Journal of Engineering and Technological Sciences

Research Paper

Lessons Learned in Interfacial Tension Prediction Using a Mixture of Sulfonate- and Ethoxylate-based Surfactants in a Waxy Oil-brine System

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Abstract

The chemical-enhanced oil recovery (CEOR) method is applied to change reservoir rock or fluid characteristics by injecting alkaline, surfactant, and polymer or a combination of two or three of the compounds. Surfactant flooding improves oil recovery by reducing the interfacial tension between oil and water. Selecting reservoir surfactants, especially microemulsions, requires careful screening. This study predicted waxy oil system interfacial tension using surfactant mixtures at below- and above-optimum salinity. To predict the interfacial tension, microemulsion types, HLB, ideal salinity, and HLD were used. The study predicted oil-surfactant-water interfacial tension using SAE, FEO, and their mixtures. We improved the Huh equation by adding a fitting parameter, β, to accommodate the transition from type III to type II microemulsions as salinity increases. With increasing salinity, anionic surfactant's hydrophilic-hydrophobic interactions change, affecting the C_{H_o} values and surfactant layer thickness. This study improved hydrophilic-lipophilic deviation (HLDN) by establishing a fixed interval for nonionic surfactants. Van der Waals attraction, C_{H_o} values and interface surfactant layer thickness are connected, reflecting the fact that lower C_{H_o} values reduce interfacial tension better. This study also found that surfactant packing at the oil-water interface increases the order of the oil-solution ratio and the microemulsion values with polarity.

Keywords: *hydrophilic-lipophilic deviation; interfacial tension; surfactant; surfactant mixture; waxy oil.*

Introduction

There are several chemical processes involved in enhanced oil recovery (EOR); most of them are based on alkaline (A), surfactant (S), and polymer (P). These processes have been used massively to alter reservoir fluid characteristics, such as the mobility ratio and interfacial tension (IFT). Surfactant flooding significantly improves oil recovery by reducing the interfacial tension between displacing fluid and displaced fluid [1]. Screening surfactant procedures are required to find a surfactant compatible with the reservoir parameters. It has been observed that the formation of microemulsions plays a significant role in reducing interfacial tension. Many studies have predicted interfacial tension based on microemulsion types, hydrophilic-lipophilic balance values (HLB) [2-4], optimum salinity and microemulsion [5,6], the hydrophilic-lipophilic difference (HLD) [7,8], and the natural curvature of the water/oil surfactant layer [9].

Winsor (1954) [10] proposed that the natural curvature is related to surfactant lipophile-to-oil interaction energy (E_{lo}) with hydrophile-to-water interaction energy (E_{hw}). The surfactant layer characteristic curvatures tend to produce oil drops in water when (E_{lo}/E_{hw}) << 1; this microemulsion (lower-phase) has water as a continuous phase and surplus oil. When a water drop occurs in oil, the upper-phase microemulsion contains surplus water when the ratio of (E_{lo}/E_{hw}) >> 1. As the ratio of E_{lo}/E_{hw} » 1, the spherical shape of the oil drop may not be maintained; identifying the continuous and dispersed phases becomes ever more complex. No theory

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ISSN: 2337-5779

DOI: 10.5614/j.eng.technol.sci.2023.55.6.1

adequately characterizes the middle-phase microemulsion structure and equilibrium. Lamellar, bicontinuous, cylindrical tubes, and others have been observed [6]. Winsor in [11] introduced microemulsions types I, III, and II, the most often used types based on their interactions with the water or oil phase. The phase shifts from microemulsion Winsor type II to type III to type I generally occur with an increase in brine salinity [12-16], alkyl chain length of the surfactant [17-20], and the aromaticity of the oil [9,21], the addition of highly oil-soluble alcohol [8,15], and an increase in temperature [15,22,23]. In addition, the microemulsion Winsor type I phase shift can also be caused by adding highly oil-soluble alcohol (for nonionic surfactants). The changes can also occur when there is a decrease in the chain length of the oil, the number of hydrophilic groups in the surfactant, the addition of alcohol that is very soluble in water, or when the temperature decreases (for most ionic surfactants). This research on microemulsions provided one basis upon which Huh developed equations for predicting the interfacial tension values of microemulsions.

According to other research, the hydrophile-lipophile difference (HLD) may also be used to predict the type of surfactant that will generate a low interfacial tension value based on the characteristic curvatures of the surfactant, salinity, and temperature. Theoretically, HLD is a logarithmic representation of the R-ratio, so it is negative (or positive) if R is less than or higher than one [24-25]. The R-ratio is the tendency of the oil-water contact layer to become convex. However, the R-ratio is qualitative since how many oil and water molecules interact with a single surfactant molecule is unknown [25-26]. The HLD method has been widely used to synthesize particular surfactant structures to be compatible with a particular condition [27-31]. However, when the surfactant is a mixture of two or more surfactants, the HLD method is rarely used.

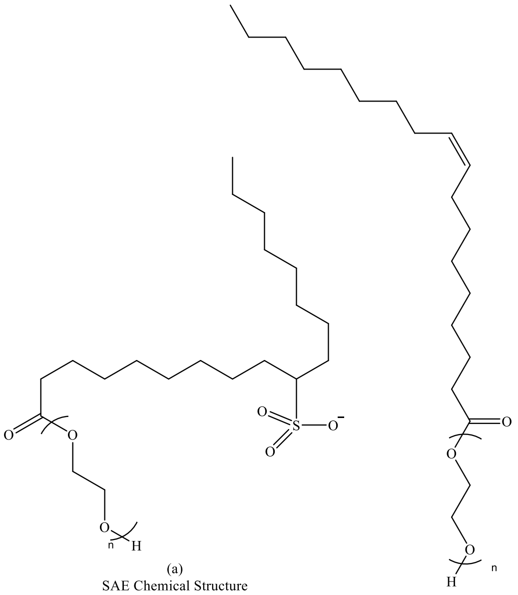
Huh [5] developed his equation by deriving three well-known forces during the microemulsion phase: van der Waals attraction, electrostatic repulsion, and entropic repulsion. He made several assumptions to determine the correlation between phase behavior and interfacial tension. Huh discovered that the oil solubilization ratio and the interfacial tension are related. Kurnia et al. [32] studied the Huh equation and discovered that the surfactant polarity influences the Huh equation constants (C_{HO} and *n*). The Huh equation underestimates the IFT value at high polarity and overestimates at low polarity, adjusting Huh's equation constants is necessary.

Furthermore, the highest oil recovery is not obtained when an individual interfacial tension – including the interfacial tension of microemulsion and oil (σ_{mo}) – is the lowest; it is obtained when the average interfacial tension of the system is the lowest. The system's average interfacial tension is the sum of the effects of each phase [1]. The study indicates that the Huh equation may forecast the interfacial tension value below optimum salinity by changing the constant values, C_{H_o} and *n*. However, these values cannot predict interfacial tension values above the optimum salinity. The C_{H_o} and *n* values could differ for a different surfactant but cannot predict the interfacial tension in a higher optimum salinity range [32-34]. Therefore, the main objective of the present research was to provide an approach to predict interfacial tension below and above the optimum salinity of the surfactant used in waxy oil when using surfactant mixtures. This study's approach should provide a more comprehensive surfactant screening procedure and probable injection situations during field application when the reservoir salinity changes.

Materials

This study used three mixtures of sulfonated alkyl ester (SAE) and fatty ester oleate (FEO) surfactants. The SAE and FEO were synthesized in the Bioorganic and Organic Synthesis laboratory of the Chemistry Study Program at Institut Teknologi Bandung [35–37]. As shown in Error! Reference source not found.**,** the SAE surfactant has two head groups (ethoxylate-based nonionic and sulfonate-based anionic), and the FEO surfactant is an ethoxylate-based nonionic surfactant [38]. The SAE and FEO surfactants were blended in a weight ratio of 1:1, 1:2, and 2:1 hereinafter referred to as 01A, 01B, and 01C, and used in all measurements. The optimum salinity of 01A, 01B, and 01C was 1.149, 0.913, and 1.637 mEq/mL, respectively, as measured using an oil sample that contained 36 %wt of wax content [32,37].

DOI: 10.5614/j.eng.technol.sci.2023.55.6.1



(a)
SAE Chemical Structure

(b)
FEO Chemical Structure

Figure 1 Chemical structure of the surfactants (a) SAE and (b) FEO.

Methods

It can be seen in Figure 1 that the SAE surfactant has two head groups (ethoxylate-based nonionic and sulfonate-based anionic) and that the FEO surfactant is an ethoxylate-based nonionic surfactant [38] when used as a single surfactant. This study included the laboratory data on the oil solution ratio and interfacial tension of 01A, 01B, and 01C, measured in brine salinity ranging from 0.171 to 3.422 mEq/mL, to represent the above- and below-optimum salinity of each surfactant mixture. Following the chart in Figure 2, these data were utilized to develop an approach for predicting the interfacial tension and improve the equation used in the prior research conducted by Kurnia [32] to estimate the interfacial tension value in the below-optimum salinity region.

The Huh equation [5] was used in this study to predict the value of interfacial tension from phase behavior data. The Huh equation was modified by adding important parameters that affect the interfacial tension changes in oil-surfactant-water systems, i.e., the HLDN [8,30,40-42] and EACN [15,43-46]. Theoretically, the EACN influences the microemulsion phase's intermolecular forces between the oil and the surfactant. Furthermore, the HLD value is influenced by the intermolecular force between the surfactant, oil, and water.

The interfacial tension prediction method proposed in this study improves the equation proposed by the previous study [32]. It is a generalized equation form in which the C_{H_o} value corresponds to the van der Waals force, indicating the interaction of the oil and brine layers and is assumed not to change significantly when there is a change in salinity. Moreover, it is assumed that the order n would change significantly when the salinity changes, as it is related to the oil solubilized ratio. In this study, the constant C_{H_o} was introduced as a parameter to adjust the value of n in the original Huh equation.

$$\sigma_{om} = \frac{c_{H_O}}{(V_{om}/V_{sm})^n} \tag{1}$$

with C_{H_o} is oil/microemulsion IFT, V_{om}/V_{sm} is an empirical constant usually determined experimentally, V_{om}/V_{sm} is the oil solubilization ratio.

Depending on the type of microemulsion formed, HLD may have positive, negative, or zero values. The HLD value for microemulsion Winsor type I (at below-optimum salinity) is negative. The HLD value for microemulsion Winsor type II (with higher salinity) is positive. If the HLD is zero, a Winsor type III (middle phase) microemulsion will form. Furthermore, the modified Huh equation was applied in two regions: below and above the optimum salinity. At below-optimum salinity, the microemulsion occurred in Winsor type I, which indicates that the interaction of the surfactant's hydrophilic group should have a significant impact. This is due to water molecules' low competition for hydration among hydrophilic groups and ions in the aqueous phase. Therefore, it can be assumed that the salinity or concentration of ions in the water significantly impacts the surfactant's performance when the salinity is in the below-optimum range. In the region above the optimum salinity, the hydrophilic groups in the surfactant are unable to compete to be hydrated by water molecules with the increasing concentration of ions in the water phase. Therefore, the interaction between the surfactant's hydrophobic groups and the oil should be more significant in the region above the optimum salinity. Therefore, to facilitate this phenomenon, this study introduces a fitting parameter, β, which indicates the transition from type III to type II microemulsion due to increased salinity and increased interaction of the surfactant's hydrophobic groups with the oil. In this case, the β value is defined as:

$$\beta = (0.13 \pm 0.03) + \frac{1}{EACN} \tag{2}$$

where the constant interval value (0.13 ± 0.03) was selected based on experimental results in normalizing hydrophilic-lipophilic deviation (HLDN) [47] for nonionic surfactants. The SAE surfactant contains two hydrophilic groups that can alter depending on the salinity. The SAE surfactants behave as nonionic at salinities above the optimum [38]; as a result, all surfactants used in this study above the optimum salinity behaved as nonionic surfactants.

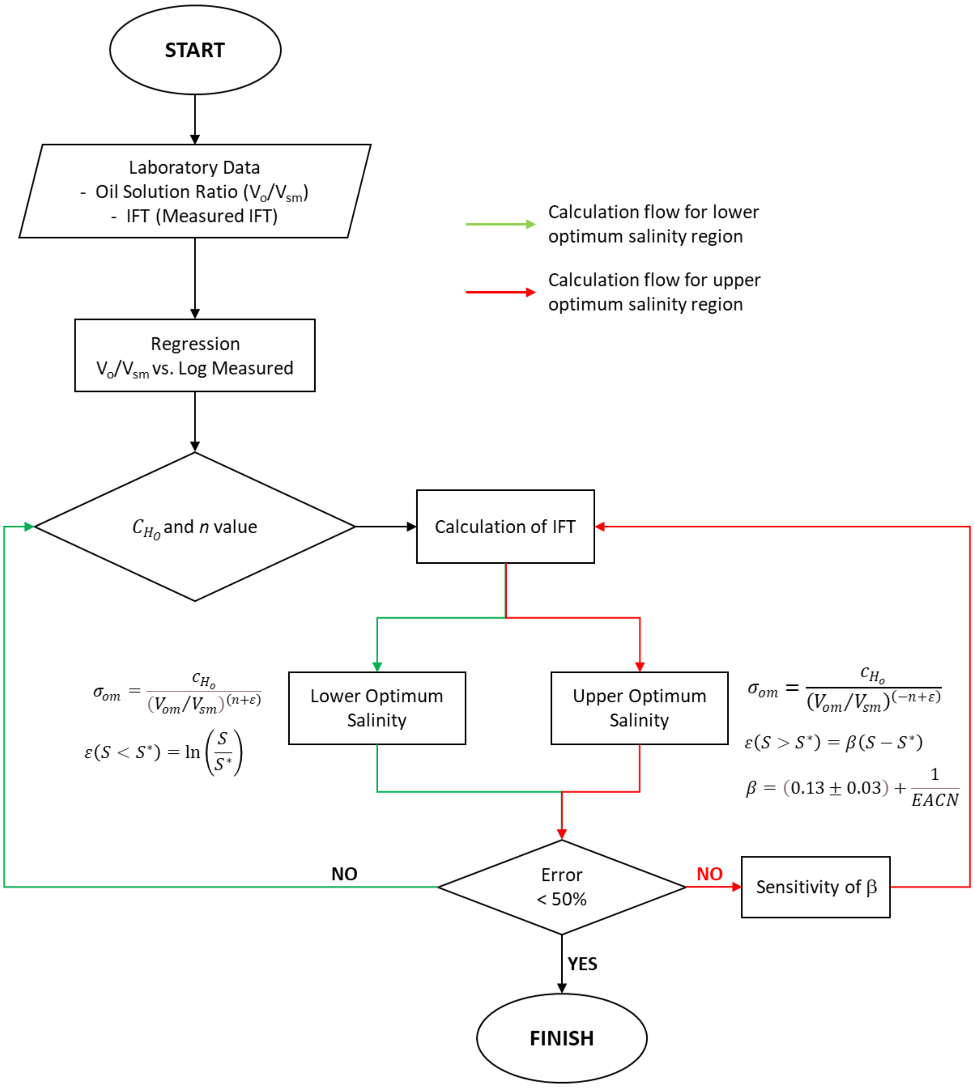


Figure 2 Research methodology to improve the Huh equation.

DOI: 10.5614/j.eng.technol.sci.2023.55.6.1

All constants introduced to Huh's equation were assumed to be temperature-insensitive and only the salinity parameters were changed. The proposed equation for predicting interfacial tension was then compared to experimental data measured under identical conditions without adding additives or solvents. The interfacial tension data were collected using a spinning drop tensiometer TX-500D at a temperature of 63 °C and all measurements were conducted twice. The constant ε for the region below and above the optimum salinity was written as follows:

$$\varepsilon(S < S^{*}) = \ln\left(\frac{S}{S^{*}}\right) \tag{3}$$

$$\varepsilon(S > S^{*}) = \beta(S - S^{*}) \tag{4}$$

The constant ε was added to the original Huh equation; hence, the proposed equation to predict the interfacial tension at below-optimum salinity is represented by Eq. (5) and at above-optimum salinity by Eq. (6).

$$\sigma_{om} = \frac{C_{H_O}}{(V_{om}/V_{sm})^{(n+\varepsilon)}} \tag{5}$$

$$\sigma_{om} = \frac{C_{H_O}}{(V_{om}/V_{sm})^{(-n+\varepsilon)}} \tag{6}$$

Results

Determination of C_{H_O} and *n* Values

Kurnia discovered in previous studies [32,39] that C_{H_O} and *n* in the Huh equation at optimum salinity does not always equal 0.3 and 2, respectively. Other studies also found a different value of C_{H_O}. Graciaa et al. [33] found that the C_H values was 0.48 ± 0.05 mN/m for alkylbenzene sulfonates and 0.34 ± 0.06 mN/m for ethoxylated alkylphenols. Barakat et al. [34] mention that C_H was 0.4 ± 0.15 mN/m for alkane and alpha-olefin sulfonates. For a further understanding of the correlation between the phase behavior data and the interfacial tension, the first step to be conducted in this study was to identify the values of $C_{H_O}$and *n*. C_{H_O} and *n* were calculated by regressing laboratory data on interfacial tension (IFT) to the oil solubilization ratio (V_{om}/V_{sm}). A collinear test point (from the IFT and V_{om}/V_{sm} values) was required to determine the C_{H_O} and *n* values used in the proposed equation. The *n* value of the divider was denoted as a negative number in the proposed equation, which can be seen in Equation (6), by following the profile of the graph of the oil solubilization ratio. The graph increases as the salinity increases, and the value of interfacial tension tends to be higher than that of the interfacial tension at optimum salinity (Figure 3). In this study, the proposed equation was compared to the results of the IFT calculation using the original Huh equation, the calculation using the values of C_{H_O} and *n* and the results of the laboratory IFT measurement.

Below the optimum salinity, the interaction of the hydrophilic group with the water phase was stronger than the interaction of the hydrophobic group with the oil phase. Variations in the thickness of the surfactant at the oil/water interface likely contributed to the different C_{H_O} values of each surfactant sample [32]. Theoretically, when the thickness of the surfactant layer is high, the C_{H_O} value will be low. In this study, we also discovered that the value of C_{H_O} is strongly related to the value of (*n* +ε) or (-*n* + ε), therefore, the value of C_{H_O} will vary according to the salinity conditions.

We found that when two surfactants were mixed at a particular ratio, the determination of C_{H_O} and *n* values would follow the surfactant with the higher ratio. This finding was also found in the previous study by Kurnia et al. [32] for the below-optimum salinity region. Moreover, if the surfactant ratio is equal, the surfactant with the higher polarity determines the C_{H_O} and *n* values. The oil solution ratio profile and interfacial tension indicate a few significant points, which are:

1. According to the Huh equation, IFT is higher at below-optimum salinity because oil per surfactant volume (V_{om}/V_{sm}) is low. Thus, electrostatic, and entropic repulsion dominate the layer interactions (brine/surfactant/oil). This increases the interfacial region per charge. In the above-optimum salinity region, oil layers swell and brine layers thin. The increasing ionic strength reduces the repulsive force of the brine layer. With oil domination, the van der Waals attraction will increase, causing oil-brine interaction

energy. Entropic and electrostatic repulsion will be weak. This influences the lipophilic chains of the surfactant molecules, causing low interfacial tension (IFT) in regions with higher optimum salinity. The ion-dipole interaction will weaken, reducing the ability for hydrophobic interaction with the oil.

2. In the below-optimum salinity region, where water solubilization predominates over oil solubilization, van der Waals attraction will be low, leading to a high C_{H_o} value, and the reverse for the higher optimum salinity region. At below-optimum salinity, which is dominated by water, hydrophilic-water interactions are strong, while hydrophobic-oil interactions are weak. This leads to a weakening of the van der Waals interaction, which will be strong when hydrophilic-oil interactions are strong since the van der Waals interaction is strong when hydrophilic-water interactions are strong. The C_{H_o} will be high if the van der Waals interaction is weak.

Calculation of Interfacial Tension Using the Developed Equation

The determined C_{H_o}, *n* and ε values were used to calculate the interfacial tension with the proposed equation. The IFT value can be accurately predicted within the optimum salinity range using the Huh equation. The calculation of IFT using the proposed equation was compared to the measured IFT. Using the developed equation, the average calculation error between the result and laboratory data was less than or equal to 20% at below- and above-optimum salinity.

Using the developed equation to predict the interfacial tension, the following summarizes several findings about the C_{H_o} and *n* values:

1. The C_{H_o} and *n* values in Kurnia et al. [32] were only proposed for the below-optimum and optimum salinity regions. However, with the improved modified equation, C_{H_o} and *n* values that could be utilized to predict the interfacial tension in the above-optimum salinity region were provided with an average calculation error equal to 20% (Figure 3).
2. As can be seen in Figure 4, the parameter C_{H_o} represents the concentration of the surfactant at the oil-water interface. The thickness of the surfactant layer at the interface can also affect the value of C_{H_o}. A thicker layer of surfactant molecules can result in a lower value of C_{H_o}, as the surfactant molecules can reduce the interfacial tension more effectively. The surfactant layer thickness is also affected by the molecular structure and the packing of surfactant molecules at the interface. For example, in general, surfactants with larger hydrophobic chains tend to form thicker surfactant layers at the interface. Since the 01C mixture has more FEO surfactant (higher hydrophobic chains), it can be said that the 01C mixture had a thicker layer of surfactant than the other mixtures. This also supports the results of the interfacial tension measurement in Figure 3, where the 01C mixture had a lower interfacial tension region than the other mixtures.
3. The *n* values follow the analysis where a higher polarity of the mixture will result in a higher *n,* as can be seen in Figure 5. The *n* value is related to the degree of surfactant packing at the oil-water interface. Specifically, *n* is related to the fractal dimension of the surfactant film at the interface, which is affected by the surfactant packing density and the surface coverage. The polarity of the surfactant can also affect the value of *n* indirectly by influencing the degree of surfactant packing at the interface. More polar surfactants tend to have a higher affinity for water and can form more tightly packed monolayers at the oil-water interface. This can lead to a higher value of *n* in the Huh equation, indicating a higher degree of surface coverage and surfactant film fractality. On the other hand, less polar surfactants tend to have a lower affinity for water and may form more loosely packed monolayers at the interface. This can result in a lower value of *n*, indicating a lower degree of surface coverage and surfactant film fractality. Overall, the polarity of the surfactant can indirectly affect the value of *n* by influencing the degree of surfactant packing at the oil-water interface.

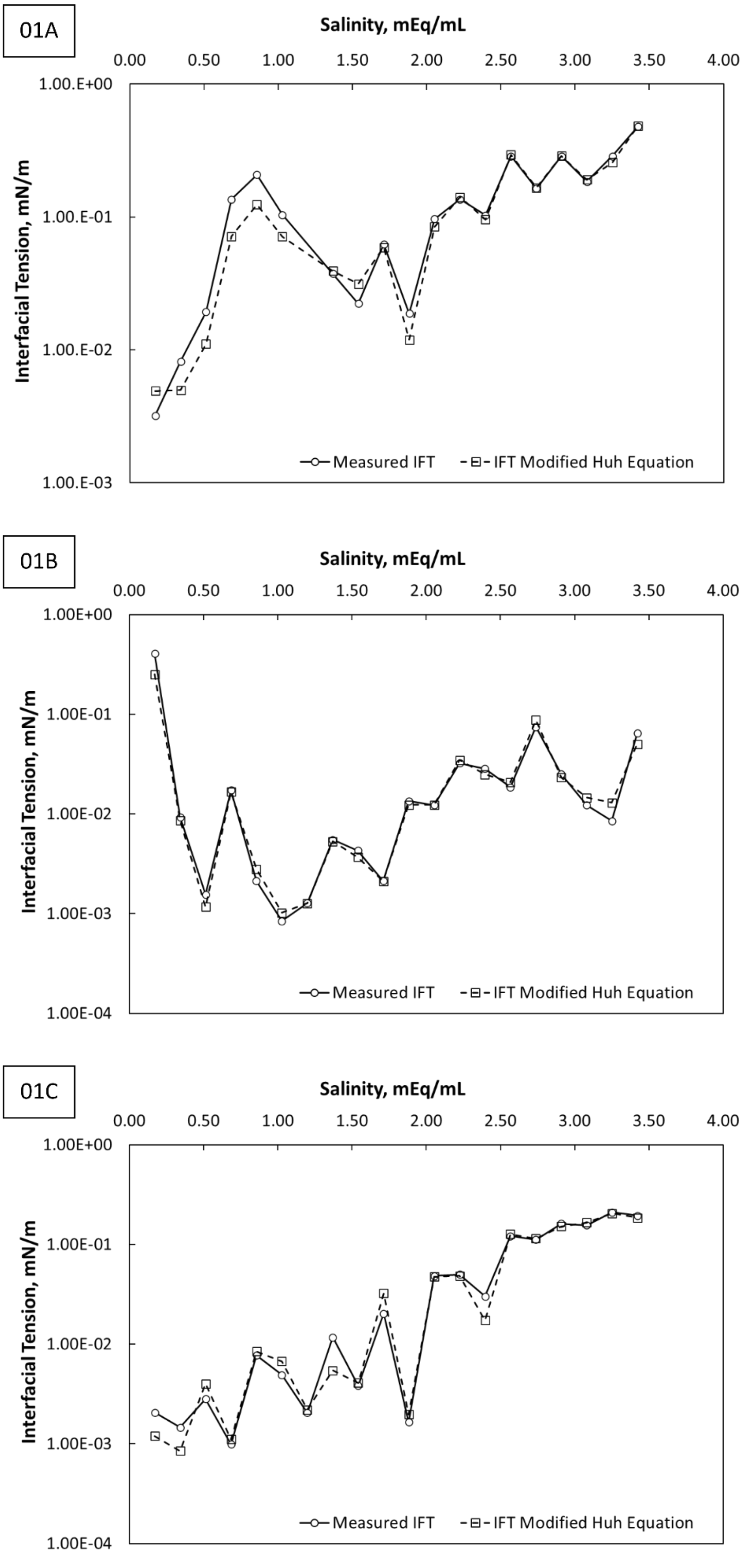


Figure 3 IFT comparison of surfactant mixtures, i.e. 01A, 01B and 01C.

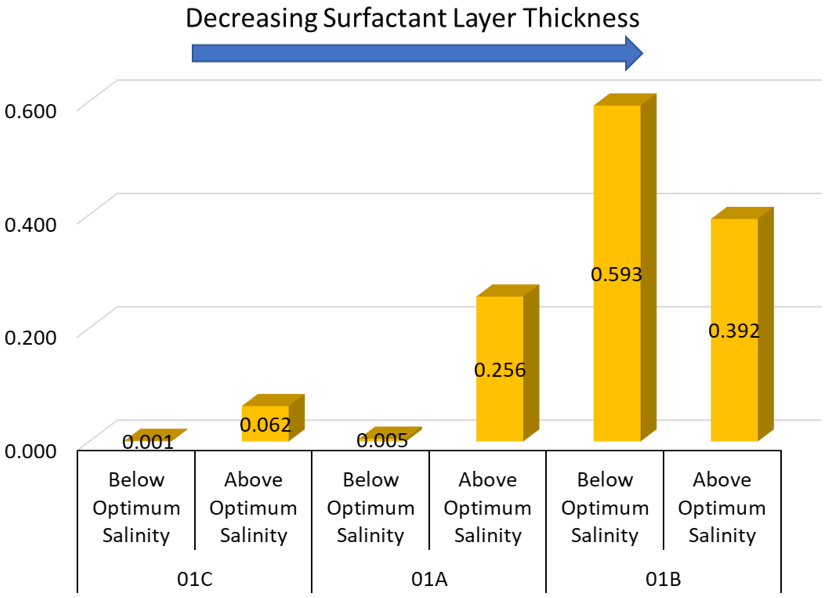


Figure 4 The C_{H_o} recommendation vs surfactant layer thickness.

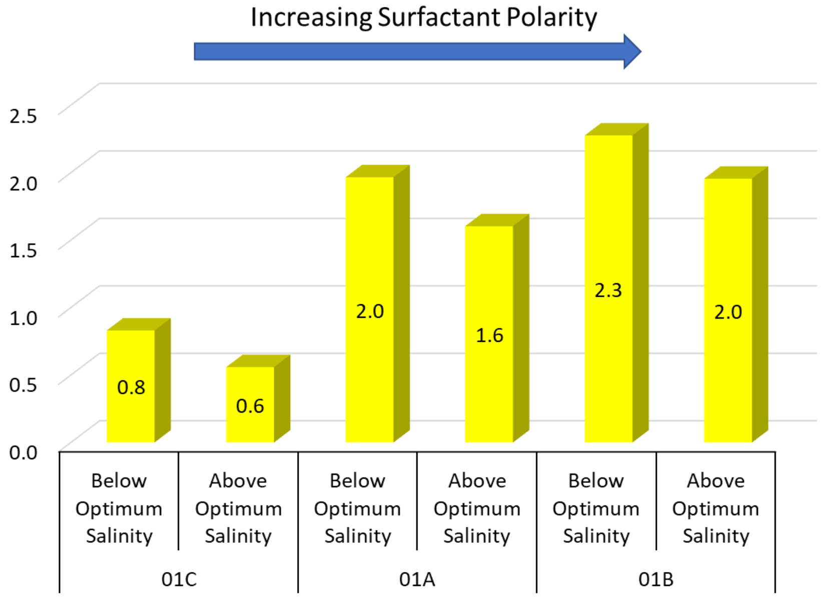


Figure 5 The *n* recommendation vs surfactant polarity.

4. The value of β for the region between the below-optimum and the optimum salinity equals 0.1, whereas it changes according to the $\beta = (0.13 \pm 0.03) + \frac{1}{EACN}$ rules for the above-optimum salinity region, as can be seen in Figure 6. At above-optimum salinity, EACNs are included in the determination of β because a higher salt concentration is required to achieve the optimal reduction in interfacial tension with a given surfactant. Generally, as the EACN of the oil phase increases, the optimum salinity of the surfactant required to achieve maximum performance in lowering interfacial tension also increases. This is because hydrophobic oils tend to have less affinity for water, which means that a higher salt concentration is required to promote their solubility and emulsification. In addition, the surfactant composition and structure can also affect the correlation between the optimum salinity and the EACN. For example, the type of headgroup and the length of the surfactant tail can affect the packing and solubility of the surfactant at the oil-water interface, which can in turn affect the optimum salinity. Overall, the correlation between optimum salinity and EACN

is related to the hydrophobicity of the oil phase and the solubility and packing of the surfactant at the oil-water interface.

5. In addition, according to Figure 6, the 01C mixture has more FEO surfactant with higher hydrophobicity than the SAE surfactant. As a result, the 01C mixture had a higher optimum salinity compared to the other surfactant mixtures (01A and 01B) as the hydrophobicity of surfactants can affect their optimum salinity in waxy oil-water systems. In general, surfactants with higher hydrophobicity tend to have higher optimum salinity in waxy oil-water systems. This is because waxy crude oils contain high amounts of long-chain hydrocarbons that tend to adsorb on the oil-water interface and create a hydrophobic layer. Surfactants with higher hydrophobicity can interact more strongly with this hydrophobic layer and displace it from the interface.

The results of this study have to be validated using reservoir fluid and surfactant samples that are more diverse. Nonetheless, it is expected that the results of this research will give further insight into the screening process in surfactant injection by considering the ratio of surfactant mixtures that can produce varied performances, how polarity influences surfactant performance, and optimum salinity. It is also important to note that the equation is an empirical correlation based on experimental data and may not be suitable for all oil-water systems.

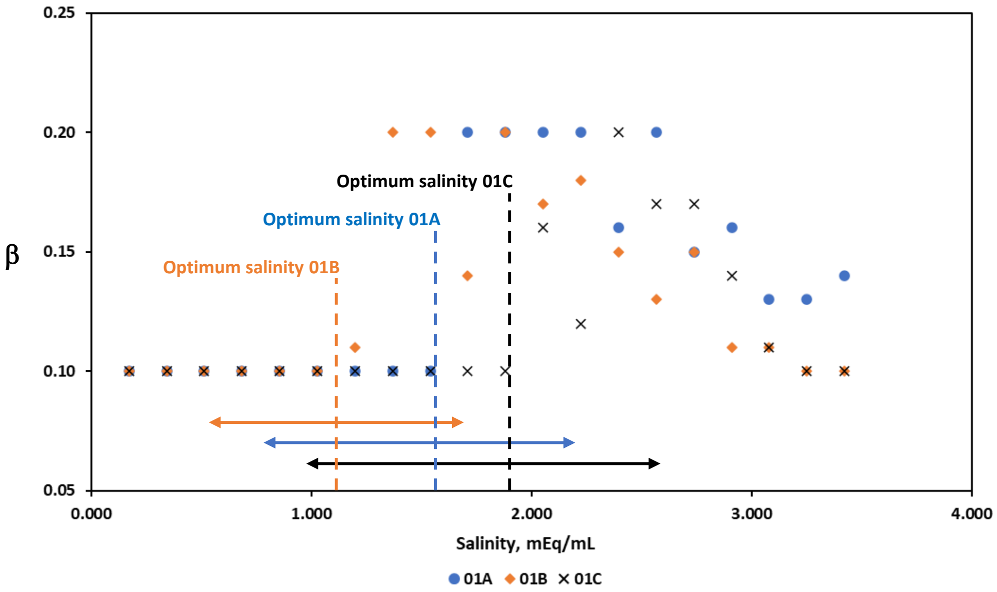


Figure 6 Distribution of β values.

Conclusions

The prediction of interfacial tension in waxy oil can be improved from the previous correlation by utilizing the Huh equation improved with the salinity parameter and EACN. Using this modified equation, the C_{H_o} and n values to be used to estimate the interfacial tension in the region of greater than optimal salinity were obtained with an average calculation error of 20%. It was also observed that the C_{H_o} and n values are proportional to the polarity of the mixture, with a higher polarity resulting in a larger C_{H_o} and n. In addition, it was observed that the optimum salinity for polar surfactant mixes is lower than that for nonpolar surfactant mixtures. However, the results of this study have to be validated using reservoir fluid and surfactant samples that are more diverse.

Nomenclature

HLB	:	Hydrophile-lipophile balance
HLD	:	Hydrophilic-lipophilic deviation
EACN	:	The equivalent alkane carbon number of the oil

σ_{om}, σ_{mo} : Refers to microemulsion/oil interfacial tension (mN/m)
V_{om} : Solubilized oil (mL)
V_{sm} : The volume fraction of microemulsion (ratio)
β : The multiplier constant for the modified equation
ε : A number that adjusts the exponential coefficient in the Huh equation
C_{H_o} : Constant representing the van der Waals attraction between hydrophilic particles and oil

Acknowledgment

This research was funded by ‘Capacity Building for Young Lecturer’s Research – Institut Teknologi Bandung’ (2021) and ‘Lecturer Internship in Research – Institut Teknologi Bandung’ (2022).

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Manuscript Received: 14 April 2023
1st Manuscript Revision Received: 9 November 2023
2nd Manuscript Revision Received: 7 December 2023
Accepted Manuscript: 11 December 2023