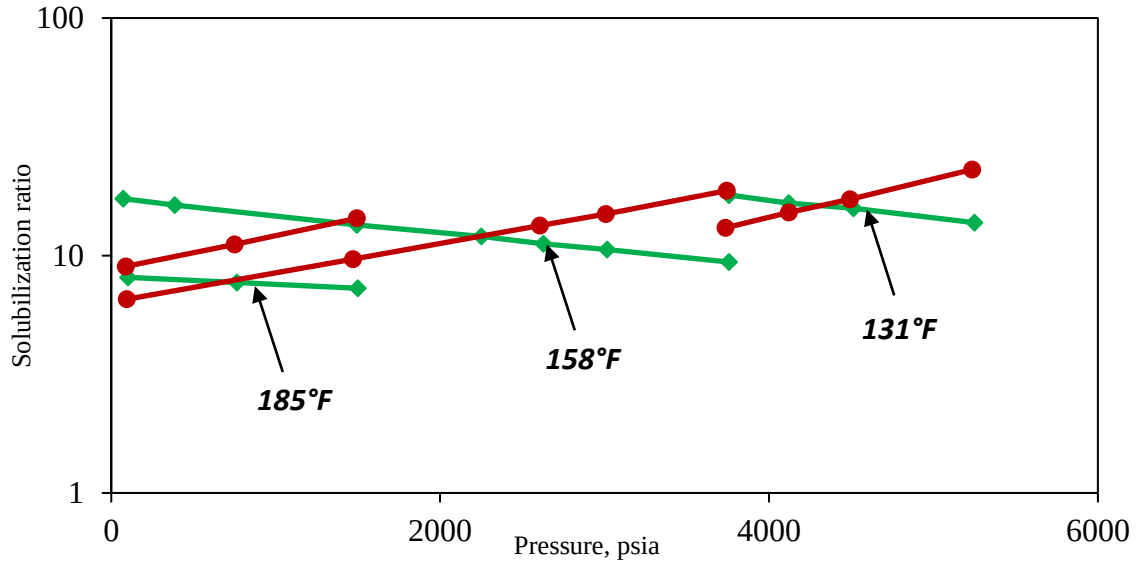


Figure 19: Optimum solubilization parameters [60]

Jang, [23] quantified the separate solution gas and pressure impacts in addition to their net effects using eight oils at a large range of pressure and temperature (up to 150 °C and 5000 psi). They reported a smaller shift in the optimum salinity due to solution gas than previously estimated using the equivalent alkaline carbon number (EACN) approach, while the pressure influence on optimum salinity was much smaller than the effect of solution gas and can often be neglected. They also reported a higher solubilization ratios and lower IFT for live crude oil samples compared to dead crude oil samples. Error! Reference source not found. summarizes the pressure and live oil influence on PB reported by different researchers.

Table 1: Summary of the pressure and live oil influence on PB.

References	Effect of live-oil	Effect of pressure
Puerto & Reed, [44]	Reduction in S*	A shift of PB to Type I
Roshanfekr, [62]	Reduction in S* and A shift of PB to Type II	Increase in S* with A shift of PB to Type I
Austad & Strand, [54]	Increase in S* and A shift of PB to Type I	Water SR in ME increased with A shift of PB to Type I
T. Austad et al, [55]	-	Water SR in ME increased with A shift of PB to Type I
Sassen, [56]	-	Water SR in ME increased with A shift of PB to Type I
Sandersen, [61]	-	Water SR in ME increased with A shift of PB to Type I
Southwick, [59]	Lower IFT values and the optimum SR increase	-
Skauge & Fotland, [50]	-	Increase in S* O/ME SR decrease
Nelson, [34]	Reduction in S* Negligible effect on PB	Negligible effect on PB
Jang, [68]	Optimum SR increased	Negligible effect on PB
Marliere & Creaton, [38]	S* decreased with increasing GOR	Negligible effect on PB
Monette & Nguyen, [47]	Decrease of S*	Decrease of S* Optimum SR increased
Sui et, [58]	Decrease of S*	Negligible effect on PB

O – oil; W – water; ME – microemulsion; PB – Phase Behavior; SR – solubilization ratio; S – optimal salinity*

4.3 Equivalent Alkane Carbon Number Approach

In this section, we will review some literature focusing on the investigation of application of EACN in EOR processes. EACN of crude dead oil containing alkanes in the composition (pure components) can be calculated from the following equation [61] [62][40].

$$EACN = \sum_{i=1}^{Nc} x_i EACN_i \quad (4.1)$$

EACN of crude oil may substantially influence the ME PB. Microemulsions are systems composed of oil, water, and surfactants, and they can exist in different phases depending on the relative concentrations of these components. In general, as EACN of the oil phase

increases, the trend for the microemulsion to form a water-in-oil (W/O) phase increases. This is because high EACN hydrocarbons are typically more hydrophobic and less water-soluble, so they tend to form droplets in the phase with water. However, as EACN enhances, the W/O microemulsion stability decreases [61]. On the other hand, as EACN of the oil phase decreases, the tendency for the microemulsion to form an oil-in-water (O/W) phase increases. This is because hydrocarbons with low EACN are typically more hydrophilic and more water-soluble, so they tend to form droplets in the water phase. EACN approach in chemical EOR support a direct correlation between optimal salinity logarithm, crude oil EACN and optimum SR. Salager, [40]. pioneered in this notion presenting the dependency of optimal salinity on several parameters in microemulsion phase behavior (**Equation 4.2**). Creton and Mougin, [64] modified the equation by including clear dependency of optimal salinity from the temperature alteration.

$$\ln S^* = K(EACN) + f(A) + \alpha(T - T_{ref}) - Cc$$

(4.2)

Where S^* is the optimal salinity, $f(A)$ is the indication of the quantity of the alcohol and also its type, T_{ref} equals to 298.15 K, α is the coefficient of temperature and Cc is related to the tendency of surfactant to create micelles in the solution, which was redefined by [65]. According to [66] K and α have the fixed values for specific surfactants and the correlation of Cc is well established. Ghosh and Johns, [67] further modified this equation by adding the consideration of pressure changes in the phase behavior system (**Equation 4.3**).

$$\ln S^* = K(EACN) + f(A) + \alpha(T - T_{ref}) + \beta(P - P_{ref}) - Cc \quad (4.3)$$

Jang, [68] investigated the solution gas influence on microemulsion phase behavior at elevated temperature and pressure and reported the variation of S^* based on the EACN concept. They surrogate oil was obtained by mixing toluene in the dead oil in order to avoid the asphaltene precipitation, and live oil. The quantity of toluene that was added to each of the dead oils to mimic the crude oil EACN containing methane was calculated by a molar average based on the approach of [40]. The optimum salinities of these surrogate crude oil samples were much lower than the S^* of live oils. Furthermore, negligible difference between the values of S^* for live and dead oils was observed. According to [68], the reduction in S^* for surrogate oils that were diluted with toluene (EACN = 1.0) [69][70] is less than the decrease of S^* of dead oils that possess relatively large EACN. Another important conclusion is that the correlation between S^* and EACN for heavy hydrocarbons is more valid than the dependency with EACN for lighter hydrocarbons such as methane. Moreover, the alterations in S^* proved to be negligible as a function of oil composition. Roshanfekr and Johns, [62] also discovered that at high pressure the trends of optimum parameters of microemulsion phase behavior (solubilization ratio, salinity) correlate linearly with the EACN. This conclusion is in the agreement with multiple other publications [71-72]. An approach to predict S^* and SR from EACN of live oils that possess methane in their composition using only experimental information of dead crude or crude diluted with alkanes was later developed by [62]. The steps to predict S^* for dead and live oil at elevated pressures using EACN of pure components (alkanes) can be described as follows:

1. Plotting the trend of S^* logarithm with increasing EACN at normal pressure (Figure 20).

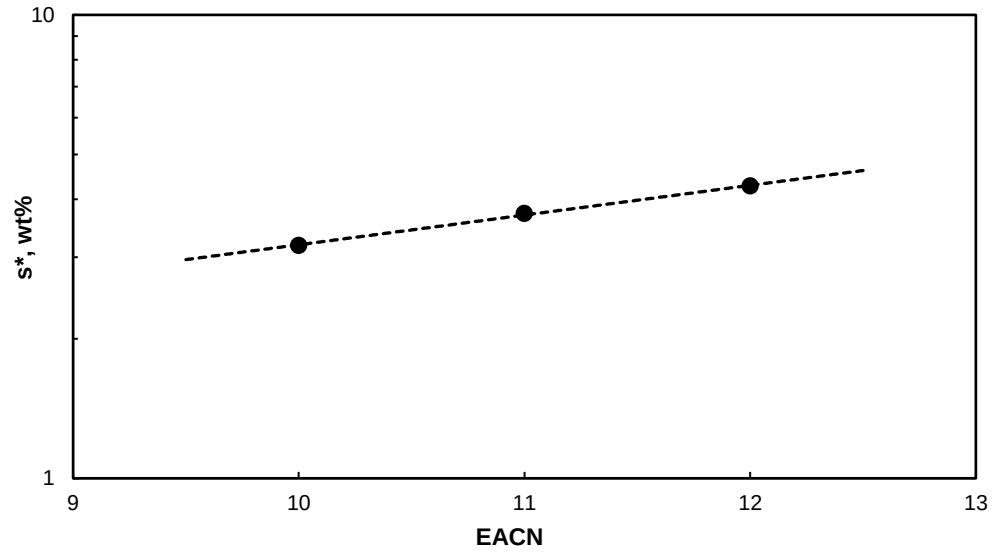
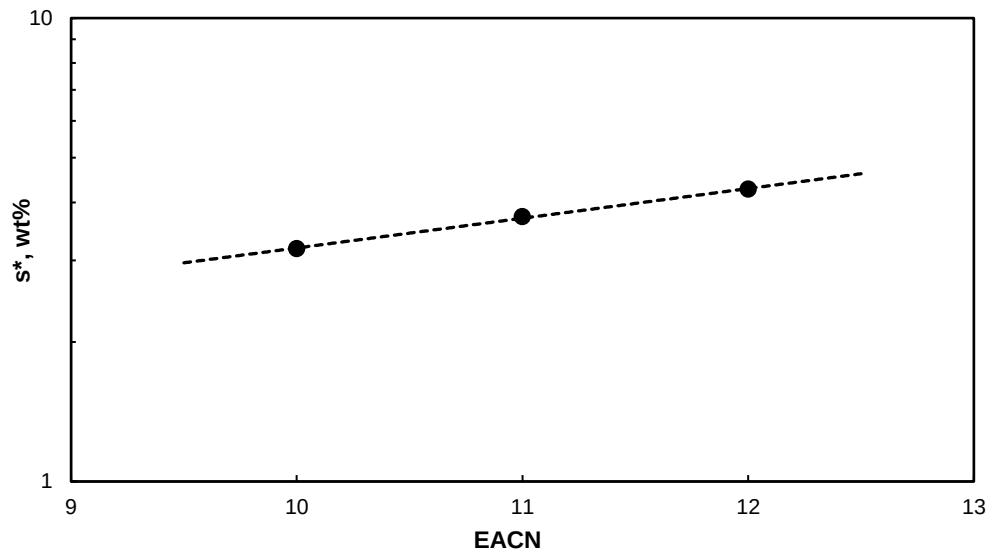


Figure 20



2. Plotting the trend of S^* logarithm with increasing density of pure components, not a mixture. This plot can be utilized for any pressure (**Figure 21**).
3. Determination of the densities of these components at high pressure using EOS.
4. Finding the new S^* using the graph data utilizing the obtained value of density at elevated pressure.

5. Plotting the obtained S^* logarithm with increasing Equivalent Alkane Carbon Number.
6. Repeating these steps to calculate S^* for each component using correlation between S^* and density at high pressure levels.
7. Using the obtained curve of S^* versus EACN to determine S^* for a live crude oil (**Figure 22**). The EACN for live oil will be determined by considering dead oil as a first component and the methane that is added to the system as a secondary component. Equation 5 was applied to determine the EACN for the live oil:

$$EACN_{live\ oil} = (1 - x_{CH_4})EACN_{dead\ oil} + x_{CH_4} \quad (5)$$

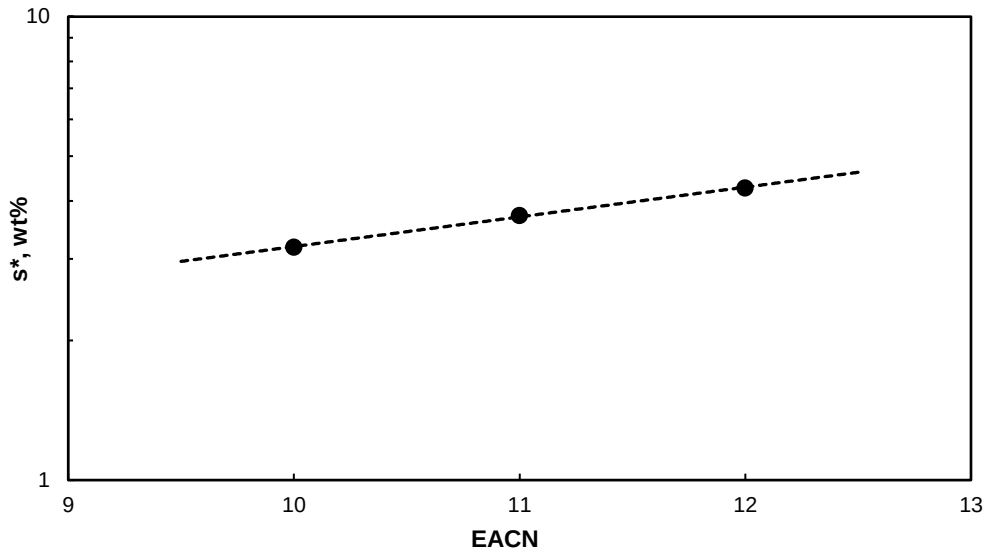


Figure 20: The linear trend between the crude oil EACN and S^* [62]

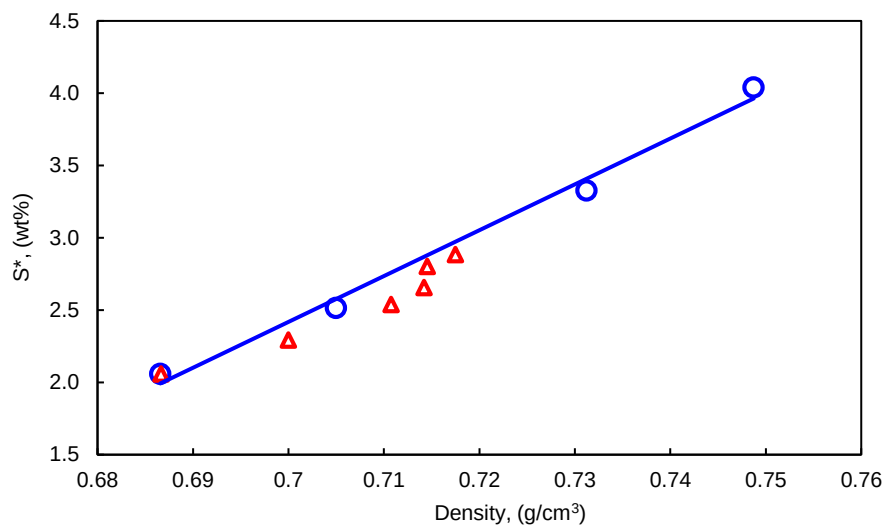


Figure 21: The relationship between the pure components density and the S^* [62]

Pressurizing the dead oil increases the optimal salinity specially for crudes with a lower EACN values (**Figure 22**). On agreement with that, [62] also reported that S^* slightly increased as the pressure was increased from 1.01 bars to 75.80 bars with more significant increase of S^* in case of low EACN range.

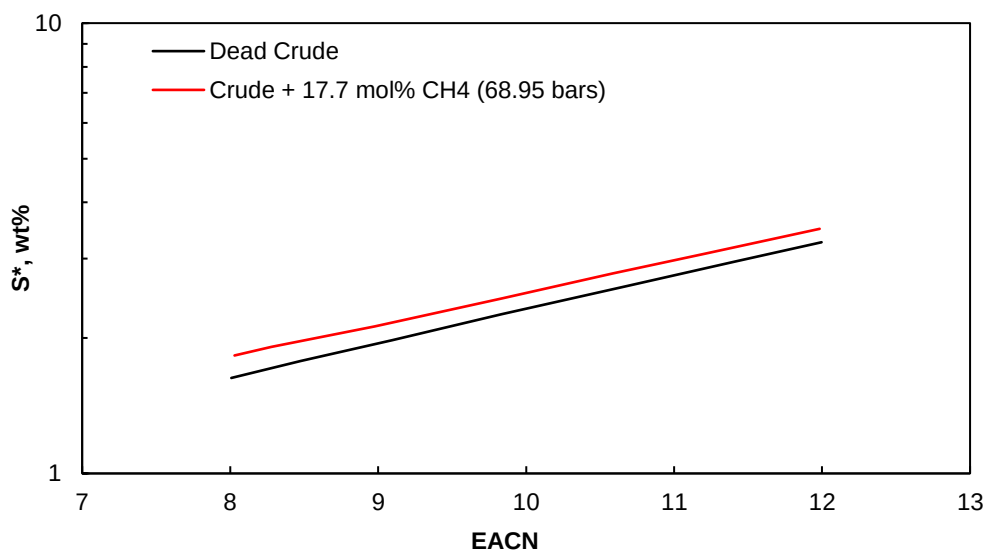


Figure 22: S^* versus EACN [62]

Chang, [66] address microemulsion phase behavior using EACN concept and data for the structures of co-surfactant and surfactant along with the equation proposed by [63] and modified by to predict the optimum salinity for a surfactant/brine/crude system. Wan, [74] modified **Eq. 4.4** to the normal temperature conditions without alcohol presence for zero hydrophilic-lipophilic-deviation (HLD) as:

$$\ln S^* = K(EACN) - Cc \quad (4.4)$$

Wan, [74] categorizes methods to determine EACN of crude oil as indirect and direct. Indirect method involves titrating the oil mixture which has the known EACN and the oil which does not have the known EACN value in the first place and also titrating a surfactant formulation that has determined magnitudes of $f(A)$, K , α , Cc with presence of NaCl for determination of S^* and then using it in **Eq. 4**. Relying on the magnitudes of values of Equivalent Alkane Carbon Number of the predetermined oil, the unknown oil Equivalent Alkane Carbon Number could be determined. In the direct method, on the other hand, author uses AOT and iso-butanol as a surfactant formulation to evaluate the EACN of oil. Solairaj, [75] also confirmed the linear dependency between oil EACN and S^* . With increasing hydrophobe size S^* decreases for the same EACN (**Figure 23**). Guerbet alkoxy sulfates (GAS) is more efficient with crude oil samples with high EACN promoting formation of ultralow IFT [76]. Skauge and Fotland, [50] investigated the effect of EACN on S^* and pertained the changes of the ME PB to the alteration of oil density. A similar conclusion was given by [62] where the EACN estimation for live oils at high pressure was executed by calculation of densities of pure components - alkanes.

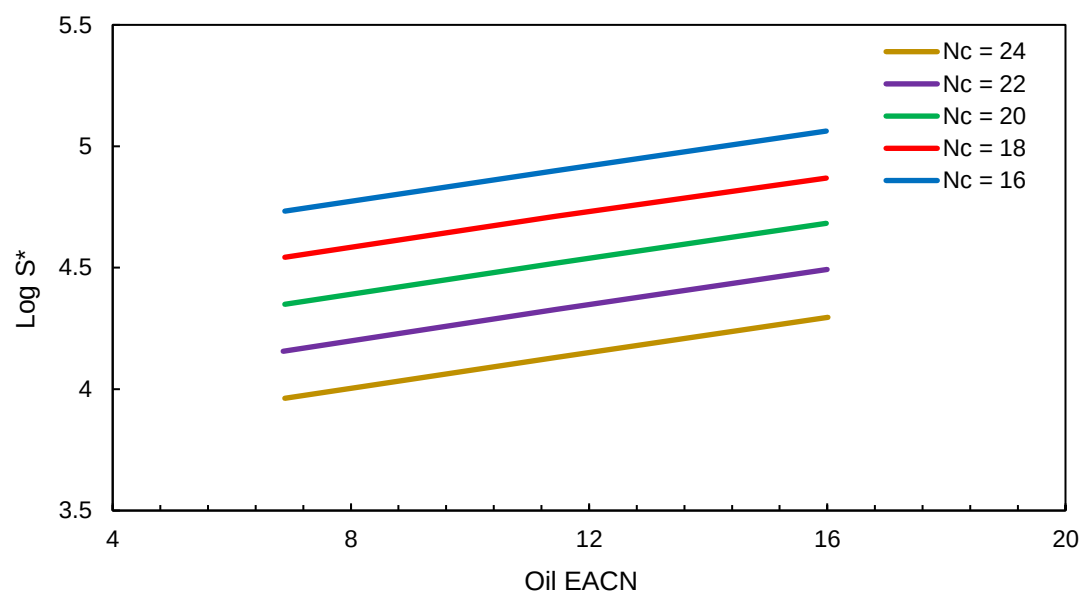


Figure 23: Plot of optimal salinity versus oil EACN

CHAPTER 5

METHODOLOGY & EXPERIMENTAL PROCEDURES

5.1 Interfacial Tension Experiments (IFT)

During the contact of two immiscible liquids with each other, they are separated by an interface with a small thickness. Because of the reason that molecules inside the fluid possess higher attraction between one another than on the boundary with the molecules of the contacting fluid. Hence, an inward acting force is present there which tends to decrease the surface by turning it into the sphere shape. This action on the surface forms a thin film of molecules, which are in tension due to the interface specific free energy [77]. The IFT is measured with the force per unit area [mN/m], but more frequently the dimension used to estimate IFT used in the literature is dynes/cm, which is in number equal to $[(N * 10^{-3})/m]$ or [mN/m] and it is designated by the symbols σ or γ . Interfacial tension plays a substantial role in various procedures where two phases are in contact with each other:

- *Emulsions and emulsifiability*: The IFT contributes to the emulsifiability and the separation of two phases from each other.
- *Flooding (for example in enhanced oil recovery)*: The organic phase can be mobilized after surfactant injection to decrease the interfacial tension with water
- *Quality tests of hydrophobic liquids*: Usually, aging of a hydrophobic liquid is accompanied by a decrease in its interfacial tension with water. An important quality test in such cases is measuring the interfacial tension, as with transformer oil.

Numerous tools have been developed contributing to IFT determination. Some of them are exhibited below:

Table 2: Most common IFT measurement techniques

Ring method	Plate method	Rod method
Drop volume method	Pendant drop method	Spinning drop technique

The IFT determination in this research will be carried out using spinning drop technique with the *Spinning Drop Tensiometer (SDT)*. This drop is set in rotation by a horizontal capillary filled with the heavy phase and the light phases. Centrifugal force causes the drop to be drawn lengthwise, resulting in a circular form that correlates with interfacial tension. With the SDT, ultralow, low, and extremely high interfacial tensions can theoretically be measured from 10^{-6} to 2000 mN/m because of its design [78]. The function of Vonnegut will be applied in the ADVANCE software which is attached to SDT. It also enables to observe the accurate image of the drop in the capillary. In the enclosed design of SDT, all functions and instrument components are located. Display, control dials and touch-sensitive buttons are on the right-hand control unit. The control dials are used to monitor the rotation of the capillary, the inclination, the lightning, and the position of the observing camera. The SDT menu gives access to the fundamental settings such as rotation speed and temperature of the capillary.

Mechanism of the Spinning Drop Tensiometer includes at first filling the closing plug outside of the sample chamber with the sample drop. Afterwards, by means of the piston and the piston rod, the heavy phase is drawn into the capillary. Once this capillary is sealed, it is placed onto the filled closing plug. Using a capillary and a piston rod, the capillary is

allocated in the SDT. The piston tip, which is the calibration object, is a component of the piston that remains in the capillary during calibration [78]. Immediately, upon the ending of the calibration, the IFT measurement in SDT takes place. Spinning Drop Tensiometer has a module called Drop Positioning for ADVANCE, which keeps the sample drop in the middle of the camera image automatically. Finally, after adjustment of the temperature, lightning, rotation speed (RPM) the IFT measurement is commenced and estimated in the ADVANCE software. Numerically, it can be demonstrated in the following equation:

$$\sigma = \frac{1}{4}r^3\omega^2(\rho_H - \rho_L) \quad (5.1)$$

σ – Interfacial tension (IFT)

r – Radius of the drop

ω – Rotational frequency of the capillary

ρ_H – Density of the heavy phase (water)

ρ_L - Density of the liquid phase (oil drop)



Figure 24: Spinning Drop Tensiometer (SDT)

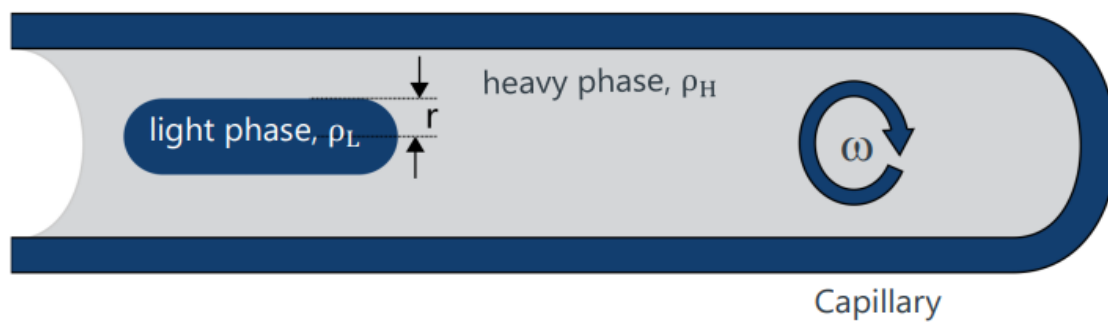


Figure 25: Representation of the IFT measurement [79]

5.2 Phase Behavior Experiments at Atmospheric Pressure

Phase behavior or salinity screening experiments are usually performed to obtain the optimum chemical formulations for SP/ASP methods (**Furia, 2021; Suniga et al., 2016; Hirasaki et al., 2011**) . In the ordinary phase behavior experiment, surfactant will be mixed with the brine and oil, which will be prior diluted with toluene to imitate properties of reservoir oil, such as viscosity. This mixture will then be stored in glass pipettes to observe the creation of microemulsions at atmospheric pressure and reservoir temperature ($>90^{\circ}\text{C}$). Also, the aqueous stability will be conducted where surfactant is mixed only with brine to determine the limit of aqueous solubility with enhancing salinity. Moreover, co-solvents and co-surfactants are also used along with the main surfactant for ideal behavior of microemulsion. Co-solvents will contribute to the reduction of microemulsion viscosity which is viable for EOR techniques. The observation of solutions might be practical if decent time is allowed to keep them in ovens at reservoir temperature. For example, months can be spent on storing and observation of solutions to await all phases reach equilibrium. Phase behavior at equilibrium state is substantial to mimic the procedure in the reservoir.

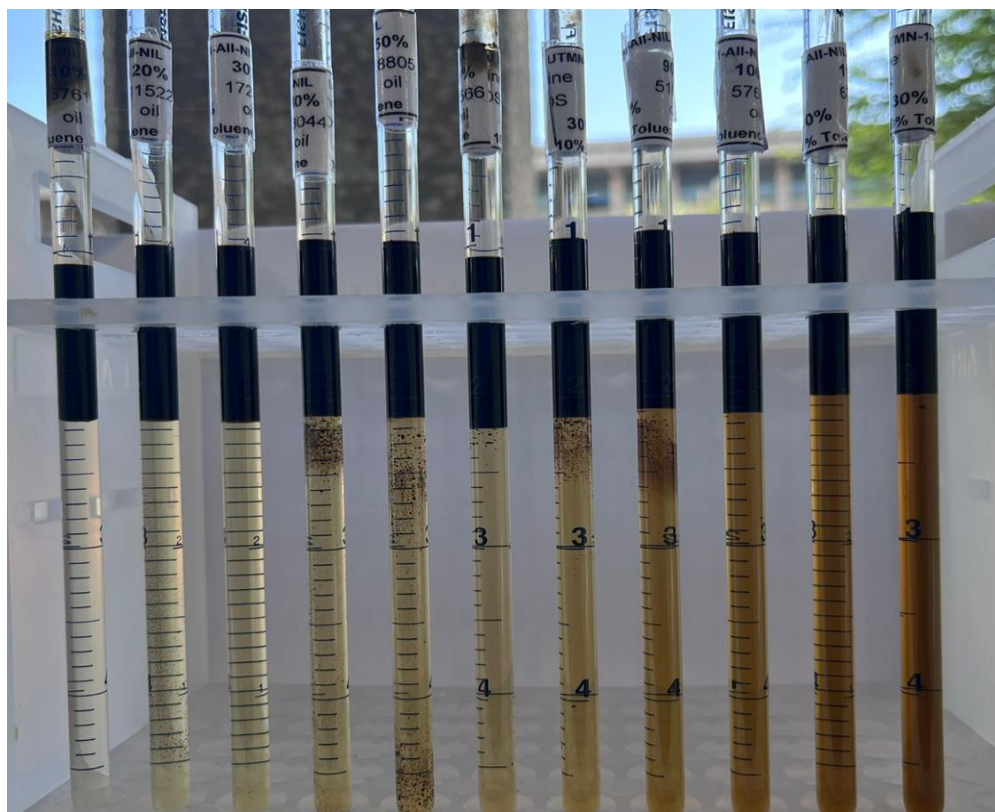


Figure 26: Phase behavior experiments with salinity increasing from left to right.

As soon as the optimum formulation is determined out of all solutions with the desired optimum parameters (optimal salinity, IFT, low microemulsion viscosity, optimum solubilization ratio), it can then be utilized for the experiments of phase behavior at high-pressure, high-temperature conditions (HPHT) with live-oil.

5.3 HPHT Sapphire Cells for EOR Surfactant Formulation

After the promising formulation has been identified from ordinary salinity screening at normal pressure, it is utilized for high pressure observation of behavior of phases. The equipment used for phase behavior experiments in this research will be 5 M9715 High Pressure/High Temperature PVT Visualization Cells. It possesses following characteristics:

- Max Operating condition: 350 bar @150°C

- Internal diameter of the sapphire tube (mm): 11 mm
- Length of the sapphire tube (mm): 150 mm
- Total cell volume: 15 ml
- 2 flat lids with low dead volumes
- 3 connectors on each lids Construction in Hastelloy HC for the 2 lids.
- Cell support and axis for an easy rotation/mixing of the cell on the support.
- 1 HP valve at the top
- 2 HP valves at the bottom
- 1 pressure gauge and 1 safety head at the top



Figure 27: Five sapphire cells for HPHT testing for surfactant formulations

5.4 PVT 300/700 Cell for Live-Oil Preparation

PVT 300/700 FV cell has been utilized in this work to dissolve certain amounts of methane in a dead oil under high pressure and high temperature to create a live oil with a particular GOR.

- Max. Pressure: 700 bar
- Max. Temperature: 180°C
- Total Volume of the Cell: 300 ml

Characteristics:

- Constant Temperature control system
- Automatic Valves
- Stirring by magnetic coupling
- Data acquisition and control system
- High pressure valves, pipes and filters



Figure 28: PVT 300/700 Cell

- **Methane injection**

Firstly, 60 ml of methane was introduced to the PVT cell from the cylinder at a pressure of 2000 psi. After finishing the transfer of the whole volume, the pressure in the cell was increased to 2500 psi in order to reduce the volume of methane to 40 ml.

- **Dead oil injection**

Afterward, the dead oil sample that contributed to the generation of Type III microemulsion at atmospheric pressure was prepared for injection into the PVT cell. Before starting the experiment, the accumulator used for dead oil was tested with water using the ISCO Syringe Pump at a maximum of 5000 psi to ensure that no leaks were observed. As the leak test has shown to be successful, 150 ml of dead crude oil was introduced into the accumulator. Then, the accumulator was connected to the pump from the bottom and to the PVT cell from the top in order to maintain an injection at high pressure. The water from the pump has been injected at a pressure which was continuous at 2550 psi from the bottom

to push the internal piston up to displace and inject 121.6 ml of dead oil into the PVT cell that contains methane inside at 2500 psi. In order to maintain a pressure drop during transferring procedure, a 50-psi difference in pressures in two cells has been retained.

Firstly, the following data is obtained and given as an input: Initial Volume of gas (V_{gi}), Pressure (psi), Temperature ($^{\circ}\text{C}$) and required GOR. Using Excel data with the equations given below, the required volume of oil is injected into the PVT cell.

Formation Volume Factor:
$$B_g = \frac{0.02827 * T_g}{P_g}$$

Volume of Gas at standard conditions:
$$V_{g.st.} = \frac{V_{gi}}{B_g}$$

Required Volume of Oil:
$$V_o = \frac{V_{g.st.}}{GOR}$$

- **Mixing**

After reaching a total volume of 161.6 ml in the cell at 2500 psi, 50 $^{\circ}\text{C}$, the live oil was stirred continuously until no bubbles of free gas were present in the cell. The mixing procedure was visualized with the camera of the PVT cell.

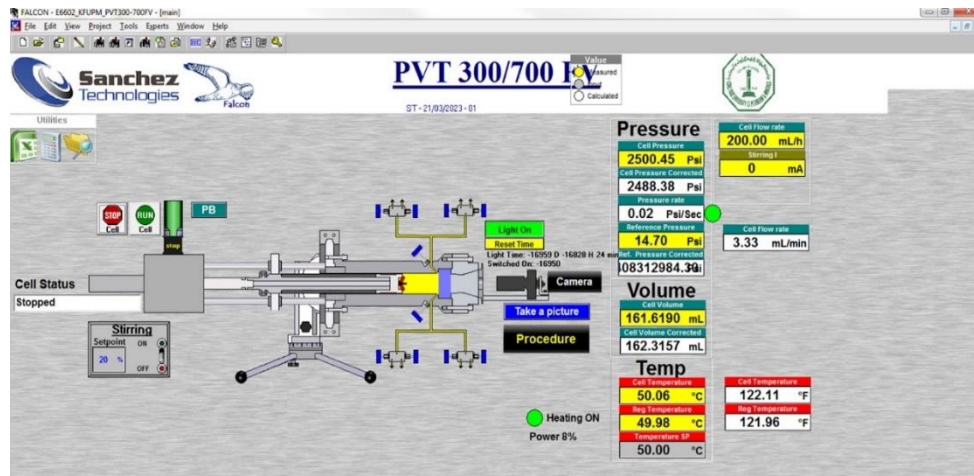


Figure 29: Principal main showing the final PVT data for Live-oil

- **Transfer of Live-Oil to the HP Accumulator**

Upon the continuous observation and confirmation of the successful experiment, the sample of live-oil (280 GOR) was transferred to the accumulator and kept at constant high pressure (2500 psi).

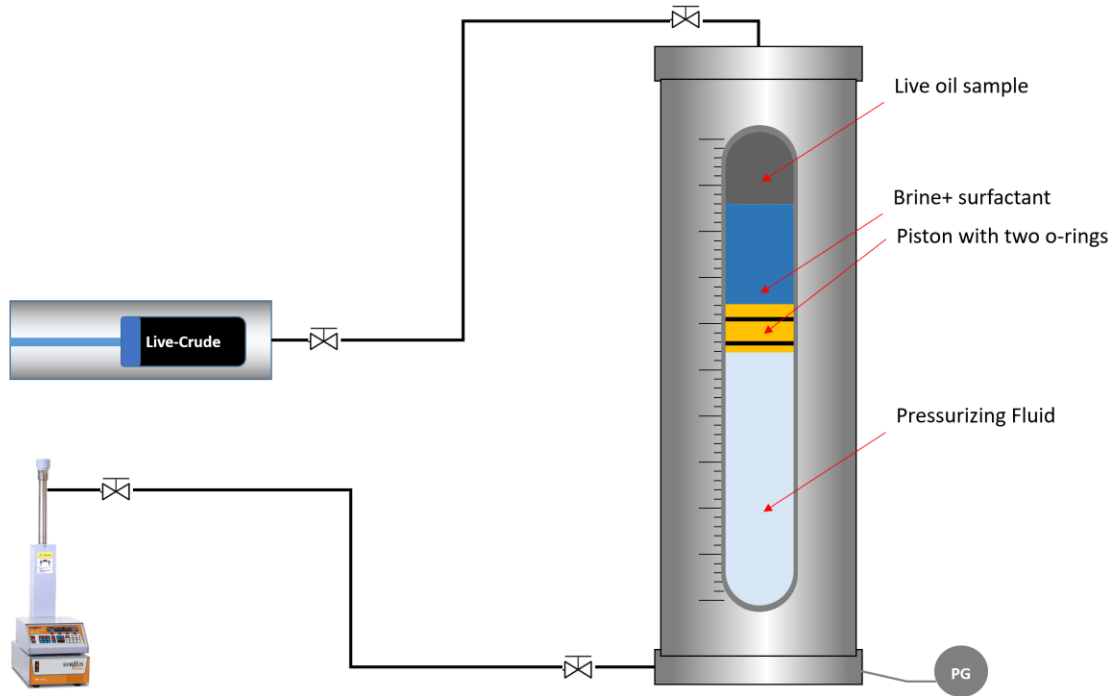


Figure 30. Setup for transfer of live-crude from PVT cell to HP accumulator

5.5 Fluids

Fluids that have been used in this thesis include Light Saudi crude oil, Seawater (Injection Brine), and Formation brine. The composition and properties of the fluids given as follows:

The Anton Paar digital density meter was utilized for density measurements of crude LS and at various levels of temperature and results are presented in **Figure 31**. According to this measured, the LS crude oil samples has API value of 29.4 at 15 °C respectively. Different constant temperatures, such as 25°, 50° and 75°C were used as data points (**Figure 32** and **Figure 33** for LS dead oil and surrogated oil respectively).

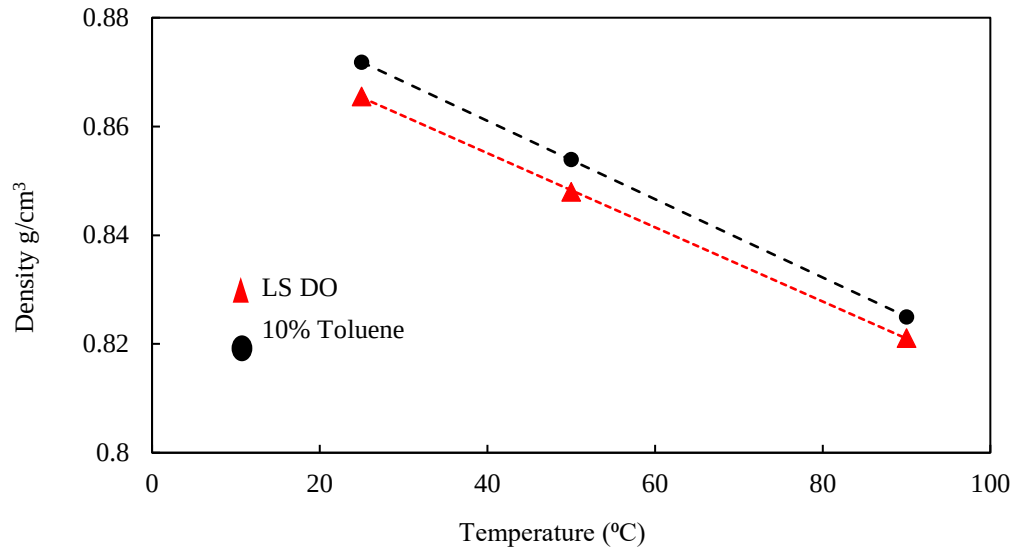


Figure 31: Density of LS dead Crude oil and surrogated crude oil

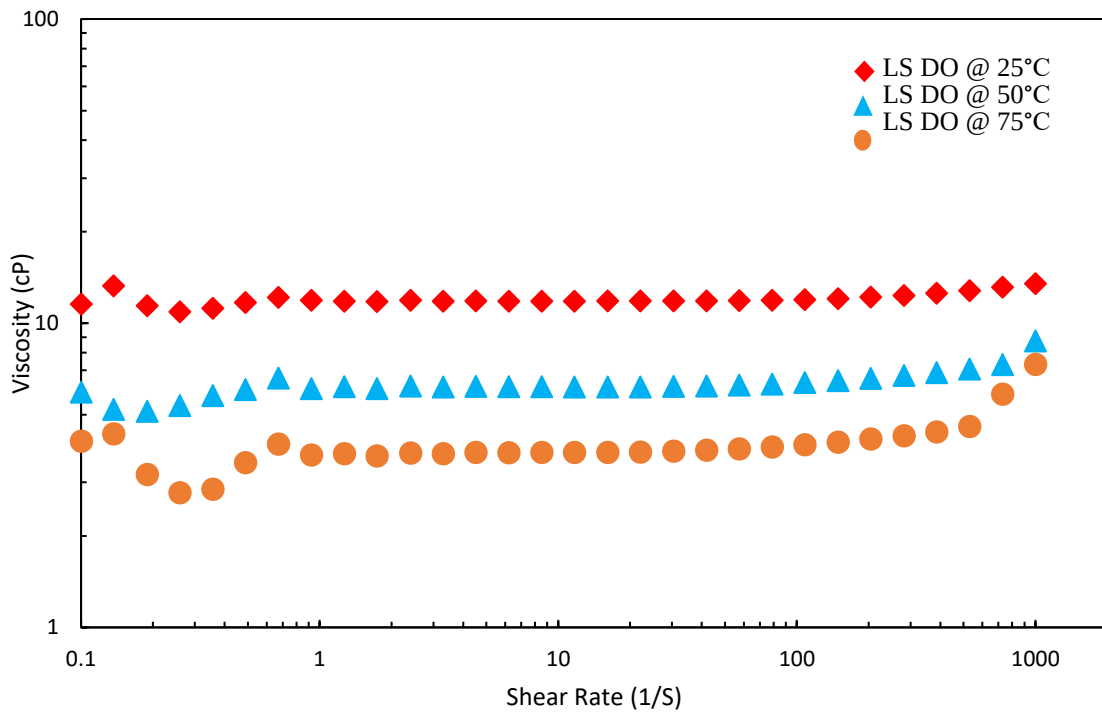


Figure 32: LS viscosity oil at temperatures at various levels.

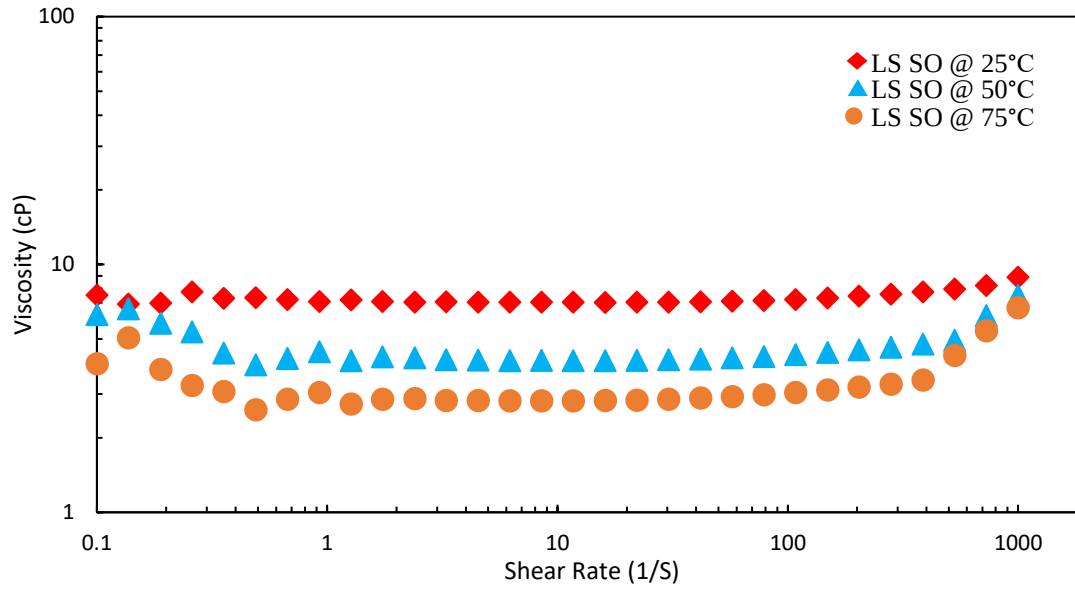


Figure 33: LS viscosity surrogated oil at different temperatures.

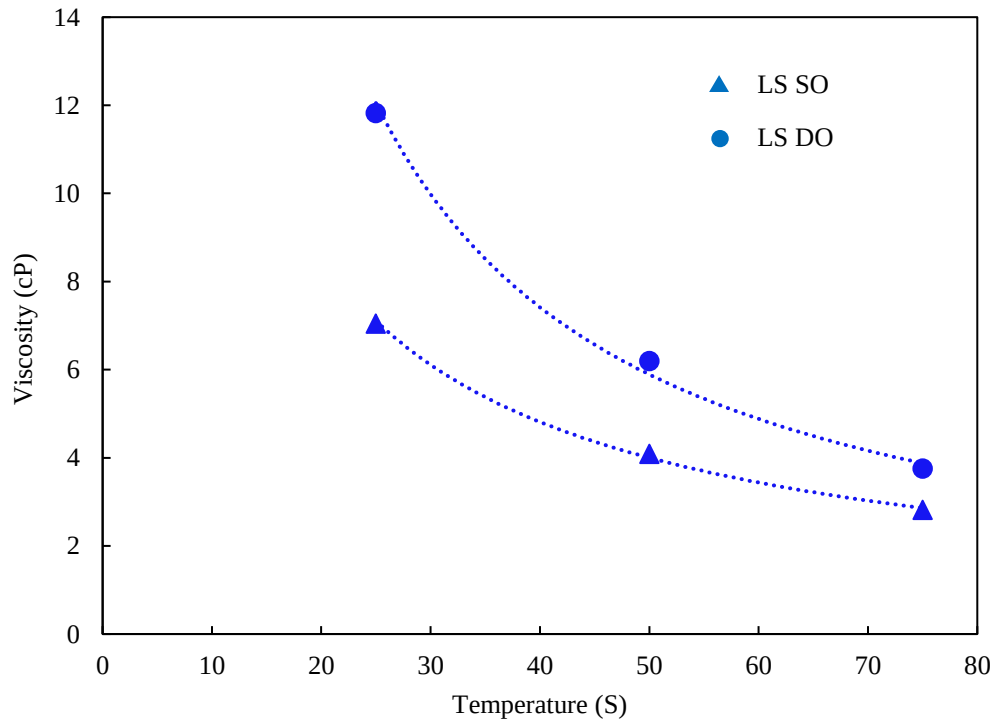


Figure 34: The viscosity of LS crude at various temperatures.

In addition to the properties of oil, the IFT between LS crude and various aqueous solutions was measured using spinning drop tensiometer at different temperature as a

reference for the performance of surfactant formulations. IFT values of the crude oil samples with Deionized water, seawater, and formation brine are listed in **Table 3**.

Table 3: IFT measurement between crude oil

Aqueous solution	Temperature (°C)	IFT (mN/m)
		LS
DI water	25	31.03
	50	33.33
	90	34.24
Seawater	25	33.65
	50	34.38
	90	35.74
Formation Brine	25	24.33
	50	25.08
	90	26.32

Table 4: LS Dead Crude oil properties

Gravity (°API)	25.4
Density @ 100°C (kg/m³)	845.8
Viscosity @ 100°C (mPa.s)	3.4
TAN (mg KOH/g)	0.38
TBN (mg KOH/g)	0.6

Table 5: LS Dead crude oil composition

C₄ - C₂₀	38.0%
C₂₀₊ Saturates	16.5%
C₂₀₊ Aromatics	18.2%
C₂₀₊ Resins	23.2%
Asphaltenes	4.1%

Table 6: Salinity of Injection water and Formation brine

Ionic Species (ppm)	Injection water	Formation Brine
Na⁺	18,300	59,491
K⁺	0	0
Ca²⁺	650	19,040
Mg²⁺	2,110	2,439
Sr²⁺	0	0
Cl⁻	32,289	132,067
SO₄²⁻	4,290	350
HCO₃⁻	120	354
TDS	57,759	213,741

CHAPTER 6

RESULTS AND DISCUSSIONS

6.1 IFT Measurement and Salinity Scan at Atmospheric Pressure

6.1.1 ARM-Surfactant-1

The IFT between LS crude oil and first surfactant formulation was measured to guide the salinity screening experiments at 90 °C, ambient Pressure, and 1.0 wt% of the ARM-surfactant-1 using RDO (dead oil+ 10 % Toluene). IFT measurements as function of salinity and times is shown in Figure 35 and stabilized IFT values are listed in **Table 7**.

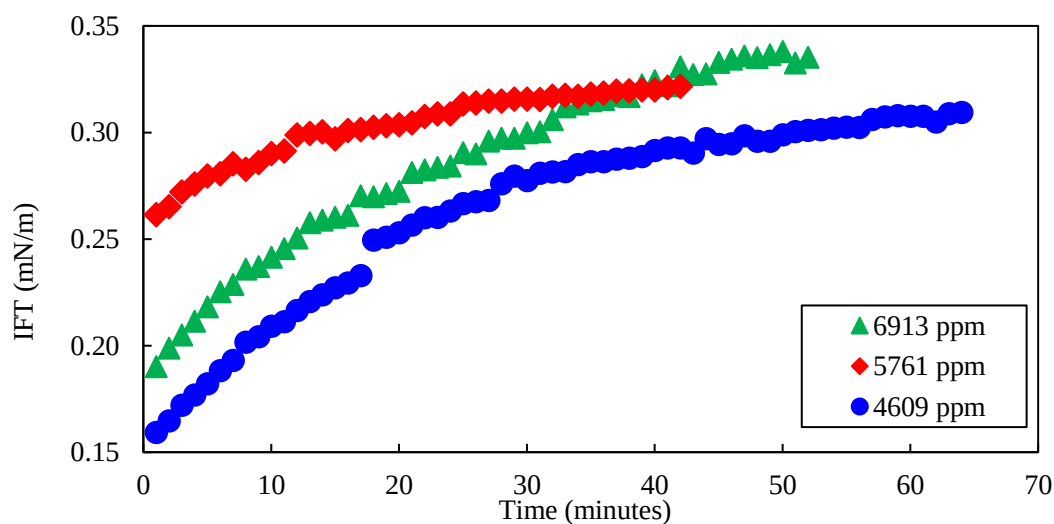


Figure 35: IFT between LS crude oil and 1.0 % ARM-Surfactant-1

Table 7: Stabilized IFT values

Salinity (g/L)	IFT (mN/m)
4.60	0.304
5.76	0.321
6.91	0.335

Ten samples were prepared to cover the low salinity range made by diluting seawater (1.15-13.8 g/L). The salinity scan shown in **Figure 36**. The entire salinity range showed Type I microemulsion which agrees with the IFT measurements reported in **Table 7**. The salinity scan was repeated at higher salinity range (5.7-69.1 g/l) using seawater and the same Microemulsion type (type I) developed at the whole range salinity range **Figure 37**. Moreover, the NaCl salinity scan showed the same Microemulsion “type 1” as shown in **Figure 38**.

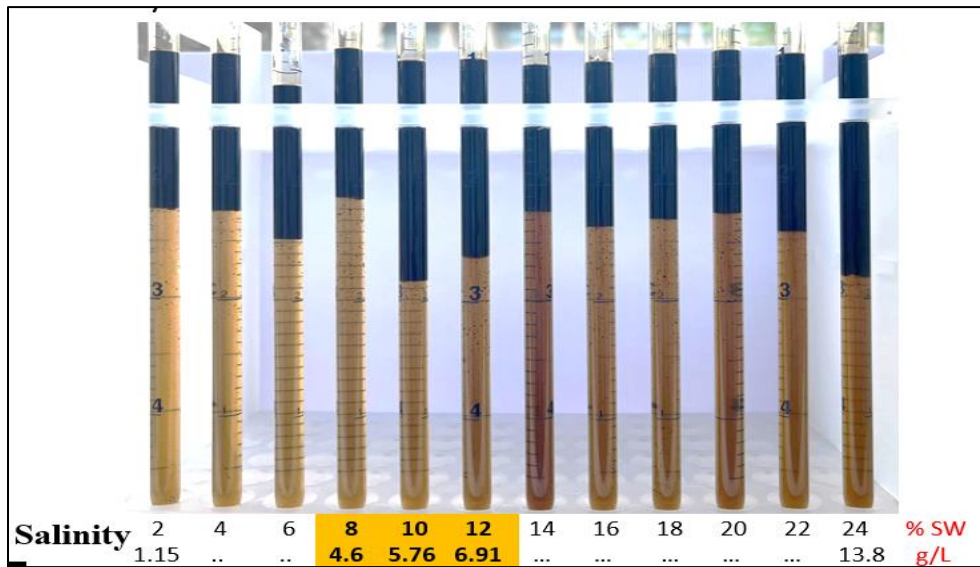


Figure 36: Salinity scan using low salinity

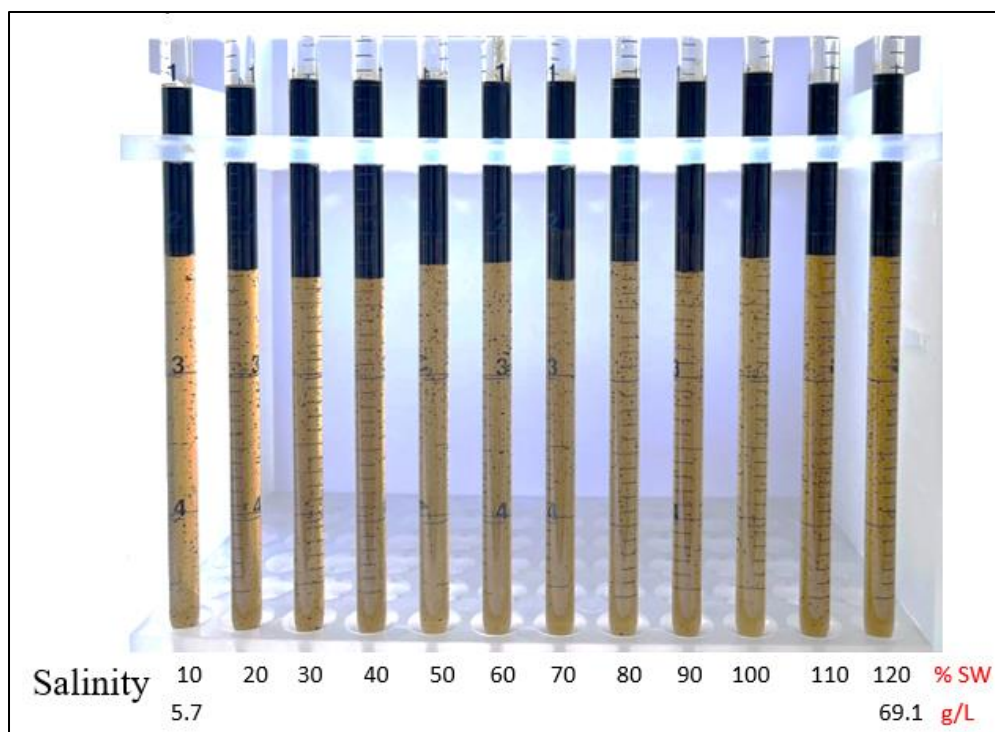


Figure 37: Salinity scan using high salinity

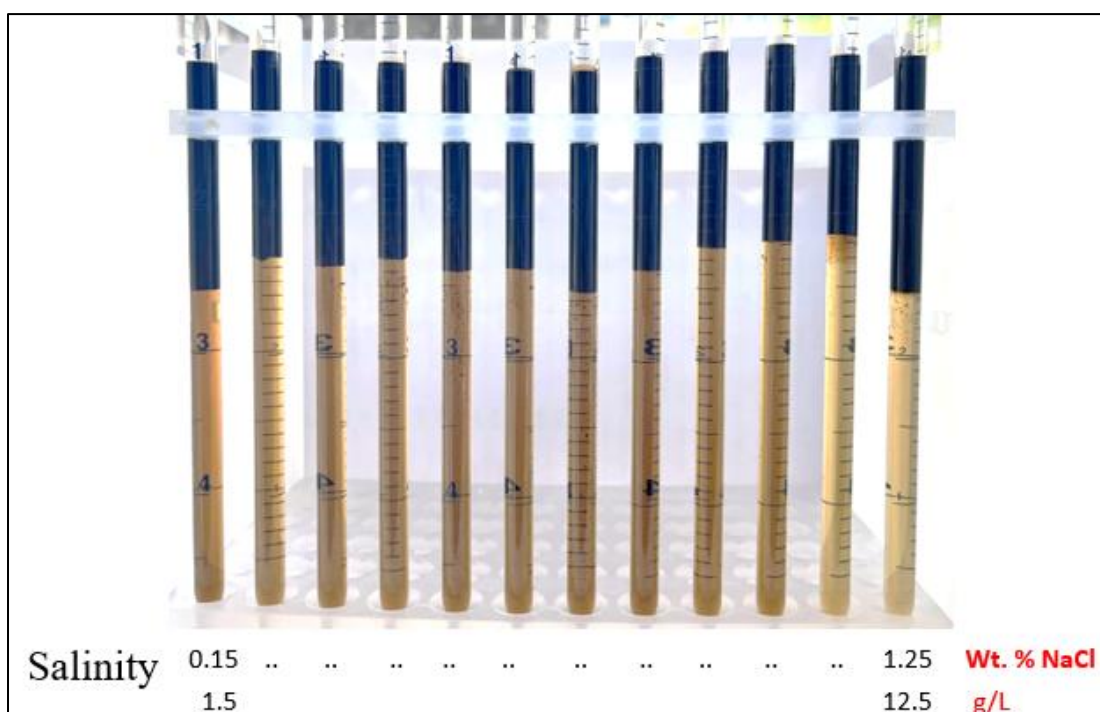


Figure 38: Salinity scan using low salinity

6.1.2 ARM-Surfactant-LS

Table 8: Summary of the salinity scans using 0.25 wt% ARM-Surfactant-LS

Scan	Crude Oil	Min. Salinity		Max. Salinity		Comments
		% SW	(ppm)	% SW	(ppm)	
LS#11	LS	10	5761	100	57610	No ME (Figure 39)



Figure 39: Salinity scans using 0.25 wt% ARM-Surfactant-LS

6.1.3 UT Surfactant Formulation

Additional salinity screening experiments have been carried out using surfactant blend UT consisting of different concentrations of Carboxylate (C28); IOS15-18; IOS19-23; Phenol. LS crude has been used to measure the potential of microemulsion generation using the following sets of surfactant formulations with different concentrations of the components

Table 9: LS -UT1 Surfactant formulation

Component	Name	Activity (%)	wt%
Surfactant	C28-35PO-50EO	10.00%	0.50%
Co-surfactant 1	C15-18 IOS	22.80%	0.35%
Co-surfactant 2	C20-24 IOS	19.53%	0.15%
Co-solvent	Phenol-1PO-5EO	100.00%	0.50%

Table 10: LS -UT2 Surfactant formulation

Component	Name	Activity (%)	wt%
Surfactant	C28-35PO-50EO	10.00%	0.50%
Co-surfactant 1	C15-18 IOS	22.80%	0.35%
Co-surfactant 2	C20-24 IOS	19.53%	0.15%
Co-solvent	Phenol-1PO-5EO	100.00%	0.20%

Ionic Liquid has been added to the surfactant formulation to contribute to the microemulsion generation.

Table 11: LS -UT3 Surfactant formulation

Component	Name	Activity (%)	wt%
Surfactant	C28-35PO-50EO	10.00%	0.50%
Co-surfactant 1	C15-18 IOS	22.80%	0.35%
Co-surfactant 2	C20-24 IOS	19.53%	0.15%
Co-solvent	Phenol-1PO-5EO	100.00%	0.05%
Ionic Liquid	C12[MIM] ⁺ Cl ⁻	10.00%	0.05%

Table 12: LS -UT4 Surfactant formulation

Component	Name	Activity (%)	wt%
Surfactant	C28-35PO-50EO	10.00%	0.50%
Co-surfactant 1	C15-18 IOS	22.80%	0.35%
Co-surfactant 2	C20-24 IOS	19.53%	0.15%
Ionic Liquid	C12[MIM] ⁺ Cl ⁻	10.00%	0.05%



Figure 40: Salinity scans with LS -UT1 and surrogated LS



Figure 41: Salinity scans with LS -UT2 and surrogated LS



Figure 42: Salinity scans with LS -UT3 and surrogated LS



Figure 43: Salinity scans with LS -UT4 and surrogated LS

Table 13: Summary of the salinity scans using UT formulation

Scan	Crude Oil	Min. Salinity		Max. Salinity		Comments
		% SW	(ppm)	% SW	(ppm)	
LS -UT1	LS	10	5761	100	57610	Type II – Type I ME
LS -UT2	LS	10	5761	100	57610	Type II – Type I ME
LS -UT3	LS	10	5761	100	57610	Type II ME
LS -UT4	LS	10	5761	100	57610	Type II ME

6.1.4 ARM-Surfactant-5660

The aqueous stability of three different concentration (0.25, 0.5, and 1.0 wt%) of the newly proposed surfactant where tested at 10% seawater salinity (5761 ppm) and 90 °C. Only the 0.25% formulation showed a clear solution at 90 °C as shown in **Figure 44**. A further test of 0.25 wt% formulation was done up to 100% sea water salinity (57610 ppm) as show in **Figure 45**. It has been deduced to continue with 0.25 wt% ARM-Surfactant-5660 with a

stability limit of 80% seawater (46088 ppm) with both LS crude oil samples. Table 14 summarizes the salinity scan results using 0.25 wt% ARM-Surfactant-5660.

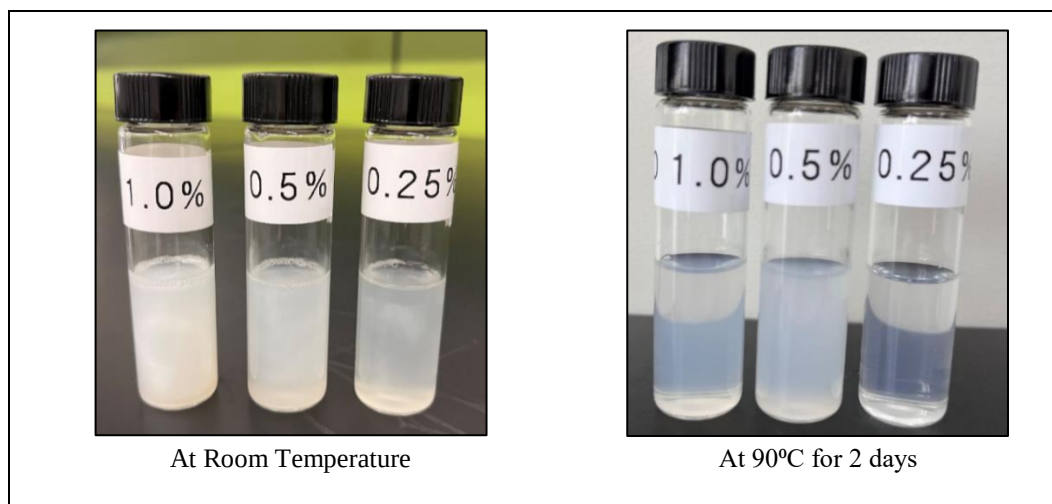


Figure 44: Aqueous stability of 0.25, 0.5, and 1.0 wt% of ARM-5660

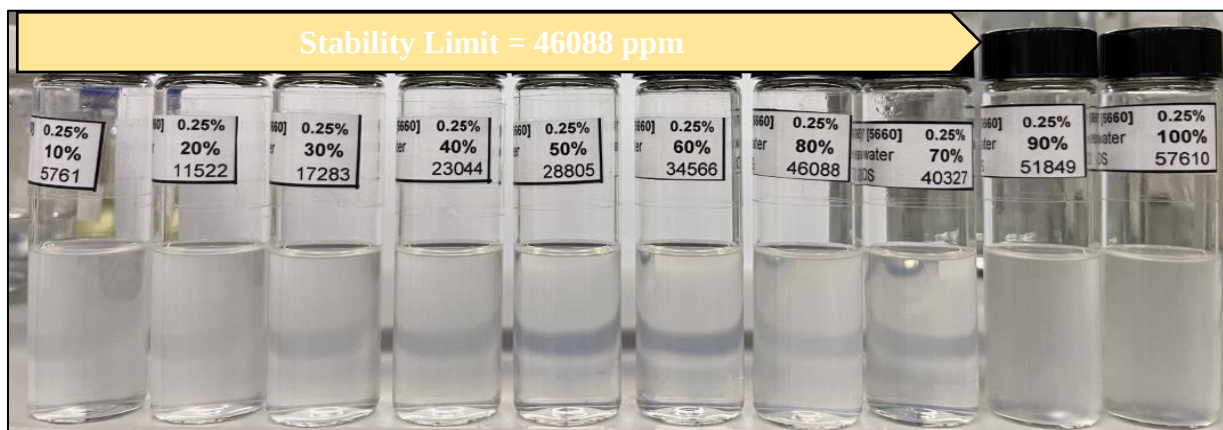


Figure 45: Aqueous stability of 0.25 wt% ARM-5660

Table 14: Summary of the salinity scans using 0.25 wt% ARM-5660

Scan	Crude Oil	Surfactant Conc. (wt%)	Min. Salinity		Max. Salinity		Comments
			% SW	(ppm)	% SW	(ppm)	
LS #7	LS	0.25	7.5	4321	30	17283	No Microemulsion except type I at higher salinity, 11283 ppm (Figure 46)
LS #8	LS	0.25	25	14403	80	46088	Mostly Type II (Figure 47)
LS #8R	LS	0.25	25	14403	80	46088	Mostly Type II (Figure 48)
LS #9	LS	0.2	10	5761	120	69132	No ME (Figure 49)
LS #10	LS	0.15	10	5761	120	69132	No ME (Figure 50)
LS #16	LS	0.25	7.5	4321	30	17283	Type III range at 11522 – 17283 ppm (Figure 51)



Figure 46: Salinity scans using 0.25 wt% ARM-5660



Figure 47: Salinity scans using 0.25 wt% ARM-5660



Figure 48: Repeated salinity scans using 0.25 wt% ARM-5660



Figure 49: Repeated salinity scans using 0.20 wt% ARM-5660



Figure 50: Repeated salinity scans using 0.15 wt% ARM-5660



Figure 51: Repeated salinity scans using 0.25 wt% ARM-5660

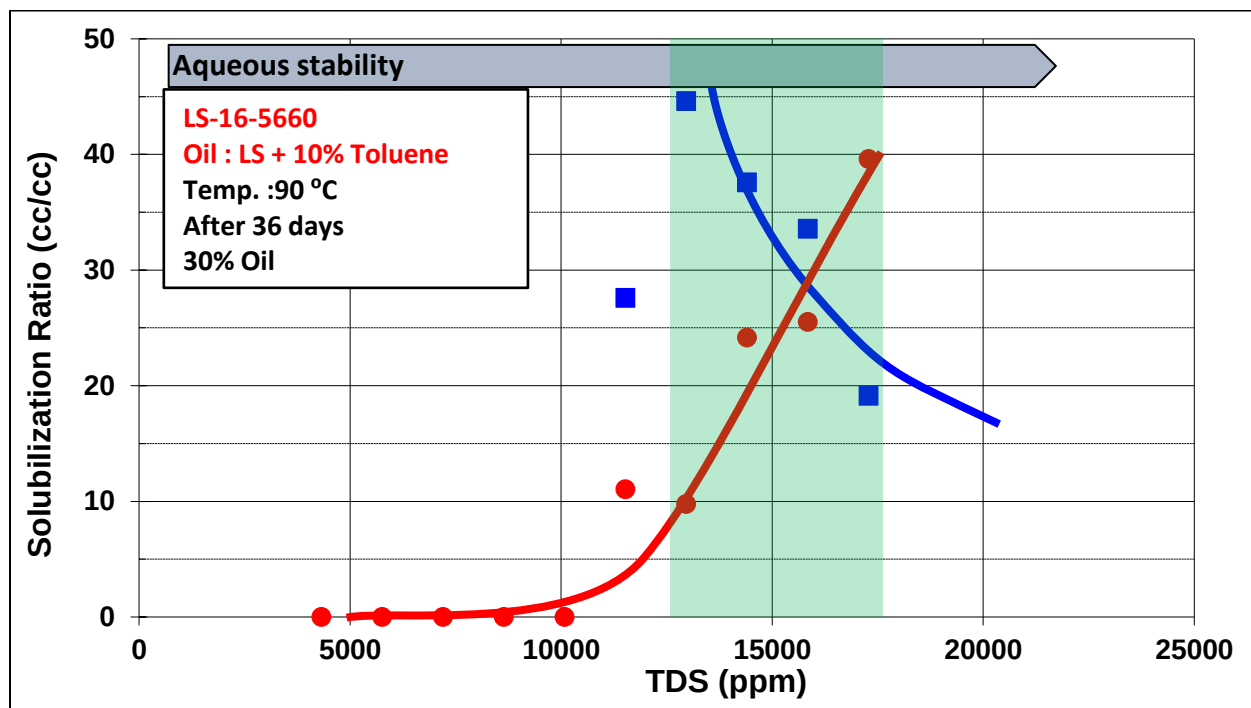


Figure 52: Solubilization ratio vs. Salinity for experiment LS -16.

To calculate the effect of absence of toluene in the composition of dead oil, the LS -16 experiment has been repeated with pure dead crude oil. As a result, it can be seen from the **Figure 53**, no Type III microemulsion has been obtained without addition of toluene in the dead oil.



Figure 53: Repeated salinity scans using 0.25 wt% ARM-5660

6.2 HPHT Phase Behavior

After determination of optimum surfactant formulation indicating Type III microemulsion as indicated in the **Figure 51**, the same surfactant formulation range has been tested with the live-oil that was prepared using PVT 300/700 HPHT Cell (**Figure 28**) at different GOR to evaluate its impact on the microemulsion PB. The total formulation volume was equal to 10 ml, 3ml of which was filled with live-oil and the remaining 7 ml was occupied by the surfactant. The experiments have been carried out at three different pressure values to

assess the pressure effect – 2500 psi, 3000 psi, 3500 psi. The results from experiments will be discussed in this section. The optimum salinity range is between 11522 ppm and 17283 ppm.

The initial set of experiments started with the live-oil containing GOR = 280 SCF/STB. First HP Phase Behavior experiment has been executed at constant pressure 2500 psi and then sequentially increased up to 3000 psi and 3500 psi and constant temperature 90°C. All the pictures are taken once the system was equilibrated.

Table 15: Experiment #1

GOR, scf/stb	280
Pressure, psi	2500
Temperature, °C	90

This experiment has been conducted in the conditions presented above. Five surfactant formulations with varying salinity levels have been filled in the High-Pressure Sapphire cells. The according salinity levels and cell numbers can be described as follows: Cell#1 – 11522 ppm; Cell#2 – 12962 ppm; Cell#3 – 14403 ppm; Cell#4 – 15843 ppm; Cell#5 – 17283 ppm.

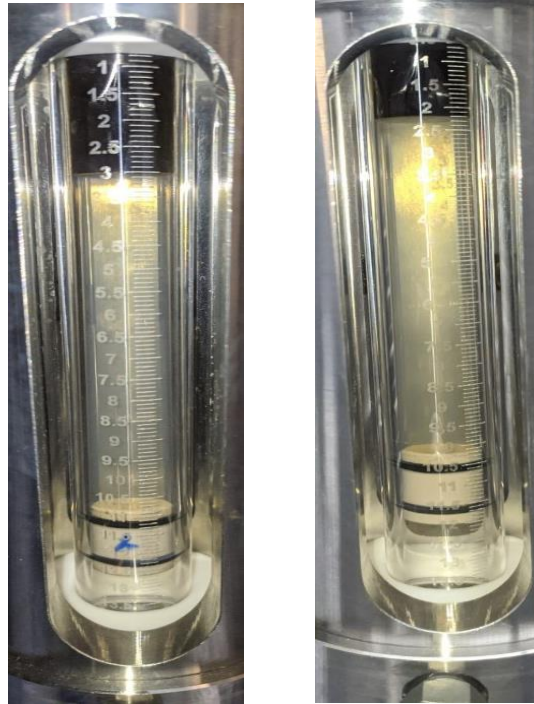


Figure 54: 11522 and 12962 ppm, GOR 280, P = 2500 psi, T = 90°C.

From the Figure xx it can be seen that at with pressurizing the system containing live-crude with 2500 psi the microemulsion is not observed at lower pressure levels, despite the fact that at atmospheric pressure and in the absence of a gas inside the crude during salinity screening experiments microemulsion has been obtained.

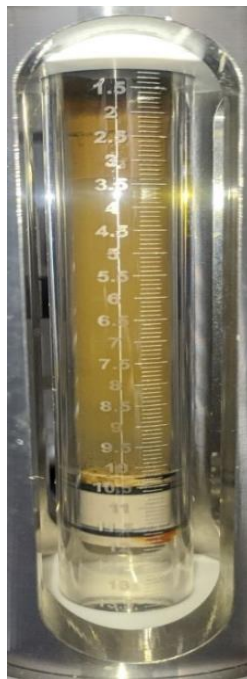


Figure 55: 14403 ppm, GOR 280, P = 2500 psi, T = 90°C.

On the other hand, the microemulsion generation has started and has been reported in the Cell#3. It can be deduced from this result that with increasing pressure the ME Phase Behavior shifts toward the Type I as agreed in the literature. In other words, with increase of pressure, the tendency of the oil to be solubilized in the surfactant enhances. It can be understood from the fact that microemulsion has been formed only at higher salinity level. Additionally, regarding the effect of gas presence in the dead crude, it can be easily observed that live-crude-oil contributes to better ME formation which means that in this case, the interfacial tension between water and oil in the reservoir would be much lower than in case of dead oil while using the relevant surfactant formulation.



Figure 56: 15843 and 17283 ppm, GOR 280, P = 2500 psi, T = 90°C.

Despite the fact that, during the initial stages of the experiment the microemulsion has been obtained in the 14403 and 15843 ppm with the highest salinity level, it was reduced after some period of time. Hence, it can be deduced from this experiment, with the increase of pressure the systems shifted towards Type I, while with the presence of gas the microemulsion quantity has increased in the Cell#3 where the optimum salinity has been reported.

Table 16: Experiment #2

GOR, scf/stb	280
Pressure, psi	3000
Temperature, °C	90

In the second part, the pressure in all the cells has been raised to 3000 psi. Generally, with increasing pressure to the system from 2500 psi to 3000 psi the tendency of the surfactant formulation to be dissolved in the middle phase increases in the Cell#3 and Cell#4.

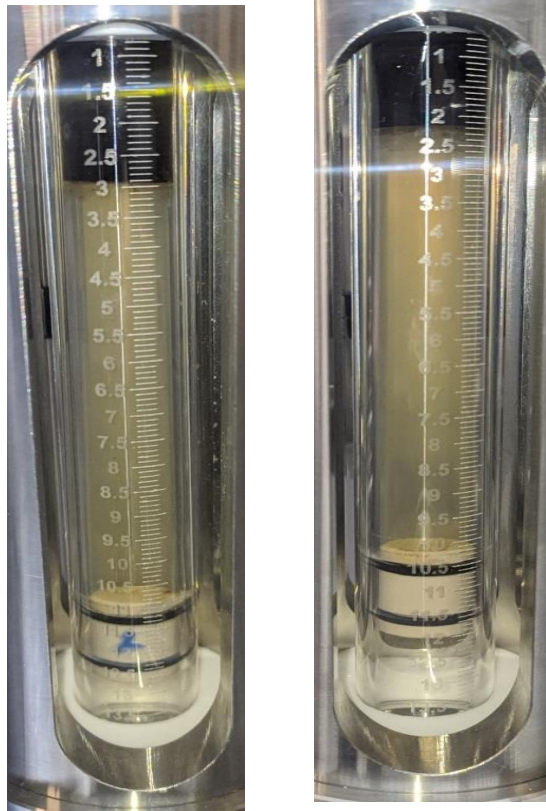


Figure 57: 11522 and 12962 ppm, GOR 280, P = 3000 psi, T = 90°C.

Similar to the result with 2500 psi pressure, the microemulsion has not been observed in the Cell#1 and 12962 ppm with increasing pressure up to 3000 psi. In fact, no changes in the interface between oleic and aqueous phases have been deduced.



Figure 58: 14403 ppm GOR 280, P = 3000 psi, T = 90°C.

As mentioned previously, the surfactant solubilization in the middle phase increased with the increase of pressure. It can be visible from the comparison of the 14403 and 15843 ppm during the experiment at 2500 and 3000 psi. While, in the **Figure 55** while the separate surfactant volume is equal to approximately to 10.2 ml, these numbers are different in the **Figure 58**. This volume reduced to around 9 ml in case of 14403 ppm and in contrast, in the 15843 ppm all the surfactant was pushed towards upper middle phase.

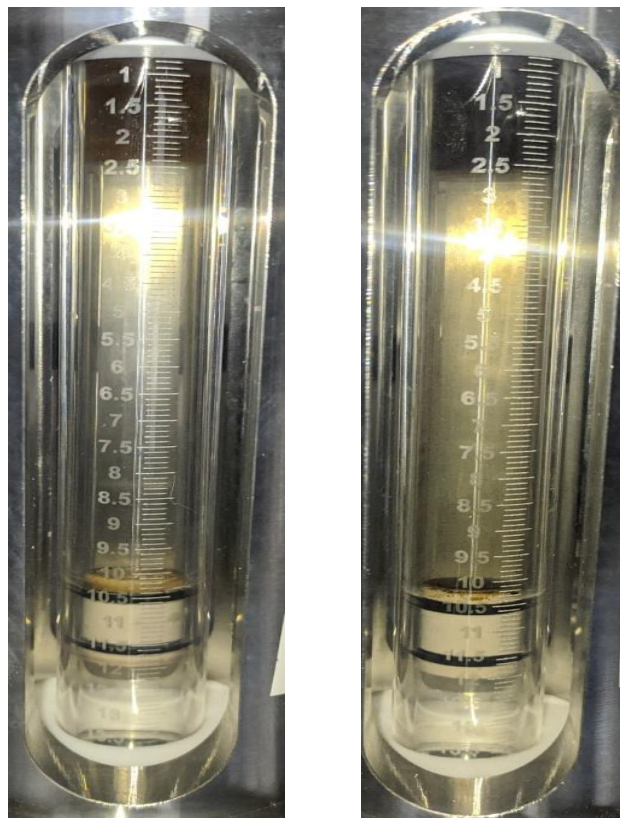


Figure 59: 15843 and 17283 ppm GOR 280, P = 3000 psi, T = 90°C.

As with the 17283 ppm, no substantial effects of increasing pressure have been deducted. The single influence is that the minor microemulsion volume that has been reported in the **Figure 56** disappeared as soon as pressure was enhanced up to 3000 psi in the cell.

Table 17: Experiment #3

GOR, scf/stb	280
Pressure, psi	3500
Temperature, °C	90

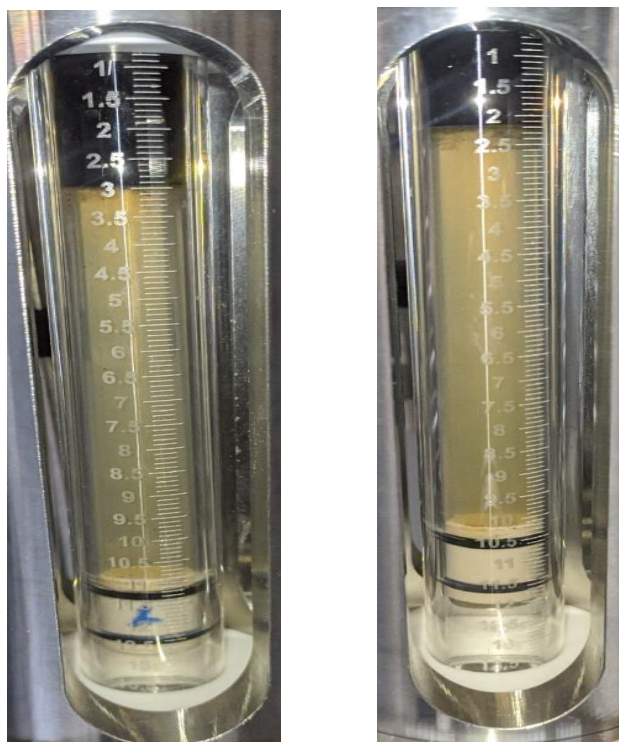


Figure 60: 11522 and 12962 ppm GOR 280, P = 3500 psi, T = 90°C.

Similar to the result with 2500 psi and 3000 psi pressure, the microemulsion has not been observed in the 11522 and 12962 ppm with increasing pressure up to 3500 psi. In fact, no changes in the interface between oleic and aqueous phases have been deduced.



Figure 61: 14403 ppm GOR 280, P = 3500 psi, T = 90°C.

Similar to the effect that has been observed from the increasing pressure from 2500 psi to 3000 psi, in this case as well, with pressure boost up to 3500 psi, more surfactant volume has been pushed towards middle phase and therefore it can be seen from the Cell#3 that the total surfactant volume reduced to almost 8.3 ml from 9 ml at 3000 psi and 10.3ml at 2500 psi. In other words, it can be deduced that with increasing pressure the solubilization ratio of water in the microemulsion increased. However, the impact of pressure on optimal salinity has been observed as negligible.

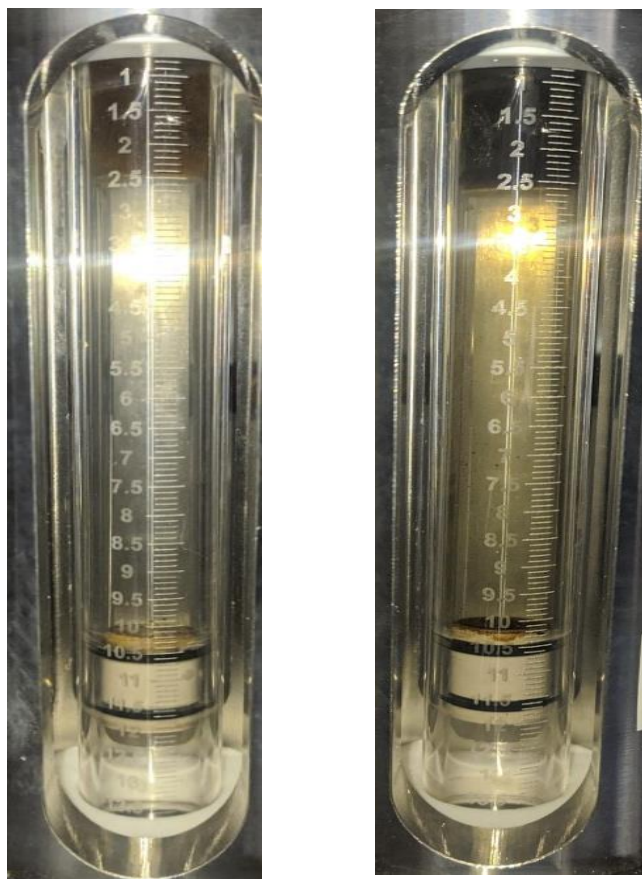


Figure 62: 15843 and 17283 ppm GOR 280, P = 3500 psi, T = 90°C.

No significant effects of increasing pressure have been reported for the 11522 and 12962 ppm. It can be seen from the comparison with the **Figure 59** that the interfaces between oleic and aqueous phases have not changed.

Table 18: Experiment #4

GOR, scf/stb	180
Pressure, psi	2500
Temperature, °C	90

The next experiment has been conducted with Live Oil GOR 180 in order to study the impact of GOR on optimum parameters of microemulsion phase behavior. The same set of surfactant formulations has been set up in the oven at reservoir temperature 90°C and 2500 psi for the first experiment. The results are discussed in the following section.



Figure 63: 11522 ppm GOR 180, P = 2500 psi, T = 90°C.

Similar to the experiment with high GOR 280, it has been observed again with low GOR 180 at the same constant pressure 2500 psi, the microemulsion generation has not been confirmed.

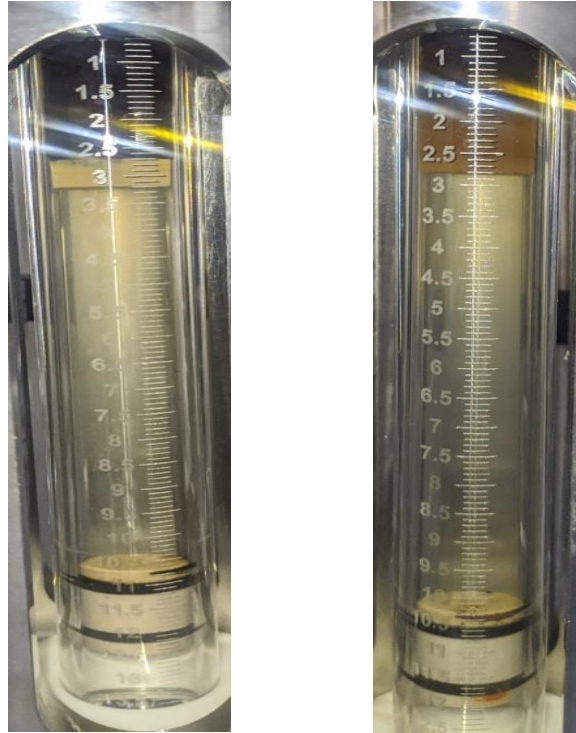


Figure 64: 12962 and 14403 ppm GOR 180, P = 2500 psi, T = 90°C.



Figure 65: 15843 and 17283 ppm GOR 180, P = 2500 psi, T = 90°C.

Table 19: Experiment #5

GOR, scf/stb	180
Pressure, psi	3000
Temperature, °C	90



Figure 66: 11522 and 12962 ppm GOR 180, P = 3000 psi, T = 90°C.

With increasing pressure from 2500 psi to 3000 psi, the formulation in the cell with 11522 ppm salinity remained unchanged with no microemulsion generation. However, as can be seen from the **Figure 66**, water solubilization in the surfactant has increased in the cell with 12962 ppm salinity. For comparison, the same behavior has not been observed in the experiment with GOR 280 SCF/STB at the same salinity level.



Figure 67: 14403 and 15843 ppm GOR 180, P = 3000 psi, T = 90°C.

The similar behavior has been reported in the formulations with 14403 and 15843 ppm salinity. As can be seen from the **Figure 67** the cell with 14403 ppm salinity which was reported as optimum in the experiment with 280 GOR did not show any microemulsion formation with decreasing GOR value to 180 SCF/STB. Nevertheless, the cell with 15843 ppm salinity showed similar to the 12962-salinity level formulation, which is the enhancement of water solubilization ratio.



Figure 68: 17283 ppm GOR 180, P = 3000 psi, T = 90°C.

The Cell with 17283 ppm salinity has been reported as optimum from the experiment at 2500 psi. However, with increasing pressure, the water solubilization ratio increased dramatically, while the opposite happened to oil solubilization ratio. This behavior confirms the effect of pressure on solubilization ratio together with the result from 280 GOR experiment.

Table 20: Experiment #6

GOR, scf/stb	180
Pressure, psi	3500
Temperature, °C	90

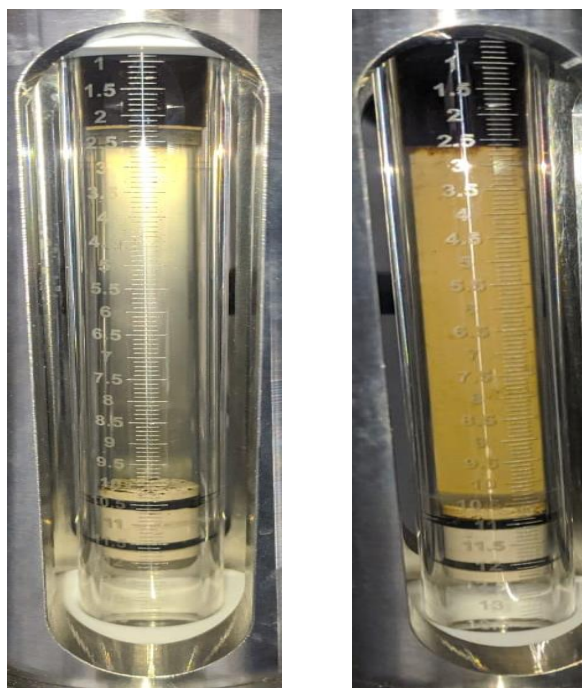


Figure 69: 11522 and 12962 ppm GOR 180, $P = 3500$ psi, $T = 90^{\circ}\text{C}$.

With increasing pressure from 3000 psi to 3500 psi, the formulation in the cell with 11522 ppm salinity remained unchanged with no microemulsion generation. However, as can be seen from the **Figure 69**, water solubilization in the surfactant has increased in the cell with 12962 ppm salinity. For comparison, the same behavior has not been observed in the experiment with GOR 280 SCF/STB at the same salinity level.

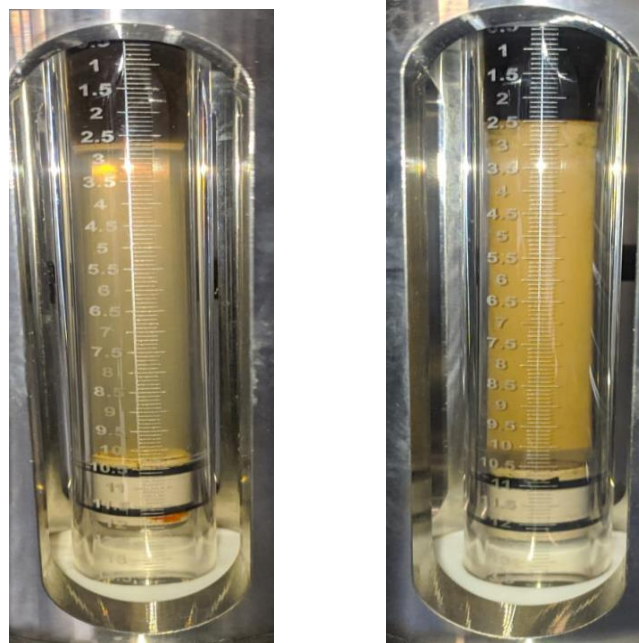


Figure 70: 14403 and 15843 ppm GOR 180, P = 3500 psi, T = 90°C.

The similar behavior has been reported in the formulations with 14403 and 15843 ppm salinity. As can be seen from the **Figure 70** the cell with 14403 ppm salinity which was reported as optimum in the experiment with 280 GOR did not show any microemulsion formation with decreasing GOR value to 180 SCF/STB. Nevertheless, the cell with 15843 ppm salinity showed similar to the 12962-salinity level formulation, which is the enhancement of water solubilization ratio.

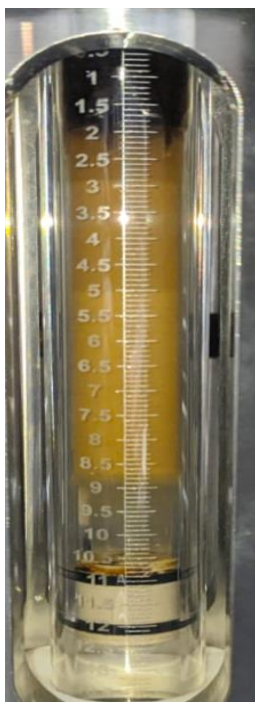


Figure 71: 17283 ppm GOR 180, P = 3500 psi, T = 90°C.

The Cell with 17283 ppm salinity has been reported as optimum from the experiment at 2500 psi. However, with increasing pressure, the water solubilization ratio increased dramatically, while the opposite happened to oil solubilization ratio. This behavior confirms the effect of pressure on solubilization ratio together with the result from 280 GOR experiment. The plot of effect of pressure at the experiment with 180 GOR is presented in the **Figure 78**.

Table 21: Experiment #7

GOR, scf/stb	380
Pressure, psi	3000
Temperature, °C	90

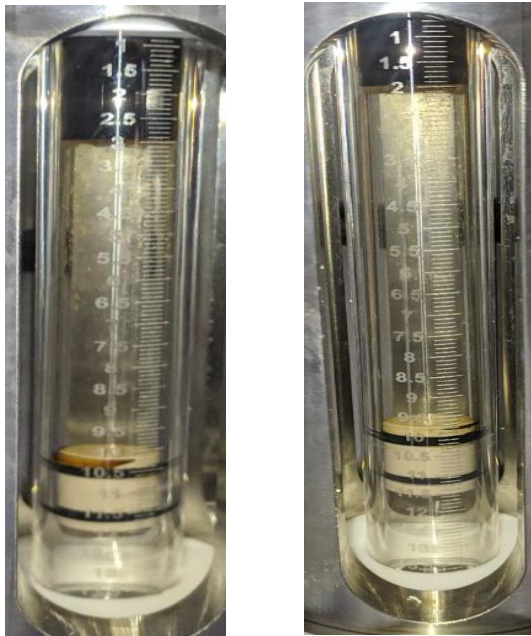


Figure 72: 11522 and 12962 ppm GOR 380, P = 3000 psi, T = 90°C.



Figure 73: 14403 and 15843 ppm GOR 380, P = 3000 psi, T = 90°C.



Figure 74: 17283 ppm GOR 380, P = 3000 psi, T = 90°C.

After completion of the HPHT Phase Behavior experiments with Live-Crudes containing GOR 180 scf/stb and 280 scf/stb, the next Live Crude containing GOR 380 scf/stb has been prepared in the PVT 300/700 cell for the last set of experiments at high pressure. During the GOR 380 Live Oil preparation procedure it has been deduced that minimum bubble point pressure at which total volume of methane is solubilized in the dead crude was equal to 3000 psi, even though it was 2500 psi for the experiments with lower GOR values. For this reason, the set of experiments with GOR 380 Live Crude has been executed at three different pressure levels: 3000 psi, 3500 psi, and 4000 psi in order to investigate the effect of pressure. The first experiment has been commenced at 3000 psi and the results are presented in the **Figure 72**, **Figure 73**, and **Figure 74**. From the aforementioned results it is visible that no microemulsion has been observed at any salinity level from 11522 ppm to 17283 ppm. As agreed with the previous results, it can also be concluded here that with

increasing GOR, the optimum salinity range shrinks or salinity range at which microemulsion generation occurs decreases.

Table 22: Experiment #8

GOR, scf/stb	380
Pressure, psi	3500
Temperature, °C	90

Table 23: Experiment #9

GOR, scf/stb	380
Pressure, psi	4000
Temperature, °C	90

In the next experiments, the pressure on the system has been enhanced to 3500 psi and 4000 psi. However, as the optimum salinity was not obtained at the lower pressure of 3000 psi, the effect of pressure on the system was not deduced as no changes took place between the oleic and aqueous interfaces at all salinity levels. It is assumed that, due to the high GOR value (380 scf/stb) and corresponding high bubble point pressure (3000 psi), the system generates the optimum salinity at higher salinity levels that are not observed in this research. Hence, the effect of pressure on the system containing Live Crude with GOR 380 can be measured at the salinity levels higher than 17283 ppm.

6.3 Discussions and recommendations

As can be deduced from the results mentioned above, it can be noticed that in comparison with the results including the presence of Live Crude with GOR 280 at 2500 psi, the

microemulsion generation has occurred in a large salinity range. To illustrate, it can be seen that during the experiment with Live Oil 280 GOR the microemulsion was formed only in the 14403 ppm (**Figure 55**). However, after reduction of Live crude GOR to 180 scf/stb, it is visible that the range of microemulsion formation has extended. To illustrate, it can be noticed that from the **Figure 64** and **Figure 65** that the 11522 – 17283 ppm has shown a clear microemulsion.

The discussion of the results and the effects of GOR and Pressure can be continued by comparing the optimum parameters of microemulsion phase behavior between two experiments.

Firstly, the effect of GOR can be visible from the comparison of the results from experiments at 2500 psi, 90°C in the Cell#3 with the salinity of 14403 ppm which was reported as optimum salinity due to equal solubilization of water and oil (30.8). As can be seen from the **Figure 55** the solubilization ratio of water and oil is higher in when comparing it to the **Figure 64** where the optimum SR of oil and water decreased in the 14403 ppm with the optimum salinity. It can be visualized in the **Figure 75**.

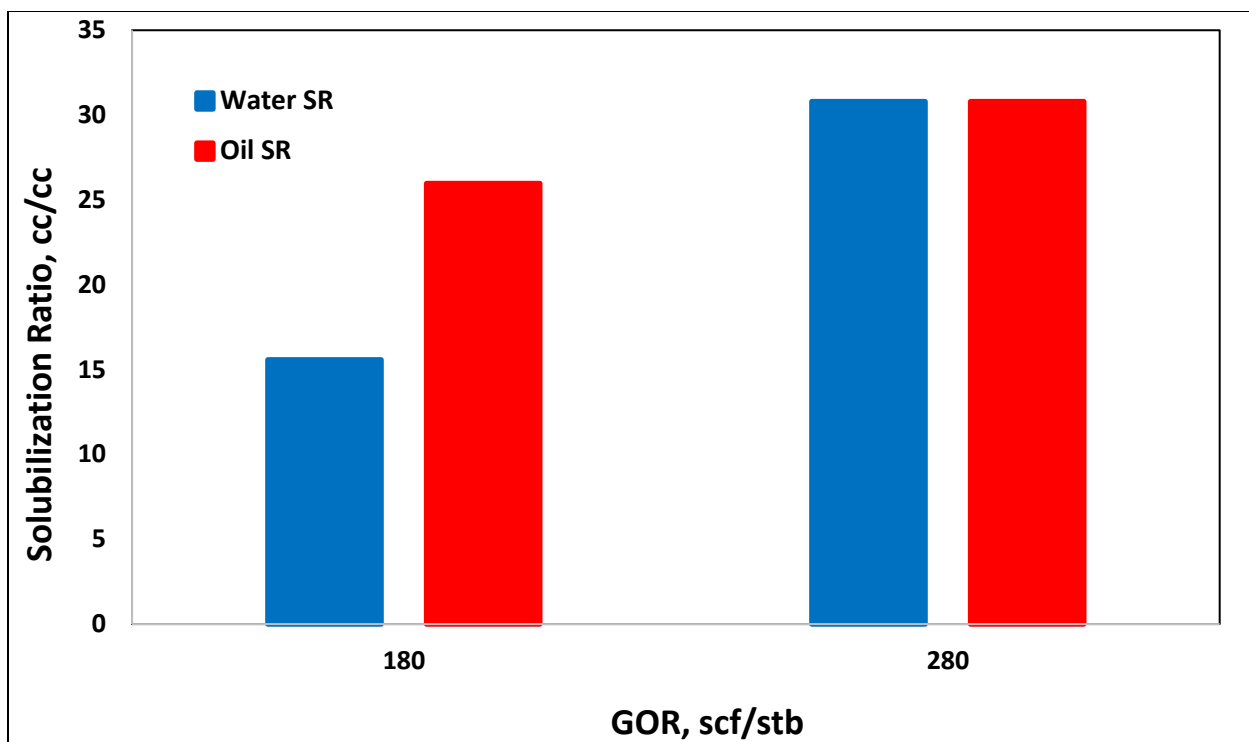


Figure 75: Optimum SR for GOR 180 and GOR 280 at 2500 psi, 90°C.

It can be deduced that at the constant pressure conditions of 2500 psi and temperature 90°C the optimum solubilization ratio decreased linearly for both oil and water solubilization ratios.

Additionally, it has been discussed that as an effect of decreasing GOR of Live Crude, the range of microemulsion generation has increased at 2500 psi. While only 14403 ppm has shown microemulsion in the experiment with GOR 280, the range from 11522 to 17283 ppm has shown clear microemulsion formation. It proves that with decreasing GOR, the tendency of surfactant formulation to create microemulsion at lower and higher salinity levels increases. Lastly, it was observed that with increasing GOR from 180 scf/stb to 280 scf/stb, the optimal salinity of ME Phase Behavior decreased from 17283 ppm to 14403 ppm (**Figure 76**). Nevertheless, as the GOR of the system increased to 380 scf/stb, no

microemulsion was observed at any salinity level, hence the optimum salinity was not determined.

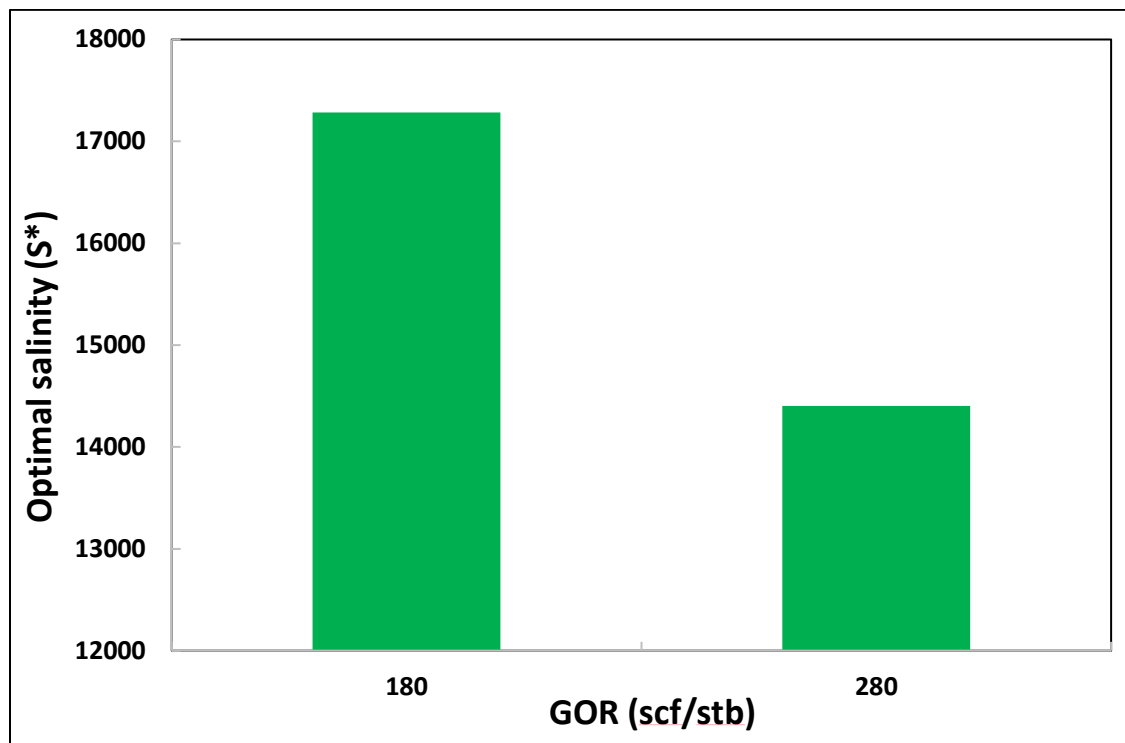


Figure 76: The optimal salinity of the system as a function of increasing GOR.

Secondly, the effect of pressure can be discussed by comparing one experiment at constant GOR 280 at constant pressure – 2500 psi and temperature 90°C. By comparing **Figure 55**, **Figure 58**, and **Figure 61** it can be concluded that with increasing pressure from 2500 psi to 3000 psi and 3500 psi the water solubilization ratio increased dramatically, while the opposite was true for oil solubilization ratio. It can be explained by the fact that; the presence of the gas inside crude oil contributes to the tendency of microemulsion to solubilize more water than oil at high pressures. From the comparison of the microemulsions at three different pressure levels, the **Figure 77** demonstrates the dramatic increase of water SR and reduction in SR of oil. The similar behavior has been observed at

the highest salinity 17283 ppm during experiment with GOR 180. This is demonstrated in the **Figure 78**.

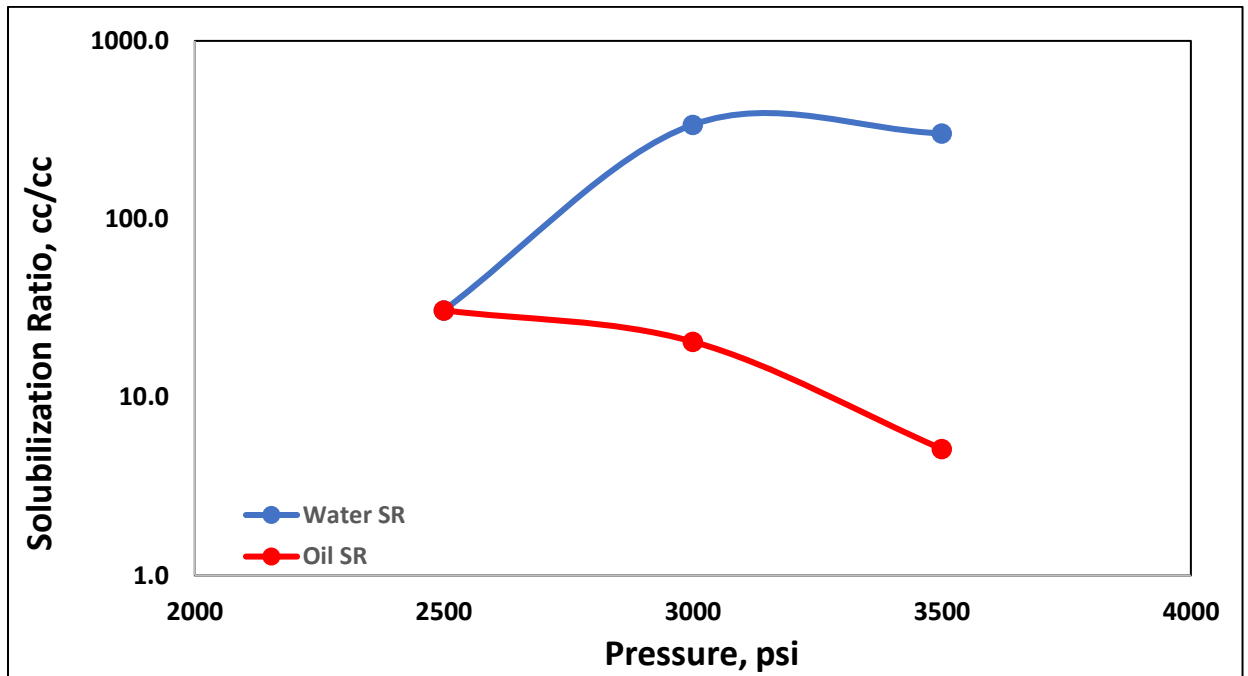


Figure 77: Water and Oil SR for GOR 280 at 2500 psi, 90°C.

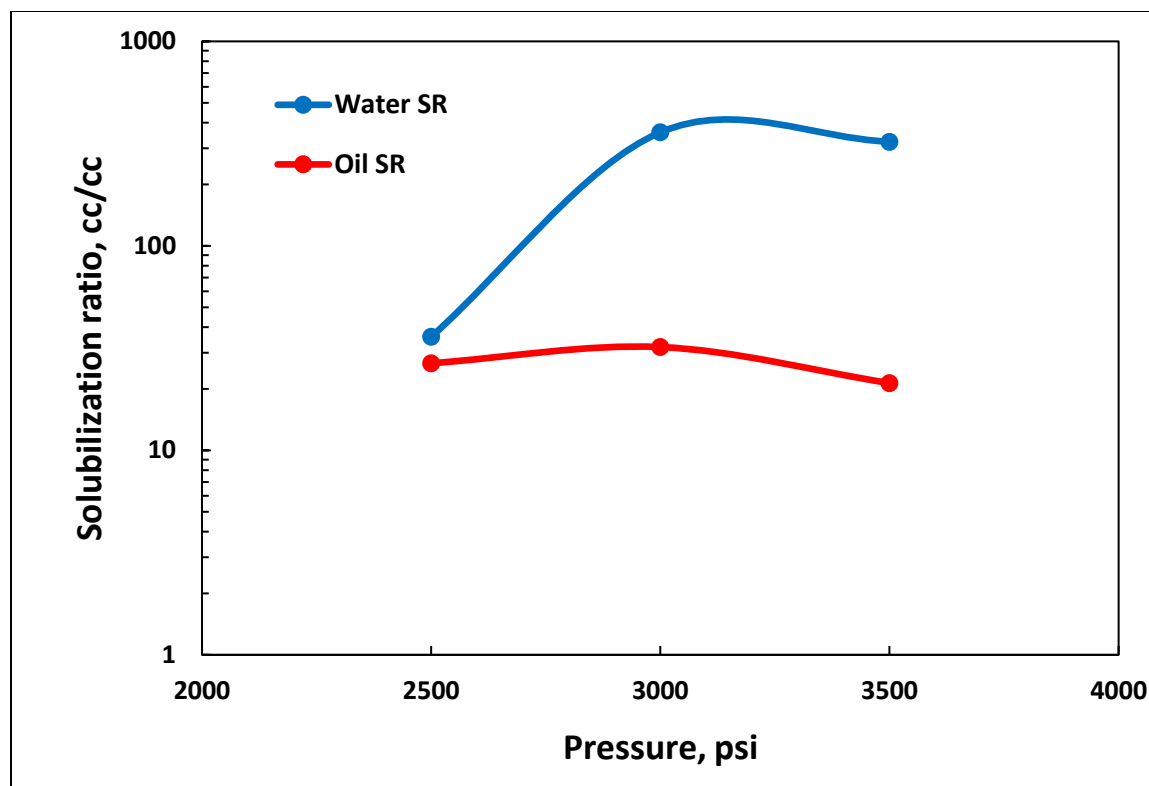


Figure 78: Water and Oil SR for GOR 180 at 2500 psi, 90°C.

This thesis focuses on the first stage of optimum surfactant formulation development – Phase behavior. However, there are multiple stages that can confirm efficiency of surfactant formulation and suitability for the use at the field scale. This work can be furthered to the next step of the optimum surfactant formulation design which involves core flooding experiments at high pressure and high temperature. Different salinity levels of the selected surfactant formulation can be used in order to evaluate the effect of Live Crude Oil at varying GOR conditions. Additionally, the influence of the properties of the crude oil can be investigated by using varying crudes. Moreover, the impact of mineralogy of the core sample on the efficiency of the oil recovery using optimum surfactant formulation is a promising way to conclude the suitability of the selected formulation for the use in an oil field EOR procedures.

CHAPTER 7

CONCLUSIONS

To sum up, multiple salinity screening experiments have been performed at reservoir temperature and atmospheric pressure in order to determine the optimum surfactant formulation at the optimum salinity range. Two types of surfactant blends with varying concentrations have been prepared and used for ambient pressure phase behavior tests. After numerous experiments the optimum salinity has been identified in the Phase Behavior with crude oil and optimum surfactant formulation diluted with 10% toluene in the range of 20% - 30%, 11522 – 17283 ppm correspondingly. Upon determination of the optimum surfactant formulation range, the followings have been concluded:

1. Salinity screening has been conducted without any presence of hydrocarbons and with the addition of 10% toluene in the dead oil to obtain a surrogated crude. It was concluded that surrogated crude oil contributes to better ME generation and imitates the reservoir oil viscosity.
2. From the HP Phase Behavior experiments with five optimum surfactant formulations, it was reported that increasing GOR at a constant pressure and temperature contributes to the increase in optimum SR and reduction in optimal salinity.
3. The pressure enhancement at a fixed GOR of Live-Crude-Oil in the surfactant formulations has a negligible effect on the changes in optimal salinity.

4. The increase of pressure on the system while keeping the same GOR influences on the dramatic increase of water SR in the microemulsion and the reduction of solubilization ratio of oil.
5. With increasing GOR, the tendency of surfactant formulation to generate microemulsion at lower and upper salinity levels decreases. To illustrate, at the GOR 180 scf/stb, the microemulsion has been generated in four salinity levels, whereas only in one surfactant formulation at a particular salinity level the microemulsion was reported with GOR 280 scf/stb. Additionally, while increasing GOR value up to 380 scf/stb no microemulsion has been observed at any salinity level.
6. At the GOR 380 scf/stb, the bubble point pressure necessary to dissolve total volume of methane in the dead crude increased from 2500 psi to 3000 psi and therefore the corresponding next experiments at higher pressure levels have been conducted at 3500 psi and 4000 psi. Nevertheless, as the microemulsion generation did not take place with this GOR value of Live Crude, the effect of pressure on the system with given salinity range was not visible. It is assumed that, at the GOR 380 scf/stb, the optimum salinity and corresponding effect of pressure can be determined at salinity levels higher than 17283 ppm.
7. The amount of microemulsion increases when using live crude for phase behavior tests, which means that the IFT between oil and water is much lower in this case than between the water and dead oil.

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