

Bio-Surfactants with Various Types of Functional Groups of Fatty Acid Derivatives from Palm Oil which can be applied as EOR Surfactants from Low to High Temperature Reservoirs

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Abstract. Despite the sustainable development of energy sources, crude oil and natural gas resources remain important elements of the international economy. With global demand for petroleum and liquid fuels continuing to increase, increasing the efficiency of extraction from existing petroleum reserves is of paramount importance as the world gradually shifts from fossil fuels to more sustainable sources. To that end, Enhanced Oil Recovery (EOR) techniques have been developed and used to minimize the amount of crude oil and petroleum left in underground reservoirs from conventional drilling extraction methods. Surfactants that are widely used in the implementation of EOR are mostly petroleum-based which have challenges from availability, so that many studies have carried out the synthesis of surfactants using palm oil-derived fatty acids as hydrophobic groups and various functional groups as hydrophilic groups.

In this paper, three types of surfactants derived from palm oil will be testing, namely Alkyl Ester Alkoxy, Alkyl Ether Alkoxy, and Internal Ketone Sulfonate surfactants. The surfactants were filtered at 5000, 18000, and 20000 ppm salinity conditions at 60 and 110 °C. Screening carried out includes compatibility tests, IFT, and thermal stability. The type of oil used varies for each surfactant, namely the type of medium oil with 34.39 °API and heavy with 24.8 °API.

Based on experiments that have been carried out in the laboratory where Alkoxy Surfactants are surfactants that were tested at 1800 ppm salinity, 60 °C temperature, and 34.39 °API oil, they were able to produce IFT values up to 10⁻³ dyne/cm, with slightly cloudy compatibility. However, for thermal stability, this surfactant can only last up to 1 month. Whereas the Alkyl Ether Alkoxy surfactants which were tested under the same conditions were able to survive for 3 months of heating. In contrast to the Internal Ketone Sulfonate surfactant formula, the test was carried out at 20000 ppm salinity, 110 °C temperature, and heavy oil with 24.8 °API. Experiments carried out in the laboratory represent that the performance of surfactants derived from plants is capable of providing an IFT value of up to 10⁻³ dyne/cm, with slightly cloudy compatibility, and able to stable no degraded up to 3 months of thermal stability testing.

This shows experimentally and chemically structure, surfactants derived from vegetable materials can be applied as Chemical EOR up to a high-temperature reservoir of 110 °C. The activity of a surfactant does not only depend on where the raw material comes from but how the structure and functional groups are created from the raw material to produce surfactant molecules that have powerful abilities. However, it is

important to note that each type of surfactant with the same functional group but different carbon chain lengths and skeletal shapes will produce very different performances.

Keyword(s): Surfactant, Functional Group, Palm Oil, Chemical EOR

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1 Introduction

Most of the current world oil production comes from mature fields. Increasing oil recovery from the aging resources is a major concern for oil companies and authorities. In addition, the rate of replacement of the produced reserves by new discoveries has been declining steadily in the last decades. Therefore, the increase of the recovery factors from mature fields under primary and secondary production will be critical to meet the growing energy demand in the coming years [1].

A large amount of petroleum resources cannot be recovered by conventional methods. In general, the recovery can reach only 30–50% of original oil in place (OOIP) after water flooding. Inventions of new methods are required in order to supply the increased energy demand when the production with conventional method starts to decline. Oil and service companies have invested a lot in increasing recovery and productivity of mature reservoirs, especially in enhanced oil recovery (EOR) processes [2].

The literature information is not consistent regarding whether polymer flooding can lower residual oil saturation over waterflooding. Even though polymer flooding may reduce residual oil saturation [3,4], a significant portion of oil will remain in the reservoirs. To produce the residual oil, surfactants have to be injected. Therefore, surfactant EOR is a fundamental method.

The main functions of surfactants are to reduce interfacial tension and wettability alteration [5]. Surfactant EOR mechanisms are discussed separately according to these two functions.

The concept of applying surfactants in enhanced oil recovery was introduced in the early 1900's. The initial unsuccessful efforts led to the creation of a new revolutionary theory related to the possibility of producing in-situ surfactants. This idea was initiated from the fact that naphthenic acids exist in the reservoir, naturally. The main question to be answered about this technique was whether the soap or, in other words, the surfactant would be produced once an alkali is injected into the pore space of the rock. Although this method had the potential to reduce the cost of injecting synthetic surfactants, the results achieved were not convincing in order for the method to be announced successful. Finally in the 1960s, yet again the research in this area focused on the use of synthetic surfactants, however, this time mainly on designing surfactants tailored for each specific circumstance using the less expensive raw material. In the 1980's, combining the benefits of alkali and surfactants resulted in the invention of one of the most important methods of chemical EOR called alkaline-surfactant-polymer, (ASP). In addition, since variation in the formation water salinity, oil composition and temperature can affect the performance of the surfactants by impacting on the interfacial tension (IFT) and wettability, the optimum conditions for the application [6].

1.1 Significance of operational conditions

Decreasing interfacial tension and shifting reservoir wettability towards more water-wet are the main mechanisms of surfactant flooding in the reservoirs. To remove the alcohol and increase the solubilisation of oil and water in micro-emulsions, surfactants with branched hydrocarbon chains, adding ethylene oxide (EO), decreasing the hydrophilic propylene oxide (PO) groups to the surfactant are used [7]. Based on the



survey results, decreasing interfacial tension has long been the goal of chemists to enhance oil recovery by developing economical surfactant for sandstone reservoirs [8]. However, for carbonated reservoirs, reservoir engineers have been focusing on using cationic surfactants to drive the reservoir wettability from oil-wet to waterwet, thus accelerating the oil production rate by decreasing the residual oil saturation.

1.1.1 Temperature

Karnanda et al. [9] explained that most of the surfactant solutions have a cloud point temperature beyond which the solution becomes cloudy and measuring the IFT or other parameters become almost impossible. However, the anionic surfactants solution has a Krafft point temperature, suggesting that the surfactants would precipitate as the temperature is lower than the Krafft point temperature. At this point, a surfactant becomes ineffective and drops out of the aqueous solution. Depending on the surfactant structure the cloud point temperature can be between 30 °C and 160 °C. Temperature can affect the IFT and critical micelle concentration (CMC) of surfactant systems and this effect is greater for anionic surfactants. Surfactants' phase separation (cloud point) at high temperatures could likely lead to the decrease of surfactant's concentration, thus exhibiting poor performance to decrease IFT [7].

Also, increasing temperature can shorten the time of an interfacial tension to reach equilibrium for Gemini surfactant solutions. However, the temperature plays a minor role for a mixing surfactant system because of synergism [10]. Hiemenz and Rajagopalan [11] in their book define CMC as a concentration level, at and above which the micelles which are the aggregation of surfactant molecules starts to form. CMC is an important factor in studying surfactants. After this threshold, the surfactant behaviour, especially its surface tension, stabilizes and stays constant regardless of any increase in its concentration. Most of the experiments in the literature indicate that temperatures above 120 °C results in either degradation or precipitation of most of the surfactant.

1.1.2 Interfacial Tension (IFT)

Udeagbara [12] defines IFT as the force that exists between the molecules of the interface between two fluids. Subsequently, IFT holds these molecules together. A surfactant can reduce this force by getting adsorbed at the interface between two liquids or a liquid and a gas. Troy et al. in their book [13] explain that this force is often measured in dynes/cm and it can be affected by pressure, temperature, and the composition of each phase. Karnanda et al. [9] explained that lowering this force to low enough values can

increase the oil recovery significantly. This is because the IFT gives rise to capillary forces in the porous media which are mainly responsible for the hydrocarbon trapped in the form of residual saturation.

1.1.3 Optimal Salinity

In general, salinity has a significant effect on a surfactants' performance. In most of the cases, high salinity has an adverse impact on the efficiency of the surfactant, therefore in a high salinity situation the use of specifically developed surfactants with reasonable resistance towards this harsh environment is recommended. In an ideal situation, the goal should be to have an optimum salinity level for any particular surfactant. Hirasaki et al. [14,8] define the optimum salinity as a salinity at which equal quantities of oil



and water can be mutually solubilized into a micro-emulsion which results in equal IFTs between microemulsion phase and excess oil or excess water phase [15]. Also, the water solubilisation capacity of a particular microemulsion is closely related to the partition of co-surfactants among water, oil and interfaces, chain length and nature of oil [15-17]. Further research indicated that the IFT measured at the optimum salinity is the minimum achievable IFT during lab experiments for IFT measurements. S.I.Chou & Shah [18] observed in their experimental research that maximum oil recovery is obtained if the salinity of connate water or chemical slug is maintained at the optimal salinity of the selected surfactant.

1.1.4 *Surfactant Concentration*

Researchers all agree that concentration of the surfactant in a chemical slug always must be considerably above the critical micelle concentration so that micellization can be initiated. Hirasaki et al. [13], describe the reason as: at higher concentration more of the excess oil and water become solubilized and forms the middle phase or type III Winsor solution which leads to higher recovery. Therefore, low surfactant concentration is not desirable. Hirasaki et al. [13] reported that even if the concentration is higher than critical micelle concentrations but still close to it, the middle phase was instantaneous or not detected. On the other hand, it must be kept in mind that at a high concentration of surfactant end effect behaviour deviates from its normal. Apaydin & Kovsky [19] with their experiments showed that if the surfactant concentration is too high, it may cause the building of pressure gradient by end effect. This gradient will be from the outlet toward the inlet, against the direction of flow.

2 **Methodology**

2.1 *Materials*

The surfactants used in this study consisted of 3 types of surfactant formulas synthesized in Lemigas, Ministry of Energy and Mineral Resources, namely Alkyl Ester Alkoxy (PEG-400-Oleate) surfactant, Alkyl Ether Alkoxy OGEP-4, and from Solvay-Alliance namely Internal Surfactant Ketone Sulfonate (IKS-F). The salinities used were 10,000 ppm, 18,000 ppm, and 20,000 ppm with light, medium, and heavy oil types.

2.2 *Compatibility Test*

Compatibility tests are carried out to evaluate the solubility of surfactants as injection materials against injection water in a field that contains several mineral components, one of which is salinity. The surfactant solution was dissolved in water which had a salinity of 18000 ppm and the solubility of the injection material was observed visually at room temperature and reservoir temperature of 60 °C. Changes in surfactant solubility at 0, 1, 7, 14 and 30 days.

2.3 *Interfacial Tension Test (IFT)*

The ability of surfactant to decrease the IFT of oil and water as the main function of surfactant was evaluated by measuring the IFT using Spinning Drop Tensiometer TX-500 C/D dan SVT 25. Surfactant solution with different concentration at 10000 ppm, 18000 ppm, and 20000 ppm salinity was prepared and filled into the IFT tube. Two micro liters of oil were added and put into the IFT unit. Setting the device at 60 °C, 85 °C and 110 °C run the measurement at 6000 rpm.

3 **Result and Discussion**



The surfactants described in this paper are surfactants synthesized from vegetable materials. Previously, many studies have been carried out on chemical development for EOR, especially surfactants derived from petroleum-based. This paper shows amazing results, where surfactants derived from palm oil-based can be applied at high-temperature conditions and also only up to medium to low temperatures. Where this paper will explain that what will play an important role in the activity or ability of the surfactant itself is the final molecular shape and functional groups contained in the final molecule of the synthesis, not from the origin of the raw material.

3.1 Compatibility Test

Compatibility test is a test of surfactant solubility against injection water which will be used in dissolving surfactants for field applications. In laboratory testing, water is prepared by taking into account the hardness and salinity of the field injection water to be studied. In this study, the solubility test was carried out using water with a variation of salinity. The results of the experiment are presented in Table 1.

The compatibility test does not have a criterion value that has a threshold value, but insoluble and precipitated surfactants are considered not to meet the requirements in compatibility testing [Jia et al., 2018]. Based on observations, all experiments for the three types of surfactants with tests on different brine resulted in clear, cloudy, and milky surfactants. However, all surfactants are compatible and do not form precipitates. So that the surfactant meets the target compatibility test criteria.

Table 1. Result of Compatibility Test.

Surfactant Concentration (% w/w)	Compatibility						
	PEG-400- Oleate ^{a*}	PEG-400- Oleate ^{b*}	OGEP-4 ^{b*}	OGEP-4 ^{c*}	OGEP-4 ^{c**}	IKS-F ^{d***}	IKS-F ^{e***}
0.1	Clear	Clear	Clear	Clear	Clear	Clear	Clear
0.3	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Clear	Clear
0.5	Cloudy	Cloudy	Cloudy	Cloudy	Cloudy	Clear	Clear
0.8	-	-	-	-	-	Clear	Cloudy
1	Milky, No Precipitation	Cloudy	Cloudy	Milky	Milky	Clear	Cloudy
2	-	-	-	-	-	-	-

a) Salinity 10.000 ppm NaCl, b) Salinity 18.000 ppm Sintetic Brine, c) Salinity 18.000 ppm Native Brine, d) Salinity 20.000 ppm Sintetic Brine, and e) Salinity 20.000 ppm Native Brine
*) 60 °C, **) 85 °C, and ***) 110 °C

Based on Table 1, we can observe the behavior of the compatibility of surfactants under various brine conditions. The composition and concentration of brine affect compatibility. The presence of an average divalent ion makes the surfactant turbid (cloudy). So it is important to understand the water used for blending surfactants in chemical injection applications in the field. A salinity scan is also important in observing the compatibility of surfactants.

3.2 Interfacial Tension Test (IFT)

Surfactants to be applied as chemical EOR must be able to reduce the surface tension to a level of 10-3 dyne/cm. This paper identifies and proves that what determines the surfactant to be synthesized is not where the raw material comes from, but from the final structure of the compound being synthesized. The surfactants that were tested were surfactants from vegetable materials. These surfactants differ in the number of carbon chains and the types of functional groups they contain.



Based on Table 2, we can observe the bond strength we can conclude that the ether bond (OGEP-4) is better than the ester group (PEG-400-Oleate) which is easily hydrolyzed. Furthermore, the sulfonate group (IKS-F) with a long carbon chain (C22-C24) is also better than the ether group with a short chain (C18).

Table 2. IFT values for CMC surfactants PEG-400 Oleate, OGEP-4, and IKS-F

Surfactant Concentration (% w/w)	Compatibility						
	PEG-400-Oleate ^{a*}	PEG-400-Oleate ^{b*}	OGEP-4 ^{b*}	OGEP-4 ^{c*}	OGEP-4 ^{c**}	IKS-F ^{d***}	IKS-F ^{e***}
0.1	1.17E+00	1.20E+00	1.17E+00	1.17E+00	4.33E-01	-	-
0.3	3.10E-03	6.20E-03	3.10E-03	6.10E-03	2.70E-02	-	-
0.4	-	-	-	-	-	3.99E-03	2.21E-02
0.5	9.04E-04	2.40E-02	5.04E-03	9.04E-03	7.97E-03	1.95E-03	1.19E-02
0.6	-	-	-	-	-	1.28E-03	9.81E-03
0.8	-	-	-	-	-	1.84E-03	7.91E-03
1	1.23E-02	1.03E-01	1.98E-01	2.98E-01	3.84E-01	2.38E-03	4.12E-03
1.2	-	-	-	-	-	3.15E-03	1.06E-02

a) Salinity 10.000 ppm NaCl, b) Salinity 18.000 ppm Sintetic Brine, c) Salinity 18.000 ppm Native Brine, d) Salinity 20.000 ppm Sintetic Brine, and e) Salinity 20.000 ppm Native Brine

*) 60 °C, **) 85 °C, and ***) 110 °C

Based on Table 2, we can also see that surfactants PEG-400-Oleate, OGEP-4, and IKS derived from vegetable-based products show good performance with IFT values up to 10^{-3} dyne/cm. These results also show that surfactants synthesized from vegetable sources with several modifications and reaction steps are capable of producing IKS surfactant compounds. IKS surfactants are able to work to reduce IFT up to 10^{-3} dyne/cm at very high temperature and salinity, 20000 ppm salinity, and 110 °C temperature.

Conclusion

Based on experiments that have been carried out in the laboratory where Alkoxy Surfactants are surfactants that were tested at 1800 ppm salinity, 60 °C temperature, and 34.39 °API oil, they were able to produce IFT values up to 10^{-3} dyne/cm, with slightly cloudy compatibility. However, for thermal stability, this surfactant can only last up to 1 month. Whereas the Alkyl Ether Alkoxy surfactants which were tested under the same conditions were able to survive for 3 months of heating. In contrast to the Internal Ketone Sulfonate surfactant formula, the test was carried out at 20000 ppm salinity, 110 °C temperature, and heavy oil with 24.8 °API. Experiments carried out in the laboratory represent that the performance of surfactants derived from plants is capable of providing an IFT value of up to 10^{-3} dyne/cm, with slightly cloudy compatibility, and able to stable no degraded up to 3 months of thermal stability testing.

References

- [1] Vladimir Alvarado and Eduardo Manrique 2. 2010. Enhanced Oil Recovery: An Update Review. *Energies* 2010, 3, 1529-1575; doi:10.3390/en3091529
- [2] Wimpy Karnanda & M. S. Benzagouta & Abdulrahman AlQuraishi & M. M. Amro. 2012. Effect of temperature, pressure, salinity, and surfactant concentration on IFT for surfactant flooding optimization. *Arab J Geosci* (2013) 6:3535–3544 DOI 10.1007/s12517-012-0605-7



- [3] J.-G. Niu, P. Chen, Z.-B. Shao, D.-M. Wang, G. Sun, Y. Li, Research and development of polymer enhanced oil recovery, in: H.-Q. Cao (Ed.), *Research and Development of Enhanced Oil Recovery in Daqing*, Petroleum Industry Press, 2006, pp. 227e325.
- [4] D.M. Wang, Development of new tertiary recovery theories and technologies to sustain Daqing oil production, *P.G.O.D.D.* 20 (3) (2001) 1e7.
- [5] J.J. Sheng, Comparison of the effects of wettability alteration and IFT reduction on oil recovery in carbonate reservoirs, *Asia-Pac. J. Chem. Eng.* 8 (1) (2013) 154e161.
- [6] Chegenizadeh Negin, Saeedi Ali, Quan Xie. 2017. Most common surfactants employed in chemical enhanced oil recovery. *Petroleum* 3 (2017) 197e211. <http://dx.doi.org/10.1016/j.petlm.2016.11.007>
- [7] G. Hirasaki, C.A. Miller, M. Puerto, *Recent Advances in Surfactant EOR*, 2011.
- [8] J.J. Sheng, Status of surfactant EOR technology, *Petroleum* 1 (2) (2015) 97e105.
- [9] W. Karnanda, M.S. Benzagouta, A. AlQuraishi, M.M. Amro, Effect of temperature, pressure, salinity, and surfactant concentration on IFT for surfactant flooding optimization, *Arab. J. Geosci.* 6 (9) (2013) 3535e3544.
- [10] Z. Ye, F. Zhang, L. Han, P. Luo, J. Yang, H. Chen, The effect of temperature on the interfacial tension between crude oil and gemini surfactant solution, *Colloids Surfaces A Physicochem. Eng. Aspects* 322 (1) (2008) 138e141.
- [11] P.C. Hiemenz, R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, third ed., Taylor & Francis, New York, 1997. Revised and Expanded.
- [12] S.G. Udeagbara, *Effect of Temperature and Impurities on Surface Tension of Crude Oil*, reprint), Universal Publishers, USA, 2010.
- [13] D.B. Troy, J.P. Remington, P. Beringer, *Remington: the Science and Practice of Pharmacy*, illustrated, Lippincott Williams & Wilkins, USA, 2006.
- [14] G. Hirasaki, C.A. Miller, M. Puerto, Recent advances in surfactant EOR, *SPE J.* 16 (04) (2011).
- [15] A. Bera, K. Ojha, T. Kumar, A. Mandal, Water solubilization capacity, interfacial compositions and thermodynamic parameters of anionic and cationic microemulsions, *Colloids Surfaces A Physicochem. Eng. Aspects* 404 (2012) 70e77.
- [16] A. Bera, T. Kumar, K. Ojha, A. Mandal, Screening of microemulsion properties for application in enhanced oil recovery, *Fuel* 121 (2014) 198e207.
- [17] A. Bera, K. Ojha, A. Mandal, T. Kumar, Interfacial tension and phase behavior of surfactant-brine-oil system, *Colloids Surfaces A Physicochem. Eng. Aspects* 383 (1e3) (2011) 114e119.
- [18] S.I. Chou, D.O. Shah, The optimal salinity concept for oil displacement by oil-external microemulsions and graded salinity slugs, *J. Can. Petr. Technol.* 20 (03) (1981).
- [19] O.G. Apaydin, A.R. Kovscek, O.G. Apaydin, A.R. Kovscek, Surfactant concentration and end effects on foam flow in porous media, *Transp. Porous Media* 43 (3) (2001) 511e536.

Acknowledgments

This paper is the result of collaboration between the Research Centre for Oil and Gas Technology “LEMIGAS” and Organic Synthesis Laboratory of Chemistry, Bandung Institute of Technology. Special thanks to Prof. Yana Maulana Syah for NMR measurement. We greatly appreciate the financial support from DIPA Research Center for Oil and Gas Technology “LEMIGAS”.