J. Eng. Technol. Sci., Vol. 53, No. 5, 2021, 210501

Correlation between Phase Behavior and Interfacial Tension for Mixtures of Amphoteric and Nonionic Surfactant with Waxy Oil

Rani Kurnia[1], Deana Wahyuningrum[2], Doddy Abdassah[1] & Taufan Marhaendrajana[1*]

[1]Petroleum Engineering Study Program, Faculty of Mining and Petroleum Engineering,
Institut Teknologi Bandung, Jalan Ganesha No. 10, Bandung 40132, Indonesia
[2]Chemistry Study Program, Faculty of Mathematics and Natural Sciences, Institut
Teknologi Bandung, Jalan Ganesha No. 10, Bandung 40132, Indonesia
*E-mail: tmarhaendrajana@tm.itb.ac.id

Highlights:

- Surfactant polarity affects the Huh equation.
- The initial C_{HO} and n constant values from the Huh equation were adjusted.
- The modified Huh equation constant, C_{HO} and n power, may be used as a guide to select the optimum mixing ratio of surfactants compatible with the fluids used in this experiment to obtain a low interfacial tension.

Abstract. Phase behavior tests in the surfactant screening process for EOR applications remain one of the relatively convenient ways to design an optimum surfactant formulation. However, phase behavior studies are unable to provide quantitative data for interfacial tension, which is one of the parameters that must be considered when selecting surfactants for EOR. Several studies related to the prediction of interfacial tension through phase behavior testing have been carried out. In this paper, the Huh correlation was used to estimate the interfacial tension value based on phase behavior tests. It was found that the current form of the Huh correlation may be applied for the below-to-optimum salinity condition. Furthermore, the constants of the equation vary depending on the surfactant type and mixtures.

Keywords: *amphoteric and nonionic surfactant; Huh equation; interfacial tensions; phase behavior.*

1 Introduction

Amphoteric surfactants are rarely an option to be applied in chemical flooding of enhanced oil recovery (EOR). This study showed that a novel surfactant called sulfonated alkyl ester (SAE) has promising performance and can be considered as a chemical agent for EOR. It has a unique chemical structure, with sulfonate

Received May 8th, 2020, 1st Revision January 8th, 2021, 2nd Revision March 25th, 2021, Accepted for publication March 31st, 2021.
Copyright ©2021 Published by ITB Institute for Research and Community Services, ISSN: 2337-5779,
DOI: 10.5614/j.eng.technol.sci.2021.53.5.1

(anionic) and ethoxylate (nonionic) groups in one single compound (Figure 1). Therefore it can be categorized as an amphoteric (zwitterion) surfactant [1].

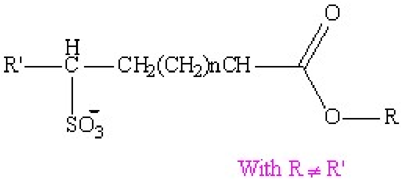


Figure 1 The chemical structure of sulfonated alkyl ester surfactant [2].

The molecular conformation of this surfactant may change depending on the water salinity and the presence of other compounds in the solution. This characteristic enables one to formulate a surfactant to obtain optimum conditions. The surfactant formulation process usually uses a single compound or mixture with other chemicals, such as a co-surfactant or co-solvent. The formulation of a surfactant was conducted to achieve optimum conditions. The optimum condition involved low interfacial tension (IFT), Winsor type III microemulsion, and a small contact angle (for oil-wet cases). Several studies have been conducted to simplify the surfactant formulation to be compatible with the reservoir characteristics. Several methods have been studied in surfactant formulation for EOR application. Some of the most popular methods are equivalent alkane carbon number (EACN) [3], hydrophilic-lipophilic balance (HLB) [2-4], hydrophilic-lipophilic difference (HLD) [5,6], and the Huh equation [7,8].

One of the best-known correlations between phase behavior tests and IFT is the Huh equation. Huh [9] developed this equation from three fundamental forces in the microemulsion phase: van der Waals attraction, electrostatic repulsion, and entropic repulsion. The correlation between phase behavior test and interfacial tension was derived using several assumptions. Huh explained that there is a relationship between the oil solubilization ratio and interfacial tension. This relationship is described with the following Eq. (1):

$$\sigma_{\mathrm{om}} = \frac{\mathrm{C_{HO}}}{(\mathrm{V_{om}}/\mathrm{V_{sm}})^2} \tag{1}$$

The Huh equation assumes that the surfactant has optimum salinity. This equation was later further developed for more complex conditions in other studies [9-13]. In the present study, the Huh equation was modified into the following more general equation:

$$\sigma_{\mathrm{om}} = \frac{\mathrm{C_{HO}}}{(\mathrm{V_{om}}/\mathrm{V_{sm}})^n} \tag{2}$$

$$C_{HO} = \frac{A_0 \cos\left({}^{\pi\phi_1}/_2\right)}{96\pi\tau^2} \text{ or } C_{HO} = 24.87\,\frac{a \cos\left({}^{\pi\phi_1}/_2\right)}{\bar{\tau}^2} \qquad (3)$$

with the value of C_{HO} explained as Eq. (3), which was derived from the van der Waals attraction between oil-surfactant-water. This attraction is caused by the interaction between surface-active hydrophilic particles in a surfactant with an oil surface [11]. In the experiment conducted by Huh, a typical constant (C_{HO}) of the equation was 0.3. The C_{HO} constant is affected by two parameters that reflect oil and surfactant properties, i.e. A_0 and τ respectively, where A_0 is the interfacial area per unit charge and τ is the apparent thickness of the surfactant layer at the oil/brine interface. The value of *n* in Eq. (2) refers to the geometry of the micro-emulsion. In the original Huh equation, the value of *n* is 2, representing that the microemulsion geometry is lamellar.

2 Materials and Methods

2.1 Surfactants, Oil, and Brine Samples

Sulfonated alkyl ester (SAE) and fatty ester oleate (FEO) surfactants synthesized at the Bioorganic and Organic Synthesize Laboratory, Chemistry study program, ITB, were used in this study [1,14]. Both surfactants were mixed with a specific weight ratio, as presented in Table 1. The oil used in this study had an API gravity of 40, wax content of 36%, viscosity of 7.9 cP (at 63 °C), and EACN of 25.2. The brine used in this study was taken from the field and had a density of 0.9847, salinity of 43 mEq/L (2,560 ppm), TDS of 4,648 ppm, pH of 7, and calcium and magnesium ions at 168 and 4.4, respectively. During the salinity scan experiment, sodium chloride was added to the field brine to achieve variable salinity of 171 to 3,422 mEq/L (or 10,000 to 200,000 ppm).

Table 1 Weight ratio of SAE and FEO surfactants as a mixture.

	Weight Ratio of	
	SAE	**FEO**
Formulation 01A	1	1
Formulation 01B	2	1
Formulation 01C	1	2

2.2 Phase Behavior Test

A phase behavior test was conducted to analyze the type of microemulsion formed in the solution mixture of oil, surfactant, and brine. In a 5-mL scaled pipette, the surfactant was diluted into the brine (percent wt) and mixed with oil at a volume ratio of 1:1. The upper part of the scaled pipette was closed using the flame-sealed method and stored in a heating oven at 63 ± 0.5 °C (reservoir temperature) for two days [1,16]. The surfactant concentration (Cs), brine salinity (A), aqueous level (B), oil level (C), top (D) and bottom (E) of the microemulsion were all measured. All data observed are shown in Table 2.

Table 2 Table of phase behavior data input.

Surfactant Concentration	Salinity meq/L	Sol. Oil mL	Sol. Water mL	Oil solution ratio mL/mL	Water solution ratio mL/mL
Cs	A	G = B-D	H = E-B	I = G/[(5-B)*Cs]	J=H/[(5-B)*Cs]

2.3 Interfacial Tension Measurement

Interfacial tension measurement was conducted using Spinning Drop Tensiometer TX-500D at 63 ± 0.5 °C (reservoir temperature) at 6000 rpm for 30 minutes (following the standard operation of the apparatus). This time was enough to obtain a stable interfacial tension (IFT) value, as shown in Figure 2. The measurement of interfacial tension followed the following procedure: (1) the surfactant was diluted into the brine at a specific concentration (%wt), (2) subsequently, the surfactant solution was injected into a glass tube by using a syringe until the tube was full, (3) the next step was injecting oil sample (± 2 μL) using a syringe into a glass tube that already contained surfactant solution; the oil must form a droplet. The spinning drop tensiometer schematic diagram and oil droplet formed in the surfactant solution can be seen in Figure 3.

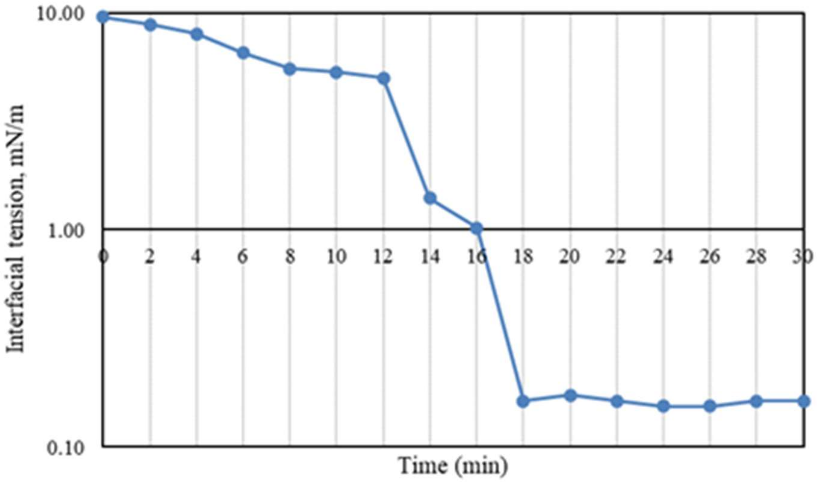
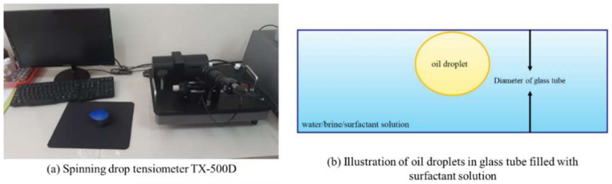
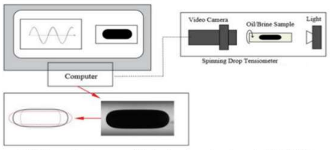


Figure 2 An example of a spinning drop tensiometer measurement with IFT versus time.



(a) Spinning drop tensiometer TX-500D

(b) Illustration of oil droplets in glass tube filled with surfactant solution



(c) Schematic diagram of Spinning drop tensiometer TX-500D

Figure 3 (a) Spinning Drop Tensiometer TX-500D, (b) illustration of oil droplets in the glass tube, and (c) schematic diagram of a spinning drop tensiometer

2.4 Partition Coefficient Measurement

The measurement of partition coefficient was conducted by using the ChemDraw software, version 18.2. The first step is to open the software until an interface appears, indicating a sheet for drawing the chemical structure of the compound to be calculated (Figure 4(a)).

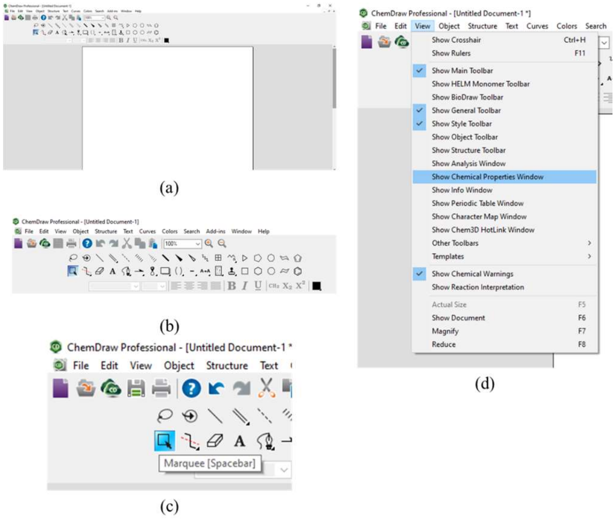


Figure 4 The ChemDraw software, version 18.2, interface for calculating the partition coefficient.

The compound's chemical structure can be calculated using the toolbar (Figure 4(b)). After the compound is drawn on the sheet, the compound is selected using marquee tools (Figure 4(c)). After that, the software generates the partition coefficient, and the measurement result can be seen by activating the chemical properties window (Figure 4(d)).

3 Results and Discussions

3.1 Polarity of Surfactants

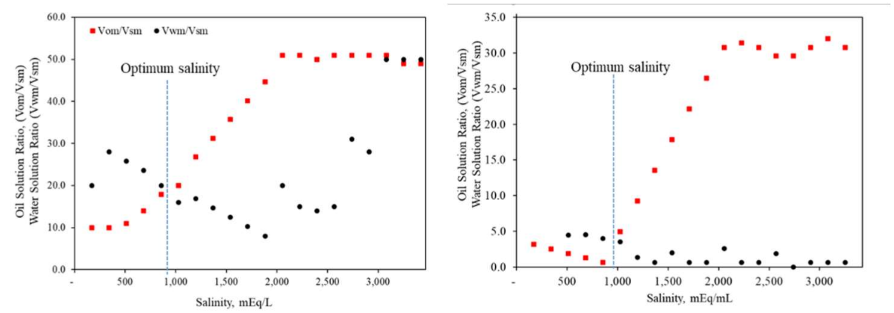
The characterization of both surfactants showed that the SAE was more polar than the FEO [17], which was confirmed by measuring the partition coefficient using ChemDraw. The partition coefficient (Log P) is the ratio of the concentrations of un-ionized compounds between two solutions calculated between an organic layer and an aqueous layer [18]. The partition coefficient value of the SAE and FEO surfactants was computed to be 0.1376 and 7.2206, respectively. The higher partition coefficient value indicates higher lipophilicity, implying that the SAE was more polar than the FEO. This polarity of the surfactant affects the interaction between a hydrophobic group of surfactants with oil and a hydrophilic group of surfactants with water. The effect of the polarity was analyzed through phase behavior tests and IFT measurements. The surfactant polarity was analyzed to study its effect on the Huh equation since it involves the van der Waals attraction in the microemulsions.

3.2 Comparison between Measured and Calculated Interfacial Tension

A comparison between the measured and the calculated interfacial tension was made. As in the Huh equation, a C_{HO} value of 0.3 and an n power of 2 was used. As mentioned above, the Huh equation assumes a middle-phase microemulsion (Winsor type III); thus, the optimum salinity of all surfactant samples was determined to support the discussion of the analysis. The optimum salinity of all surfactants used in this study is presented in Figure 5 and Table 3. A comparison of the measured and the calculated IFT was made below or equal to its optimum salinity.

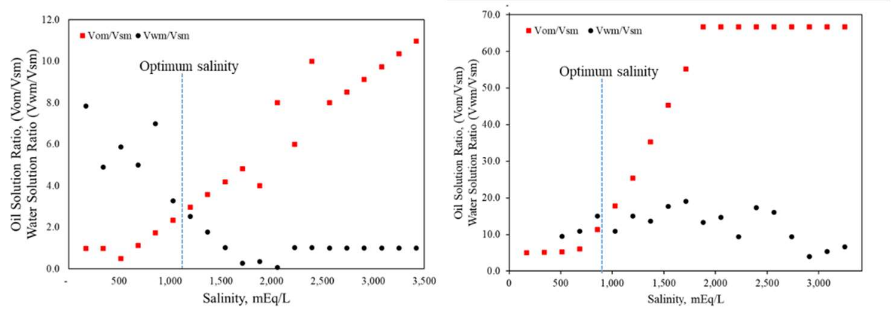
Table 3 Optimum salinity of all surfactants used.

Surfactant	Optimum Salinity, mEq/L
SAE	914
FEO	980
Formulation 01A	1,149
Formulation 01B	913
Formulation 01C	1,635



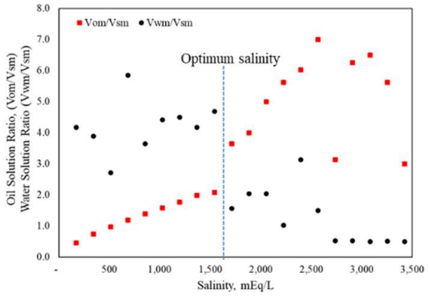
(a) SAE

(b) FEO



(c) formulation 01A

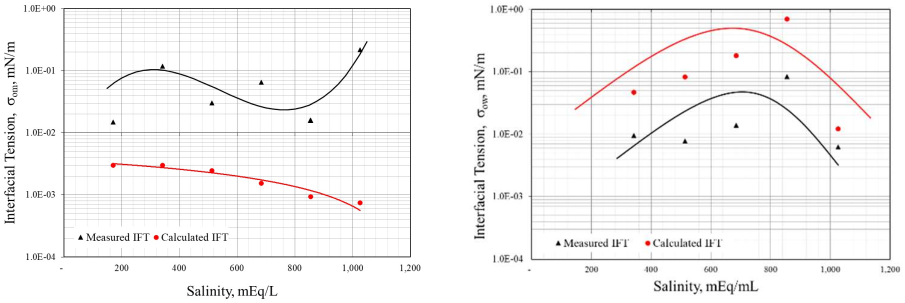
(d) formulation 01B



(e) formulation 01C

Figure 5 The effect of salinity on the phase behavior profile of SAE, FEO, formulation 01A, 01B and 01C

The first comparison used the SAE surfactant. It can be seen in Figure 6 that the calculated interfacial tension from the Huh equation had a lower value compared to the measured interfacial tension. This deviation also occurred in the FEO case. Interestingly, in general, IFT prediction by the Huh equation is closest to the measured value near optimum salinity. Another observation was that the surfactant with higher polarity had a lower prediction of the measured interfacial tension value (Figure 6(a)). Meanwhile, the surfactant with lower polarity showed the opposite behavior (Figure 6(b)). It can be inferred that the polarity of the surfactant affects the prediction of IFT using the Huh equation.



(a) SAE surfactant

(b) FEO surfactant

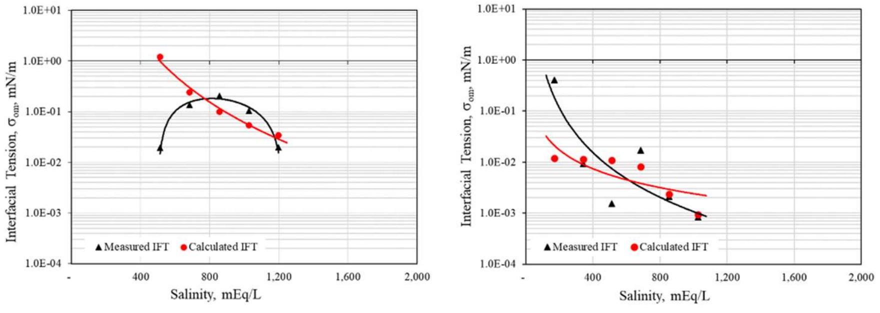
Figure 6 Interfacial tension values of measured and calculated (using the Huh equation) for (a) SAE surfactant and (b) FEO surfactant.

A comparison was also performed for the mixture of SAE and FEO surfactants. In the case of Formulation 01A, see Figure 7(a), three regions were observed. The first region was where the calculated interfacial tension had a higher value than the measured interfacial tension, which occurred below a salinity of 780 mEq/L. The second region was where the calculated interfacial tension had a lower value than the measured interfacial tension, which occurred between salinity 780 and 1,140 mEq/L. The third region was where the salinity was above 1,140 mEq/L, and the calculated IFT value returned to above the measured IFT value, as the first region. Figure 7(b) compares the predicted and the measured IFT of Formulation 01B shows a similar profile to Formulation 01A; however, Formulation 01B only had two regions. The first region followed the SAE surfactant profile, and the second region followed the FEO surfactant profile. The transition of both regions occurred when the salinity was above 600 mEq/L. The profile of Formulation 01C followed that of the FEO, where the calculated IFT was higher than the measured one. Formulation 01C had excess FEO surfactant; therefore, it was less polar than the SAE and Formulations 01B and 01A, which explains the profile shown in Figure 7(c).

Based on the comparisons discussed above, the surfactant polarity appeared to affect the IFT prediction from high to low polarity consistently. The polarity of the surfactant was in the following order: SAE, Formulation 01B, Formulation 01A, Formulation 01C, and FEO. This observation, then, became our consideration to make adjustments to the C_{HO} and the n constant values used in the Huh equation for the surfactants studied.

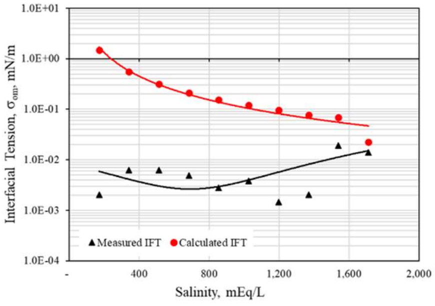
3.3 Correlation between Phase Behavior and Interfacial Tension

The value of C_{HO} and n of the SAE surfactant may be calculated using the modified Huh equation by plotting the oil solubilization ratio against the measured interfacial tension values (Figure 8). The C_{HO} number and power of n values were determined by regression of the data. The plot of the oil solubilization ratio with measured interfacial tension values was divided by two regions, i.e. at below to equal its optimum salinity of the surfactant and above its optimum salinity. The first region, i.e. the plot below to equal its optimum salinity, showed that the correlation between the oil solubilization ratio and the IFT values provides a C_{HO} number and power of n of 32.717 and 1.69, respectively. The n power resulting from the plot was close to the Huh equation, but the C_{HO} constant differed.



(a) Formulation 01A

(b) Formulation 01B



(c) Formulation 01C

Figure 7 The measured and calculated (using the Huh equation) IFT of Formulations 01A, 01B, and 01C.

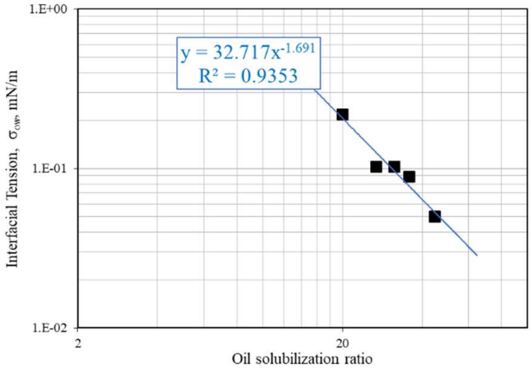


Figure 8 Correlation between oil solubilization ratio and interfacial tension values of the SAE surfactant

The IFT values were also plotted against the oil solubilization ratio versus brine salinity for the FEO surfactant, as shown in Figure 9. The C_{HO} and *n* values calculated from the phase behavior data below the optimum salinity were 0.028 and 1.34. As explained by Eq. (3), C_{HO} is affected by the surfactant and oil characteristics. The difference in C_{HO} values between the SAE and FEO surfactants, in this case, was caused by the thickness of the surfactant layer at the oil/water contact. In particular, the SAE surfactant had a thinner layer than the FEO surfactant at the oil/water interface.

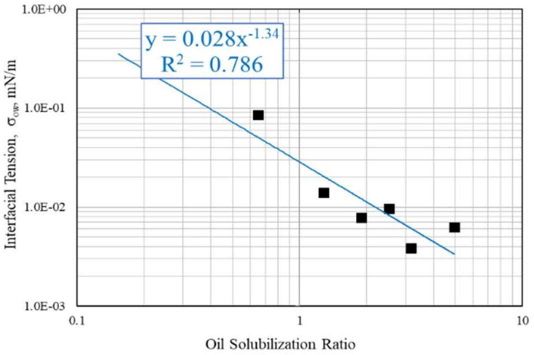


Figure 9 Correlation between oil solubilization ratio and FEO surfactant interfacial tension values.

This study also examined the effect of surfactant mixtures on the C_{HO} value, in this case, mixtures of the SAE and FEO surfactants. In Figure 10, a plot of IFT against the oil solubilization ratio below to equal optimum salinity indicates a correlation with the C_{HO} value of 0.264, which is close to the typical constant suggested by Huh's study ($C_{HO} = 0.3$). Furthermore, the *n* value of 1.67 was also near Huh's original value ($n = 2$). It can be inferred that adding FEO surfactant to SAE surfactant with a weight ratio of 1:1 increases the van der Waals attraction of the SAE surfactant and oil. Note that the *n* value of Formulation 01A was higher than FEO's, while it was lower than SAE's. These results are consistent with the polarity order of the three: from low to high, the polarity order was FEO, Formulation 01A, and SAE.

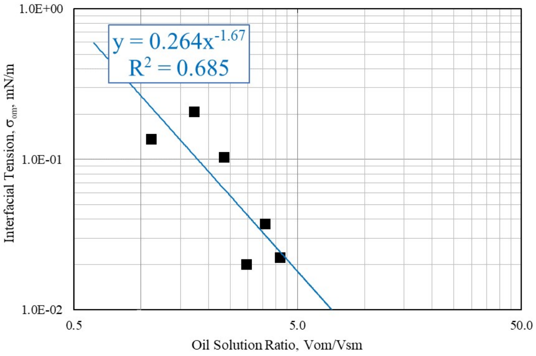


Figure 10 Correlation between oil solubilization ratio and interfacial tension values of Formulation 01A.

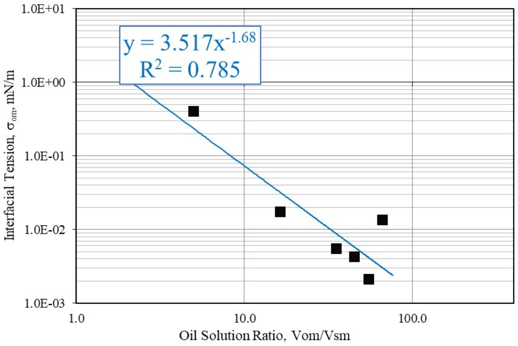


Figure 11 Correlation between oil solubilization ratio and interfacial tension values of Formulation 01B.

The effect of the SAE/FEO surfactant ratio to C_{HO} and *n* values was also analyzed for the other formulations. It can be seen in Figure 11 that Formulation 01B had a slightly higher *n* value compared to Formulation 01A, which again is consistent with their polarity. When FEO was twice SAE in the mixture (formulation 01C), the C_{HO} value was 0.005, as shown in Figure 12, indicating high van der Waals attraction. Meanwhile, the *n* value of Formulation 01C was 1.38, which is between that of FEO and Formulation 01A. It proves a strong relationship between surfactant polarity and the values of C_{HO} and *n*, as indicated in Figure 13.

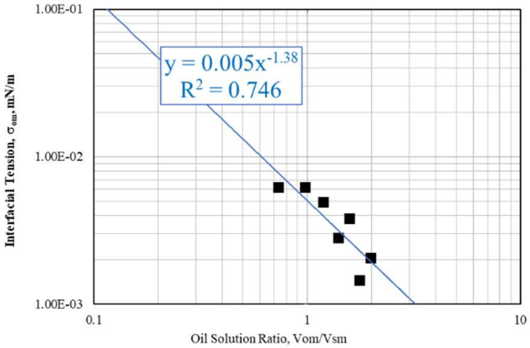
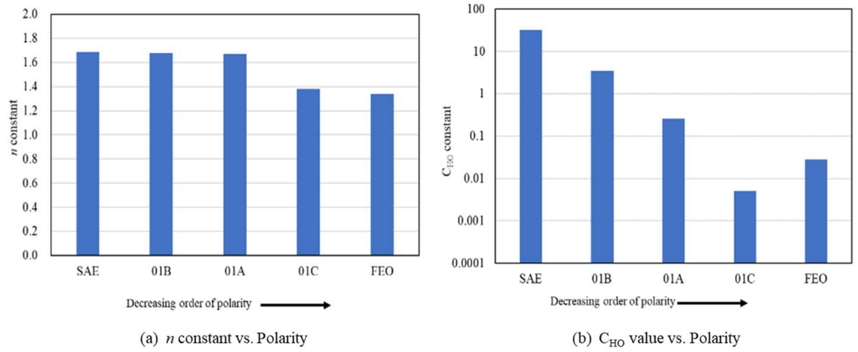


Figure 12 Correlation between oil solubilization ratio and interfacial tension values of Formulation 01C.

The C_{HO} and *n* values are summarized in Table 4. Except for Formulation 01A statistically, the correlations were reasonably acceptable, which indicates a correlation of fit, R-squared, more significant than 0.75. The formulation may need to be examined further. It might be caused by waxy oil attached to the pipette tube, which would affect the oil-surfactant-brine phase equilibrium. If we compare the C_{HO} and *n* values of SAE, FEO, and its formulations (Table 4), the closest C_{HO} and *n* values to the value used in the Huh equation occurred when Formulation 01A was used. Among the three formulations, Formulation 01A had the lowest IFT value. If Huh assumed an ideal condition, the optimum mixture of two surfactants might be represented by values of C_{HO} and *n* near to Huh's. Since the definition of C_{HO} is based on van der Waals attraction, the higher the C_{HO} value, the greater the distance between the oil and the water. This can cause instability of the microemulsion produced. However, the microemulsion would be too stable if the distance between the oil and the water was too small. This can cause problems when a microemulsion is produced on the surface because it will be a challenge to demulsify it.



(a) *n* constant vs. Polarity (b) C_{HO} value vs. Polarity

Figure 13 The relationship of C_{HO} and *n* values versus the polarity of the surfactants.

Table 4 Phase behavior and interfacial tension correlation for each surfactant and formulation.

Surfactants	**Modified Huh Equation Below/at Optimum Salinity**		**R^2**
	C_{HO}	**n**	
SAE	32.717	1.69	0.935
FEO	0.028	1.34	0.786
Formulation 01A	0.264	1.67	0.685
Formulation 01B	3.517	1.68	0.785
Formulation 01C	0.005	1.38	0.756

4 Conclusions

The Huh equation is affected by the surfactant polarity. Lower polarity decreases the *n* value, and in general, also reduces the C_{HO} value. The Huh equation tends to predict a lower IFT value at high polarity, while it tends to overestimate the IFT value at low polarity. Therefore, an adjustment of the values of C_{HO} and *n* proposed by Huh is needed.

This study discovered that C_{HO} and *n* values near Huh's value indicate the optimum mixture of two surfactants. Hence, the Huh equation constant and *n* power values can be used as a reference to choose the best mixing ratio of surfactants compatible with the corresponding fluids used in this study to achieve a low IFT.

Acknowledgment

This research was funded by *Program Riset Multidisplin,* Institut Teknologi Bandung, 2020-2021.

References

[1] Sheng, J., *Modern Chemical Enhanced Oil Recovery: Theory and Practice*, Elsevier, 2011.

[2] Marhaendrajana, T., Wahyuningrum, D., Kurnia, R. & Buhari, A., *Sulfonate Alkyl Ester based Surfactant to Lower Interfacial Tension Oil-Water in Reservoir Enhanced Oil Recovery Application*, No. P00201600324, Granted Patent, 2017. (Text in Indonesian)

[3] Wan, W., Zhao, J., Harwell, J.H. & Shiau, B.J., *Characterization of Crude Oil Equivalent Alkane Carbon Number (EACN) for Surfactant Flooding Design*, J. Dispers. Sci. Technol., **37**(2), pp. 280-287, 2016. DOI: 10.1080/01932691.2014.950739.

[4] Davies, J., *A Quantitative Kinetic Theory of Emulsion Type, I. Physical Chemistry of the Emulsifying Agent*, 2nd International Congress Surface Activity, pp. 426-438, 1957.

[5] Griffin, W.C., *Classification of Surface Active Agents by HLB*, J. Soc. Cosmet. Chem., **1**, pp. 311-326, 1949.

[6] Griffin, W.C., *Hydrophile-Lipophile Balance and Cloud Points of Nonionic Surfactants*, J. Pharm. Sci., **58**(12), pp. 1443-1449, 1969. DOI: 10.1002/jps.2600581203.

[7] Salager, J., Morgan, J.C., Schechter, R.S., Wade, W.H. & Vasquez, E., *Optimum Formulation of Surfactant/Water/Oil Systems for Minimum Interfacial Tension or Phase Behavior*, Soc. Pet. Eng. J., **19**(2), pp. 107-115, 1979. DOI: 10.2118/7054-pa.

[8] Salager, J., *Microemulsions* in *Handbook of Detergents, Part A: Properties*, G. Broze, ed., *Surfactant Science Series* Vol. 82, Chapter 8, pp. 253-302, Marcel Dekker, Inc., New York, 1999.

[9] Huh, C., *Interfacial Tensions and Solubilizing Ability of a Microemulsion Phase that Coexists with Oil and Brine*, J. Colloid Interface Sci., **71**(2), pp. 408-426, 1979. DOI: 10.1016/0021-9797(79)90249-2.

[10] Huh, C., *Equilibrium of a Microemulsion that Coexists with Oil or Brine*, Soc. Pet. Eng. J., **23**(5), pp. 829-847, 1983. DOI: 10.2118/10728-PA.

[11] Marina, P.F., Cheng, C., Sedev, R., Stocco, A., Binks, B.P. & Wang, D., *Van der Waals Emulsions: Emulsions Stabilized by Surface-Inactive, Hydrophilic Particles via van der Waals Attraction*, Angew. Chemie – Int. Ed., **57**(30), pp. 9510-9514, 2018. DOI: 10.1002/anie.201805410.

[12] Ghosh S. & Johns, R.T., *Dimensionless Equation of State to Predict Microemulsion Phase Behavior*, Langmuir, **32**(35), pp. 8969-8979, 2016. DOI: 10.1021/acs.langmuir.6b02666.

[13] Torrealba, V.A. & Johns, R.T., *Coupled Interfacial Tension and Phase Behavior Model Based on Micellar Curvatures*, Langmuir, **33**(47), pp. 13604-13614, 2017. DOI: 10.1021/acs.langmuir.7b03372.

[14] Torrealba, V.A., Johns, R.T. & Hoteit, H., *Curvature-based Equation of State for Microemulsion-phase Behavior,* SPE Journal, **24**(2), pp. 647-659, 2019. DOI: 10.2118/194022-PA.

[15] Marhaendrajana, T., Kurnia, R., Wahyuningrum, D. & Abdassah, D., *Composition of Alkyl Ester Sulfonate Surfactant (SAE) with Polyethyleneglycol Oleic Ester Surfactant (EOP) for Reducing Interfacial Tension between Waxy Oil and Water*, No. P00201809114, 2018. (Text in Indonesian)

[16] Healy, R.N. & Reed, R.L., *Physiochemical Aspects of Microemulsion Flooding*, Society of Petroleum Engineers of AIME Journal, **14**(5), pp. 491-501, 1974. DOI: 10.2118/4583-pa.

[17] Marhaendrajana, T., Kurnia, R., Wahyuningrum, D. & Fauzi, I., *A Novel Sulfonated Alkyl Ester Surfactant to Reduce Interfacial Tensions in a Wide Range Salinity with Monovalent and Divalent Ions*, Modern Applied Science, **10**(1), pp. 93-102, 2015. DOI: 10.5539/mas.v10n1p93.

[18] Di, L. & Kerns, E.H., *Lipophilicity in Drug-like Properties: Concepts, Structure Design and Methods from ADME to Toxicity Optimization,* 2nd ed., Boston: Academic Press, pp. 39-50, 2016.