PHASE BEHAVIOR STUDIES OF ALPHA OLEFIN SULFONATE (AOS), LAURYL GLUCOSIDE, AND DECANE IN CREATING WINSOR TYPE-III MICROEMULSION

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ABSTRACT

One of the methods to increase the oil recovery is by significantly increase the capillary number. This can be achieved by reducing the interfacial tension (IFT) between the oil and the water in the reservoir to an ultra-low value. There are many studies conducted that proved the ability of Winsor Type-III microemulsion to reduce the IFT to an ultra-low value. Winsor Type-III microemulsion can be created by mixing surfactant, cosurfactant or cosolvent, brine, and oil. However, there has not been any research related to microemulsion creation conducted on alpha olefin sulfonate, AOS and alkyl polyglucoside, and, APG surfactant mixture. Commonly, alcohol as a cosolvent will be added to the surfactant system to enhance the surfactant ability in creating Winsor Type-III microemulsion, but in this project, alcohol was replaced with an environmental friendly nonionic surfactant, lauryl glucoside. In this project, the phase behavior study of a novel 'green' surfactant mixture was conducted to evaluate the potential of the surfactant in creating Winsor-Type III microemulsion and determine the optimum formulations to create a stable Winsor Type-III microemulsion. The phase behavior studies were conducted in three stages which are the optimization of salinity, surfactant concentration, and cosurfactant concentration. Phase diagrams were constructed to properly analyze the phase behavior of the components in a wide range of decane volumes. From the phase behavior studies conducted, it can be concluded that the optimum formulation is 3 wt% salinity, 1 wt% AOS, and 3 wt% lauryl glucoside. Lauryl glucoside addition in the mixture could alter the HLB value of the surfactant mixture hence increasing its potential in creating Winsor Type-III microemulsion.

Keywords: *Enhanced Oil Recovery, surfactant, alkyl polyglucoside*

INTRODUCTION

Only about one-third of the hydrocarbon discovered with conventional recovery techniques can be economically recovered [1]-[2]. The conventional techniques refer to the primary and secondary recovery methods. Primary recovery methods depend on the natural drive forces that exist in the reservoir and the secondary recovery methods' main purpose is to maintain the reservoir pressure by injecting water or gas into the reservoir. The tertiary recovery method or Enhanced Oil Recovery (EOR) is one of the techniques that could improve oil and gas recovery [3]

by approximately 30% [4]-[6] of the remaining reserves in oil and gas field.

Surfactant flooding is one of the techniques that fall under the category of Chemical-Enhanced Oil Recovery (CEOR). It involves injecting chemicals, mainly surfactants, into the reservoir to increase the ultimate recovery of the field [7]. Surfactant flooding is used to recover oil that is not recovered during the waterflood process [8]. Some reasons enhanced oil recovery is needed after waterflooding are low capillary number, Ca after waterflooding process [9], reservoir heterogeneities and trapped oil ganglia from

high surface tensions [10]. A low capillary number, Ca of about 10^{-5} indicates that oil trapping due to capillary forces is most likely to happen and for a typical waterflood, the Ca value is approximately at 2.5×10^{-7} [9].

The capillary number is affected by fluid/fluid interactions and the parameters that are involved in the calculation are the velocity of the injected fluid, the viscosity of the injected fluid, and interfacial tension. Kamal et al. [11] suggested that by increasing the capillary number up until 10^{-4} or 10^{-3}, the oil saturation in the formation could be reduced by 90% and it could approach 100% if the capillary number reaches 10^{-2}. To achieve this from the typical capillary number after waterflooding process, an increase of about 1000 times needs to be obtained, and this could be possible by reducing the interfacial tension to an ultra-low value of 10^{-3} mN/m or lower. Many past researches displayed surfactant capabilities to reduce the IFT to an ultra-low value from its initial value of 20 to 40 mN/m [1],[4].

Surfactants will react with the aqueous or oil phase to form micelles [8]. According to Howe et al. [8], these micelles will solubilize some of the excess aqueous or oil phase to form a microemulsion. Microemulsion can be categorized into three types which are Winsor Type-I (lower-phase), Winsor Type-II (upper-phase), and Winsor Type-III (middle-phase) [12]-[14]. Pal et al. [12] mentioned that Winsor Type-III microemulsion could offer ultra-low IFT (10^{-2} to 10^{-4} mN/m). To achieve Winsor Type-III microemulsion, the surfactant affinity towards oil and water phases needs to be well balanced [8] hence emphasizing the need for a thorough screening process. Phase behavior study is an excellent screening tool which can efficiently determine the suitable formulation of a surfactant system to create a stable Winsor Type-III microemulsion [4],[10],[15]. There are a few methods to conduct phase behavior studies, such as using phase diagrams [16], solubilization ratio curves, and Winsor's R-ratio [10].

A surfactant mixture that consists of biodegradable surfactants was used in this project to create a 'green' surfactant system. The surfactants are alpha olefin sulfonate and lauryl glucoside. Alpha Olefin Sulfonate (AOS), commercially known as sodium linear alpha olefin sulfonate, is an anionic surfactant. According to Pratiwi et al. [3], the AOS family of surfactants can perform well in a wide enough range of pH, display good detergent ability in high hardness solution, and has a high biodegradation rate. In addition, AOS also has low adsorption on porous rock, making it a suitable candidate for EOR application [3]. However, AOS alone could not create Winsor Type-III microemulsion [3]. For anionic surfactant like AOS, hydrophilic cosolvent or cosurfactant could be used to assist the creation of Winsor Type-III microemulsion [11].

Lauryl glucoside is one of the alkyl polyglucosides. Alkyl polyglucoside (APG) is a non-ionic surfactant that is categorized as "non-toxic" for environmental threats [17]. According to Li et al. [18], APG has a great capability to improve oil recovery at a wide range of temperature and salinity instead, it performs much better in high temperature and high salinity. Li et al. [18] also mentioned that despite being a "green surfactant," it also able to demonstrate good interfacial activity and foaming performance. Ghosh and Obasi [19] suggested that APG generally has an HLB value of more than 11 and Kamal et al. [11] mentioned that HLB values of more than 11 indicate that the surfactant is hydrophilic. Hence, lauryl glucoside could be a potentially good cosurfactant for the surfactant system to create Winsor Type-III microemulsion.

Based on the above two surfactants mentioned, this project focused on investigating the performance of AOS and lauryl glucoside in creating Winsor Type-III microemulsion with the presence of decane, where AOS will act as the main surfactant, and lauryl glucoside will act as the cosurfactant. The addition of APG as cosurfactant was expected to alter the mixed surfactant HLB value so that it could efficiently create Winsor Type-III microemulsion at a wide range of decane volume.

METHODOLOGY

Aqueous Phase Preparation
The composition to create the microemulsion system consists of surfactant, cosurfactant, brine, and oil. For this experiment, the chemicals chosen for each composition are alpha olefin sulfonate (AOS), lauryl glucoside, sodium chloride (NaCl), and decane, respectively. Details of the chemicals are shown in Table 1.

Table 1 Chemicals used in microemulsion creation

Chemical	Description	Supplier	Active Content (%)
Alpha Olefin Sulfonate (AOS)	Surfactant (Anionic)	Personal Formula Resources (M) Sdn. Bhd.	97
Lauryl Glucoside	Surfactant (Non-ionic)	Personal Formula Resources (M) Sdn. Bhd.	50-53
Sodium Chloride	Salt	Merck Sdn. Bhd.	-
Decane	Oil	-	-

AOS used in this project is in powdered form, while lauryl glucoside was purchased in liquid form. For lauryl glucoside, the determination of water content was conducted by using Karl Fischer (KF) Titration method. A sample of lauryl glucoside with a mass of 0.2 g was sent to the laboratory for the KF Titration. The titration method results showed that the purchased lauryl glucoside's water content is 19.35%. Hence, the calculation to prepare the sample was done by considering the water content of lauryl glucoside to obtain a more accurate outcome.

The aqueous solution was prepared in a 250 ml beaker. For the aqueous solution, distilled water volume was fixed at 200 ml. By multiplying the density of distilled water at experimental temperature with 200 ml, the mass of solvent was obtained and incorporated into:

$$\text{Mass of solute} = \frac{\text{Mass of solvent}}{\text{wt\% solvent}} \times \text{wt\% solute} \quad (1)$$

After the solutes had been weighed and added to the distilled water in the beaker, the mixture was left to be stirred until the solution appeared to be homogenous.

Phase Behavior Study
To achieve the objectives of this project, a few published research papers that investigated microemulsion phase behavior were being referred to. For this project, the phase behavior study conducted by Jeirani et al. [16] was the main reference for the methodology in investigating the optimum conditions to create Winsor Type-III microemulsion in a wide range of decane.

There were three optimization stages which are salinity, surfactant concentration, and cosurfactant concentration optimization. Decane was pre-filled into test tubes at 1, 2, 3, 4, 5, 6, 7, 8, and 9 ml. Then, the prepared aqueous solutions were poured into the decane pre-filled test tubes. The total decane and aqueous solution volume inside each test tube was maintained at 10 ml. The samples were then shaken by an orbital shaker at a low speed of approximately 100 rpm for an hour. After that, the samples were left undisturbed for one week to allow equilibration between the phases. After one week, the decane, microemulsion, and aqueous phase volume were recorded and presented in phase diagrams. The optimum salinity was chosen based on the appearance of Winsor Type-III microemulsion in a wide range of decane volumes.

RESULTS AND DISCUSSION

Phase Behavior Studies and Aqueous Phase Optimization
This project could be considered successful through the phase behavior studies conducted by replicating the methodology of Jeirani et al. [16]. The objectives of this project were met as the optimum formulation to create Winsor Type-III microemulsion in a system of AOS, APG, brine, and decane were obtained. The assessment was conducted based on the presence of Winsor Type-III in a wide range of decane with various concentrations of AOS, APG, and brine. An example of the determination of the phases is shown in Figure 1. Phase diagrams were constructed to efficiently observe the oleic, microemulsion, and aqueous phase volume.

Salinity Optimization
From the phase diagrams constructed as shown in Figures 2 to 7, it can be seen that at a low decane volume system, the volume of the middle-phase microemulsion is relatively higher than the system with a high decane volume. According to Jeirani et al. [16], there are two ways to promote phase shifting to Winsor Type-III microemulsion, which are by
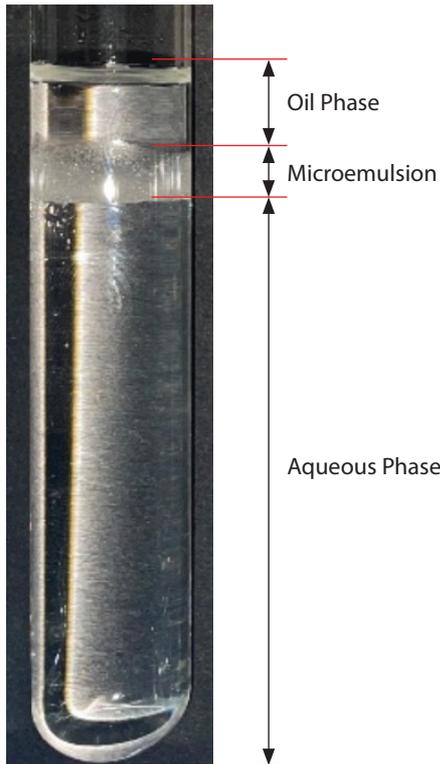
Figure 1 An example of the phases determination based on their distinct differences in appearance

increasing the hydrophobicity of the surfactant system or by increasing the hydrophilicity of the oil. The low volume of middle-phase microemulsion observed at high decane volume indicates that by adding more decane, the hydrophilicity of the oil phase to the aqueous phase will decrease.

Middle-phase microemulsion can be seen formed at almost all salinity conditions at a wide range of decane volumes. However, this is untrue for phase diagrams with 4 wt% and 5 wt% salinity. For 4 wt% and 5 wt% salinity conditions, the middle-phase microemulsion volume appears at a lower volume of decane and almost none at a higher volume of decane. According to Massarweh and Abushaikha [10], proper middle-phase microemulsion will not appear in high salinity conditions unless a high-HLB surfactant or surfactant mixture is used. This could indicate that the surfactant system containing 1 wt% AOS and 1 wt% APG did not have the required HLB value to create Winsor Type-III at a wide range of decane volume at salinity of 4 wt% and higher.

At lower salinity conditions of 0, 1, 2, and 3 wt%, considerable Winsor Type-III microemulsion volume can be seen at all decane volumes. In this first optimization stage, the aqueous solutions were prepared at low concentrations of surfactant and cosurfactant, which are 1 wt% for AOS and 1 wt% for APG. Modification of surfactant and cosurfactant concentrations in later optimization stages could show whether the volume of the middle-phase microemulsion could be increased or not. Thus, the highest salinity condition with considerable volume of middle-phase microemulsion at all of the decane volumes, which is the 3 wt% salinity, was chosen as the optimum salinity.
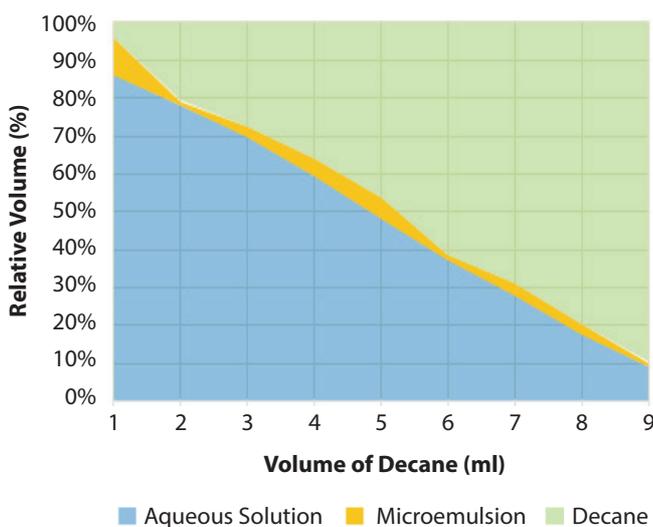

Figure 2 Phase diagram for 0 wt% salinity, 1 wt% AOS, 1 wt% APG, and decane
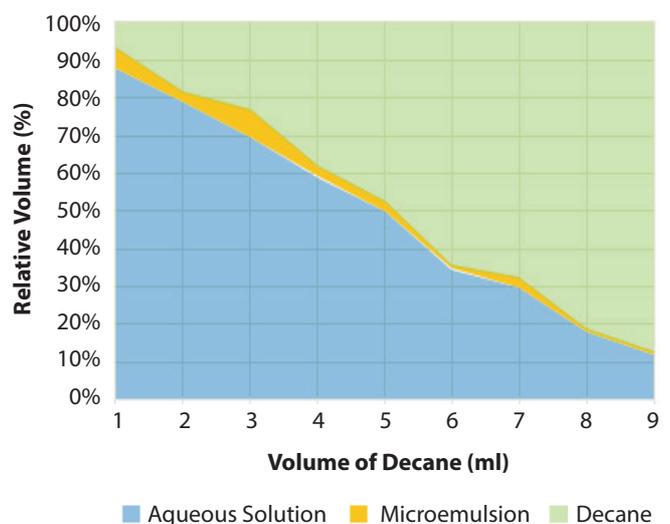

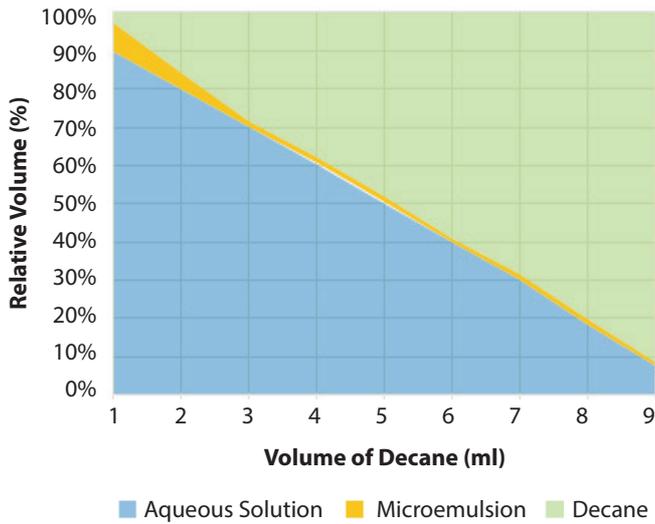**Figure 3** Phase diagram for 1 wt% salinity, 1 wt% AOS, 1 wt% APG, and decane

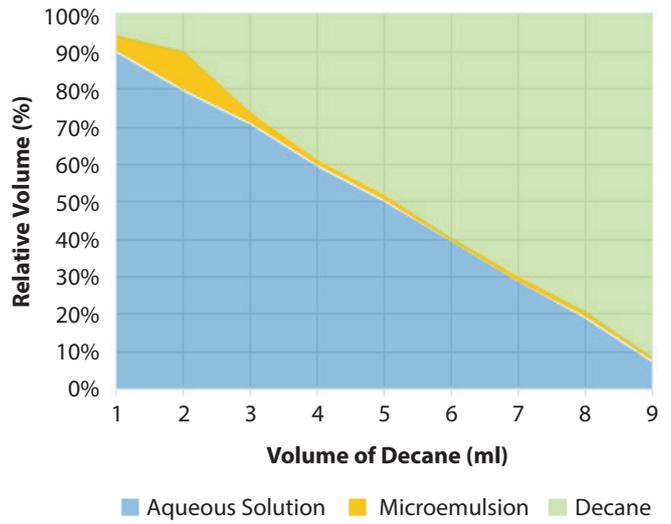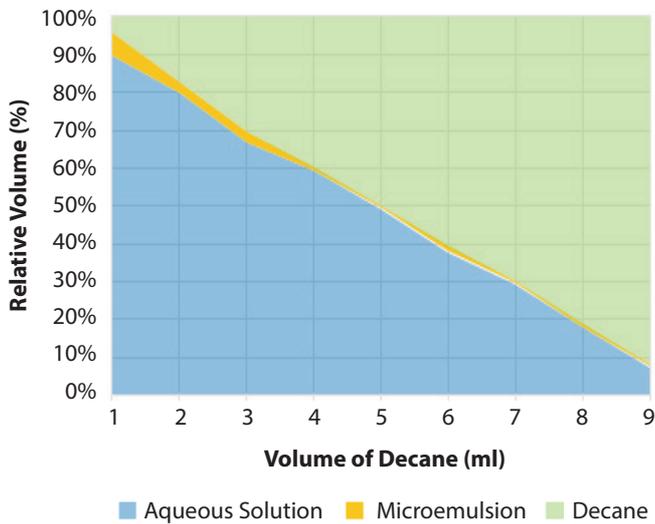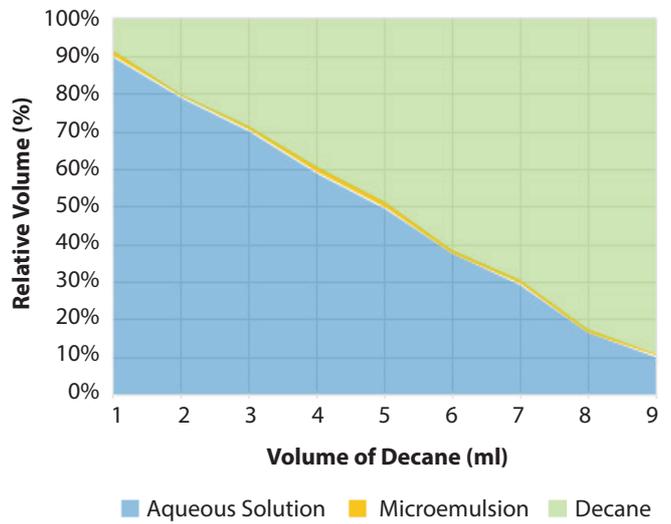**Figure 4** Phase diagram for 2 wt% salinity, 1 wt% AOS, 1 wt% APG, and decane

Figure 5 Phase diagram for 3 wt% salinity, 1 wt% APG, and decane

Figure 6 Phase diagram for 4 wt% salinity, 1 wt% APG, and decane

Figure 7 Phase diagram for 5 wt% salinity, 1 wt% APG, and decane

Surfactant Concentration Optimization

From the phase diagrams as shown in Figures 8 to 13, middle-phase microemulsion can be seen appearing almost constantly throughout the increasing decane volume. This indicates that APG alone could create Winsor Type-III microemulsion at the given condition of 3 wt% salinity. However, one of the scopes of study of this project is to evaluate the potential of APG as a cosurfactant to create a 'green' surfactant mixture to replace alcohol. Hence, the option of formulating the surfactant system without AOS is not viable in this project. Nevertheless, from the phase diagram of only APG present as the surfactant, the hydrophilic characteristic of APG can be seen where the

microemulsion formed at 10% decane mainly settled at the interface between oil and aqueous phase but mainly on the aqueous section.

Volumes for middle-phase microemulsion were observed to be relatively low at decane volumes of more than 80% for 2, 3, and 4 wt% of AOS. This might indicate that the relatively high lipophilicity surfactant system contributed by high AOS concentration is not capable of creating Winsor Type-III microemulsion at high decane volume and 3 wt% salinity and 1 wt% APG concentration. For the optimum surfactant concentration, 1 wt% AOS was chosen instead of 0.5 wt% due to the volume of
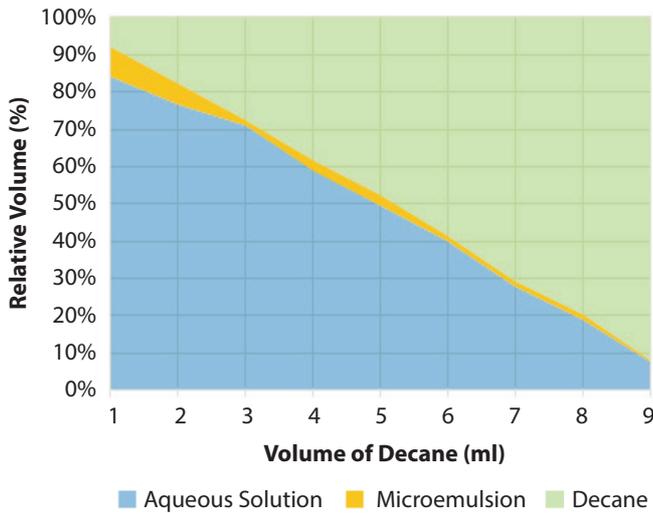
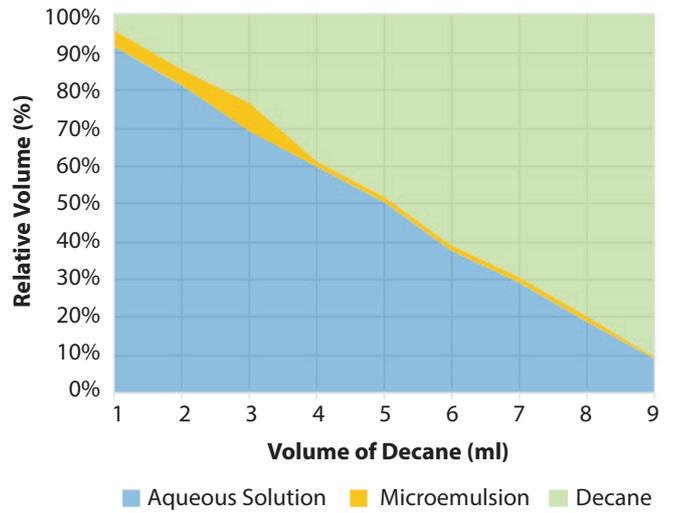**Figure 8**   Phase diagram for 3 wt% salinity, 0 wt% AOS, 1 wt% APG, and decane

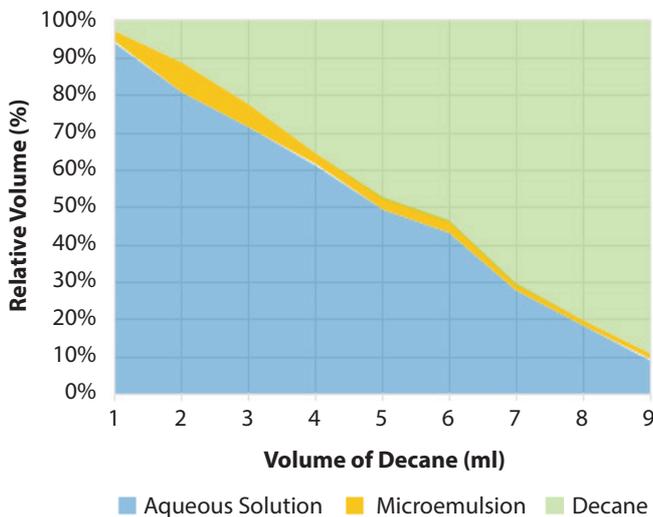**Figure 9**   Phase diagram for 3 wt% salinity, 0.5 wt% AOS, 1 wt% APG, and decane

Figure 10   Phase diagram for 3 wt% salinity, 1 wt% AOS, 1 wt% APG, and decane
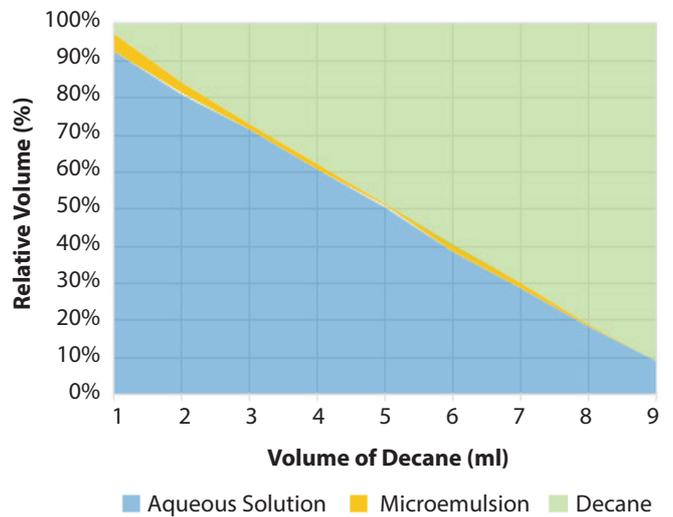

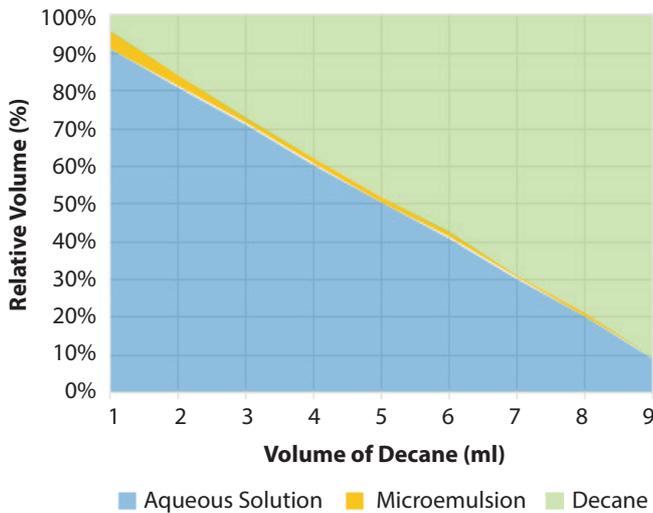**Figure 11**   Phase diagram for 3 wt% salinity, 2 wt% AOS, 1 wt% APG, and decane

Figure 12   Phase diagram for 3 wt% salinity, 3 wt% AOS, 1 wt% APG, and decane.

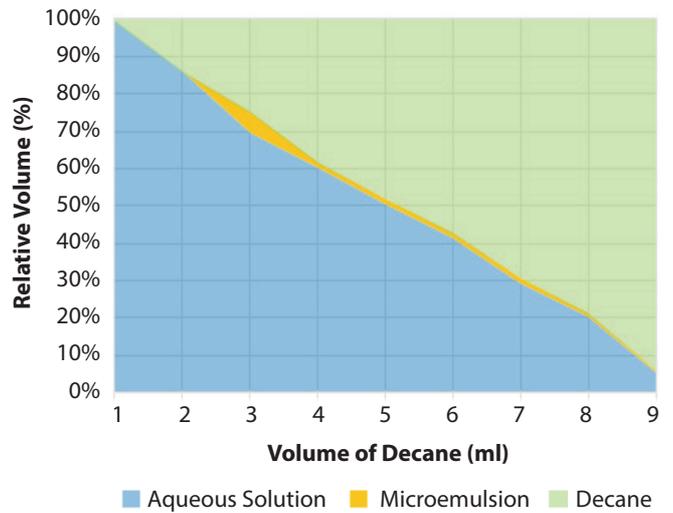**Figure 13**   Phase diagram for 3 wt% salinity, 4 wt% AOS, 1 wt% APG, and decane.

microemulsion being relatively higher throughout the decane volumes.

Cosurfactant Concentration Optimization
In the surfactant system without APG, as shown in Figures 14 to 19, middle-phase microemulsion volume was minimal throughout all decane volumes. There were only middle phase microemulsion forming at 10 and 20% decane volume and none were forming at higher decane volumes. This suggests that without the assistance of cosurfactant or cosolvent, AOS could not efficiently create Winsor Type-III microemulsion and this correlates with the research conducted by Pratiwi et al. [3].

As the concentration of APG increases in the aqueous solution, the volume of middle-phase microemulsion was also observed to be increasing. APG is more hydrophilic compared to AOS and this might contribute to the creation of Winsor Type-III microemulsion due to the HLB value of the surfactant system reached the suitable value for microemulsion creation. It can be observed at 3 wt% and 4 wt% APG concentration the volume of the middle-phase microemulsion is relatively higher compared to others and there is not much difference between the two of the systems. Hence, the lower APG concentration between both of them, which is 3 wt% APG was chosen as the optimum cosurfactant concentration.
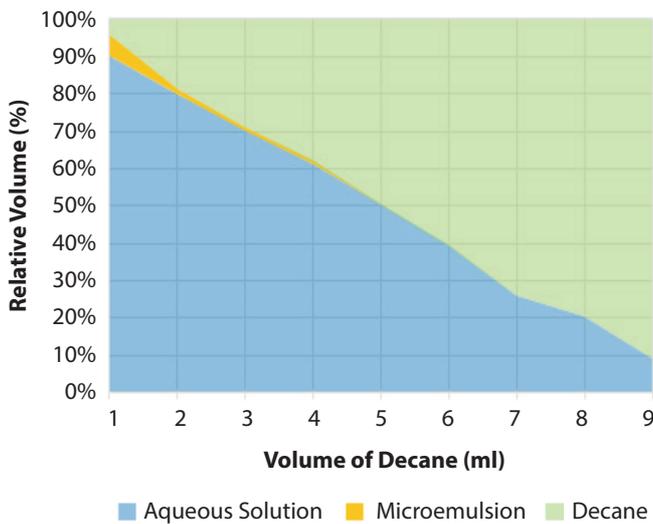

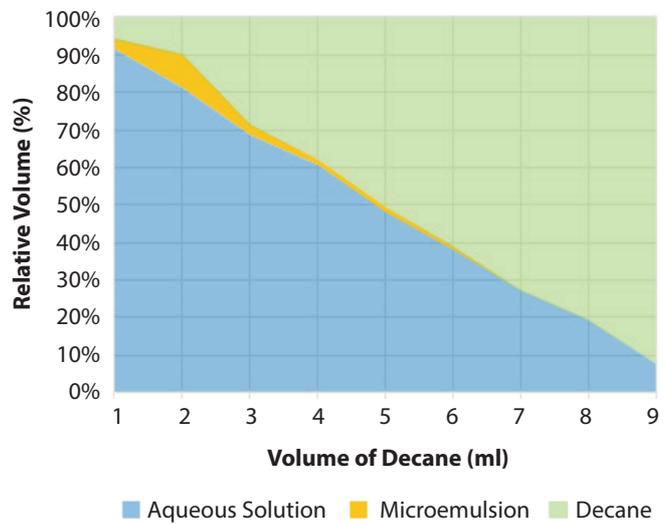**Figure 14**   Phase diagram for 3 wt% salinity, 1 wt% AOS, 0 wt% APG, and decane

Figure 15   Phase diagram for 3 wt% salinity, 1 wt% AOS, 0.5 wt% APG, and decane

Figure 16   Phase diagram for 3 wt% salinity, 1 wt% AOS, 1 wt% APG, and decane

Figure 17   Phase diagram for 3 wt% salinity, 1 wt% AOS, 2 wt% APG, and decane

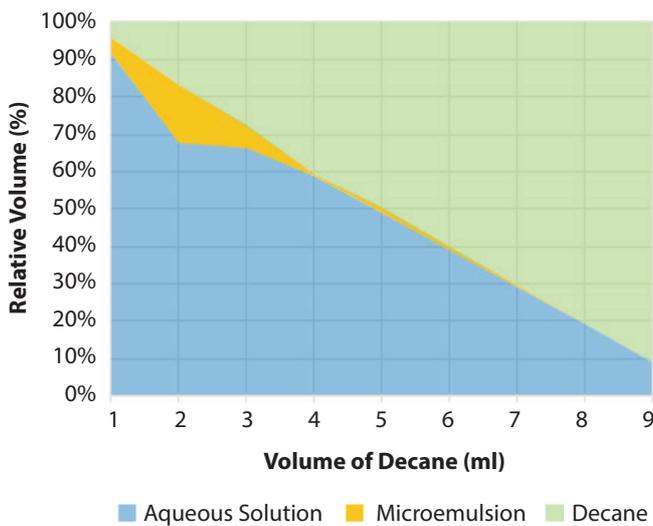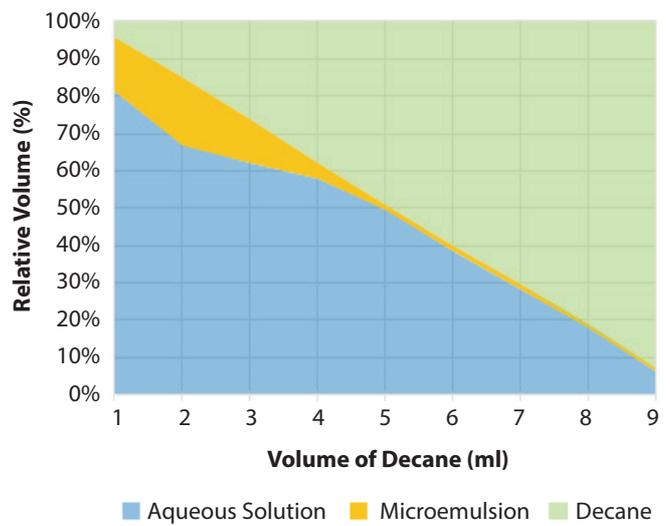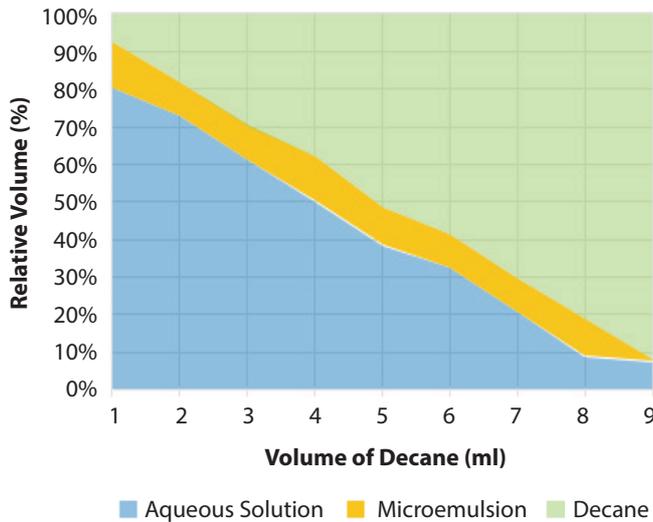**Figure 18** Phase diagram for 3 wt% salinity, 1 wt% AOS, 3 wt% APG, and decane
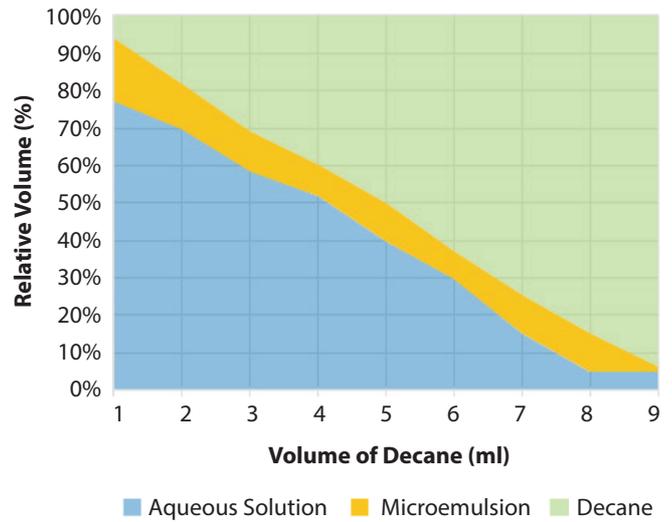

Figure 19 Phase diagram for 3 wt% salinity, 1 wt% AOS, 4 wt% APG, and decane

CONCLUSION

The results of this project showed the potential of a 'green' surfactant mixture which is the AOS and APG surfactant mixture, in chemical enhanced oil recovery application. Winsor Type-III microemulsion can be created with this surfactant mixture at a considerable high salinity condition of 3 wt%. In a research conducted by Belhaj et al. [20], it was mentioned that the water injection salinity of a Malaysia challenging oil field is at around 3 wt%. This means that the AOS and APG surfactant system could withstand the challenging condition of the Malaysia oil field.

Increasing AOS concentration will results in a reduction of the middle-phase microemulsion volume. This might be due to the high lipophilic nature of the surfactant system contributed by the high AOS concentration. 1 wt% AOS was chosen as the optimum surfactant concentration as the middle-phase microemulsion constantly appeared through a wide range of decane volumes.

For the last optimization stage, which is the cosurfactant optimization, it can be concluded that APG introduction into the surfactant system helped create middle-phase microemulsion. Without APG, AOS alone in the system could not create a stable middle-phase microemulsion hence, suggesting the need for a cosurfactant. At 3 and 4 wt% of APG, relatively high middle-phase microemulsion

volume can be seen appearing at a wide range of decane. This might be contributed by the alteration of the surfactant system's HLB value due to the introduction of APG, which is more hydrophilic than AOS. Thus, for the cosurfactant optimization, 3 wt% APG was chosen.

RECOMMENDATIONS

This project focuses on the phase behavior of a novel surfactant mixture which has AOS as the main surfactant and APG as the cosurfactant as a means to replace alcohol in creating Winsor Type-III microemulsion. This project could serve as the basis of further experiments on determining the potential of this 'green' surfactant in the application of chemical enhanced oil recovery. One of the experiments that could be done is the determination of IFT reduction between the oleic and aqueous phase with the determined optimum formulations. Supposedly, through the concept of Winsor Type-III microemulsion, ultra-low IFT values should be achieved.

In addition, further phase behavior studies can be conducted to investigate the effect of salinity hardness on the creation of Winsor Type-III microemulsion. In this project, only sodium chloride was used to synthesize the brine, and it can be considered as soft brine due to only sodium ions, Na^+ interacting with the surfactant system. Investigation of phase

behavior with hard brine such as Mg^+ and Ca^+ could display the potential or limitation of the surfactant mixture in creating Winsor Type-III microemulsion. Lastly, the effect of elevated temperature on the phase behavior could also be conducted to determine what is the limitation of the surfactant system to create Winsor Type-III microemulsion.

REFERENCES

[1] C.-D. Yuan, W.-F. Pu, X.-C. Wang, L. Sun, Y.-C. Zhang, and S. Cheng, "Effects of Interfacial Tension, Emulsification, and Surfactant Concentration on Oil Recovery in Surfactant Flooding Process for High Temperature and High Salinity Reservoirs," *Energy & Fuels,* 29, 10, pp. 6165-6176, 2015. doi: 10.1021/acs. energyfuels.5b01393.

[2] G. J. Hirasaki, C. A. Miller, and M. Puerto, "Recent Advances in Surfactant EOR," *SPE Journal,* 16, 04, pp. 889-907, 2011. doi: 10.2118/115386-pa.

[3] R. Pratiwi, R. Setiati, R. Andryan, F. Fadliah, and K. Fajarwati, "Initial screening of AOS, its performance in EOR to improve oil recovery," *Journal of Physics: Conference Series,* 1402, pp. 055013, 2019/12 2019. doi: 10.1088/1742-6596/1402/5/055013.

[4] J. J. Sheng, "Status of surfactant EOR technology," *Petroleum,* 1, 2, pp. 97-105, 2015/06/01/ 2015. [Online]. Available: https://doi.org/10.1016/j. petlm.2015.07.003.

[5] S. Adkins, G. P. Arachchilage, S. Solairaj, J. Lu, U. Weerasooriya, and G. Pope, "Development of Thermally and Chemically Stable Large-Hydrophobe Alkoxy Carboxylate Surfactants," in *SPE Improved Oil Recovery Symposium*, 2012, All Days, SPE-154256-MS, doi: 10.2118/154256-ms. [Online]. Available: https://doi. org/10.2118/154256-MS

[6] S. Liu, D. Zhang, W. Yan, M. Puerto, G. J. Hirasaki, and C. A. Miller, "Favorable Attributes of Alkaline-Surfactant-Polymer Flooding," *SPE Journal,* 13, 01, pp. 5-16, 2008, doi: 10.2118/99744-pa.

[7] C. Negin, S. Ali, and Q. Xie, "Most common surfactants employed in chemical enhanced oil recovery," *Petroleum,* 3, 2, pp. 197-211, 2017. doi: 10.1016/j. petlm.2016.11.007.

[8] A. M. Howe, A. Clarke, J. Mitchell, J. Staniland, L. Hawkes, and C. Whalan, "Visualising surfactant enhanced oil recovery," *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 480, pp. 449-461, 2015/09/05/ 2015. [Online]. Available: https://doi.org/10.1016/j. colsurfa.2014.08.032.

[9] A. Muggeridge *et al.*, "Recovery rates, enhanced oil recovery and technological limits," *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences,* 372, 2006, pp. 20120320, 2014. doi: doi:10.1098/rsta.2012.0320.

[10] O. Massarweh and A. S. Abushaikha, "The use of surfactants in enhanced oil recovery: A review of recent advances," *Energy Reports,* 6, pp. 3150-3178, 2020/11/01/ 2020. [Online]. Available: https://doi. org/10.1016/j.egyr.2020.11.009.

[11] M. S. Kamal, I. A. Hussein, and A. S. Sultan, "Review on Surfactant Flooding: Phase Behavior, Retention, IFT, and Field Applications," *Energy & Fuels,* 31, 8, pp. 7701-7720, 2017. doi: 10.1021/acs.energyfuels.7b00353.

[12] N. Pal, S. Kumar, A. Bera, and A. Mandal, "Phase behaviour and characterization of microemulsion stabilized by a novel synthesized surfactant: Implications for enhanced oil recovery," *Fuel,* 235, pp. 995-1009, 2019/01/01/ 2019. [Online]. Available: https://doi. org/10.1016/j.fuel.2018.08.100.

[13] S. N. Kale and S. L. Deore, "Emulsion micro emulsion and nano emulsion: a review," *Systematic Reviews in Pharmacy,* 8, 1, pp. 39, 2017.

[14] P. A. Winsor, "Solvent properties of amphiphilic compounds", B*utterworths Scientific Publications*, 1954.

[15] A. S. Adila, E. W. Al-Shalabi, and W. AlAmeri, "Recent Developments in Surfactant Flooding for Carbonate Reservoirs Under Harsh Conditions," in *Offshore Technology Conference Asia*, 2020, Day 1 Mon, November 02, 2020. doi: 10.4043/30318-ms. [Online]. Available: https://doi.org/10.4043/30318-MS

[16] Z. Jeirani, B. Mohamed Jan, B. Si Ali, I. M. Noor, C. H. See, and W. Saphanuchart, "Formulation and phase behavior study of a nonionic triglyceride microemulsion to increase hydrocarbon production," *Industrial Crops and Products,* 43, pp. 15-24, 2013/05/01/ 2013. [Online]. Available: https://doi.org/10.1016/j. indcrop.2012.07.004.

[17] J. A. Clark and E. E. Santiso, "Carbon Sequestration through CO2 Foam-Enhanced Oil Recovery: A Green

Chemistry Perspective," *Engineering,* 4, 3, pp. 336-342, 2018. doi: 10.1016/j.eng.2018.05.006.

[18]   G. Li, L. Chen, Y. Ruan, Q. Guo, X. Liao, and B. Zhang, "Alkyl polyglycoside: a green and efficient surfactant for enhancing heavy oil recovery at high-temperature and high-salinity condition," *Journal of Petroleum Exploration and Production Technology,* 9, 4, pp. 2671-2680, 2019. doi: 10.1007/s13202-019-0658-1.

[19]   B. Ghosh and D. Obasi, "Eco-Friendly Surfactant for EOR in High Temperature, High Salinity Carbonate Reservoir," in *SPE Enhanced Oil Recovery Conference*, 2013. All Days, SPE-165219-MS, doi: 10.2118/165219-ms. [Online]. Available: https://doi.org/10.2118/165219-MS

[20]   A. F. Belhaj, K. A. Elraies, S. M. Mahmood, R. D. Tewari, and A. A. Elryes, "A Comprehensive Surfactant Performance Assessment in Harsh Malaysian Reservoir Conditions," in *Offshore Technology Conference Asia*, 2020, Day 1 Mon, November 02, 2020. doi: 10.4043/30171-ms. [Online]. Available: https://doi.org/10.4043/30171-MS