

A Novel Sulfonated Alkyl Ester Surfactant to Reduce Oil-Water Interfacial Tensions in Wide Range Salinity with Monovalent and Divalent Ions

Taufan Marhaendrajana¹, Rani Kurnia¹, Deana Wahyuningrum² & Iqbal Fauzi¹

¹ Petroleum Engineering, Institute Technology of Bandung, Bandung, Indonesia

² Chemistry, Institute Technology of Bandung, Bandung, Indonesia

Correspondence: Taufan Marhaendrajana, Petroleum Engineering, Institute Technology of Bandung, Bandung, Indonesia. E-mail: tmarhaendrajana@tm.itb.ac.id

Received: September 8, 2015

Accepted: November 1, 2015

Online Published: December 22, 2015

doi:10.5539/mas.v10n1p93

URL: <http://dx.doi.org/10.5539/mas.v10n1p93>

Abstract

A novel sulfonated alkyl ester (SAE) was developed. The sulfonated alkyl ester has unique chemical structure that is aimed to combine the advantages of ester-based and sulfonate-based surfactant in one compound. This surfactant was studied for its performance to reduce oil-water interfacial tensions in a wide range of salinity with monovalent and divalent ions and in a light and heavy oil samples. The study showed that the sulfonated alkyl ester surfactant gives a good performance in a light oil sample in a high monovalent ion concentration and also give a good performance in a heavy oil sample in both low and high concentration of monovalent and divalent ions solution.

Keywords: sulfonated alkyl ester, light oil, heavy oil

1. Introduction

A surface active agents or commonly known as surfactant is one of chemical that has a very wide range of applications. Its ability to lower the oil-water interfacial tension and to form a micro-emulsion makes surfactant widely used in oil industries to enhance recovery. Studies in this area still continue developing to improve the effectiveness of surfactant in improving oil recovery at various oil/rock characteristics and reservoir conditions.

There are four type of surfactants based on its head group charges: nonionic, anionic, cationic and amphoteric. In its application in reservoir sandstone, nonionic and anionic surfactants are commonly used to prevent adsorption of the surfactant on the rock. Nonionic surfactant generally has a good solubility in water, low CMC (Muherei & Junin, 2008), favorable in industrial uses because of its weak foaming property, widely useful as emulsifying and dispersing agent (Fujimoto, 1985), has a good stability in high salinity condition (Muherei & Junin, 2008). However, nonionic surfactant is not really good to apply in a high temperature condition (Salanger, 2002; Fujimoto, 1985). On the other side, an anionic surfactant has a different characteristic from nonionic surfactant. Anionic surfactant has a good solubility in water and mostly stable in a high temperature condition, especially when the hydrophilic groups are coming from sulfonate or sulfate compound (Puerto, Hirasaki, Miller, & Barnes, 2011). However, there are still some disadvantages of anionic surfactant, such as it cannot be applied at an existence of divalent ion in a high concentration and has a high CMC (Critical Micelle Concentration) (Fujimoto, 1985).

Surfactant has been studied in a various parameters and it still develops to fit with a various reservoir conditions. A few recent studies investigate an effect of combining a different type of surfactant could give a better results in some aspects. Liu et al. investigated the influences given, in term of lowering an interfacial tension in water-alkanes interfaces, by anionic surfactant when it added to nonionic surfactant. The study shows that by adding a nonionic surfactant to an anionic surfactant solutions, gives a significant results in lowering the interfacial tensions.

1.1 Sulfonated Alkyl Ester

There are a lot of studies related to the development of surfactant, both in terms of structure or formulation, for its application in EOR. There are several sulfonate based surfactants that are still being developed or has been

applied for EOR purposes, including a conventional alkyl sulfonates, alkylarylsulfonates, internal olefin sulfonates, arylalkylsulfonates and methyl ester sulfonates (Figure 1).

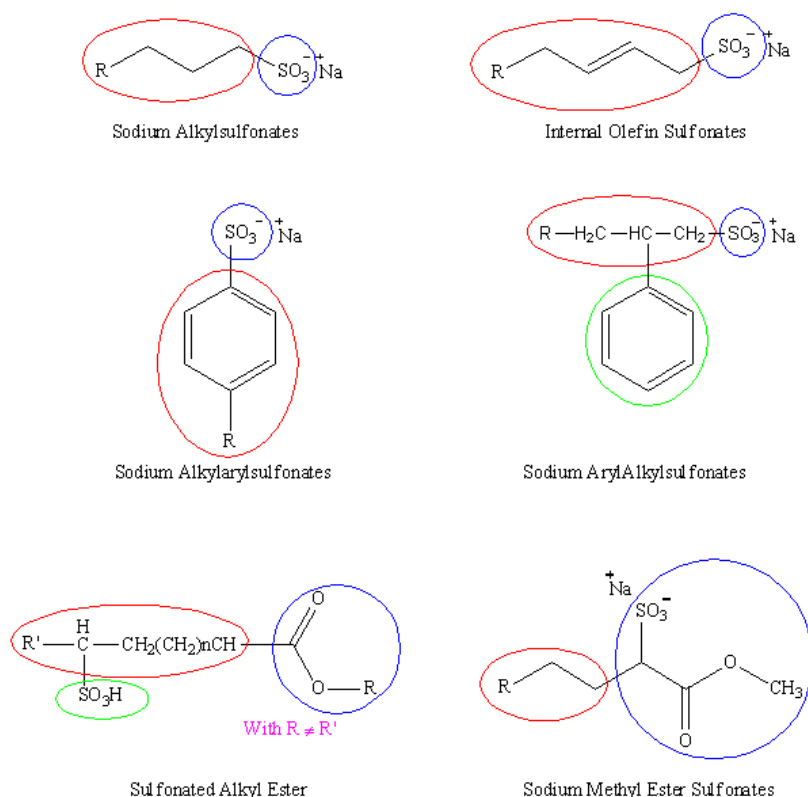


Figure 1. A chemical structure of common sulfonate based surfactant which are widely used in EOR compared to sulfonated alkyl ester; blue circle indicates hydrophilic group, red circle indicates hydrophobic group and green circle indicates side group

Sulfonate-based surfactant provides a various advantages in its application, such as a good solubility in water (Farn, 2006), can be used in acid solution (Farn, 2006) and good stability in high temperature condition (Fujimoto, 1985). However, a sulfonate-based surfactant has a high CMC value and also poor resistance through high salinity, mainly to the presence of divalent ions (Fujimoto, 1985). Depending on brine and oil characteristics, in some cases, a sulfonate based surfactant cannot reach a low interfacial tension value ($\approx 10^{-3}$ mN/m). For example, one of recent studies about development of one type of sulfonate based surfactant is methyl ester sulfonate that has been synthesized by using a non-petrochemical. It resulted a lowest possible IFT of 0.19 mN/m at concentration of surfactant of 1%wt with an addition of 0.5% wt carbonate (Majidaie, Mushtaq, Tan, Demiral, & Lee, 2012).

In this paper, the study was conducted to analyze a performance of novel sulfonates surfactant that is developed by our laboratory, called sulfonated alkyl ester (SAE). The sulfonated alkyl ester (SAE) surfactant has a unique chemical structure by combining ester groups (nonionic) and sulfonate groups (ionic) in one compound. By combining these two chemical groups, the sulfonated alkyl ester will have a head group that can act as a hydrophilic group and a side groups (branch) attached to the hydrophobic tail-group that also can act as a hydrophilic head group.

The sulfonated alkyl ester surfactant has a different chemical structure from a common sulfonate surfactant i.e. methyl ester sulfonate (MES). Unlike other sulfonates surfactant that usually use alkyl or aryl as its side chains and use the sulfonate group as its hydrophilic group, the SAE surfactant used sulfonate groups as a side chains. The sulfonate group in this surfactant is not attached to the carbon near the functional group as methyl ester sulfonate. In the MES surfactant, the sulfonate group acts as a part of head hydrophilic group and it made MES becomes an anionic surfactant (Figure 2b). In the sulfonated alkyl ester (SAE) surfactant, the sulfonate group do not act as a head group but as a branch (Figure 2a).

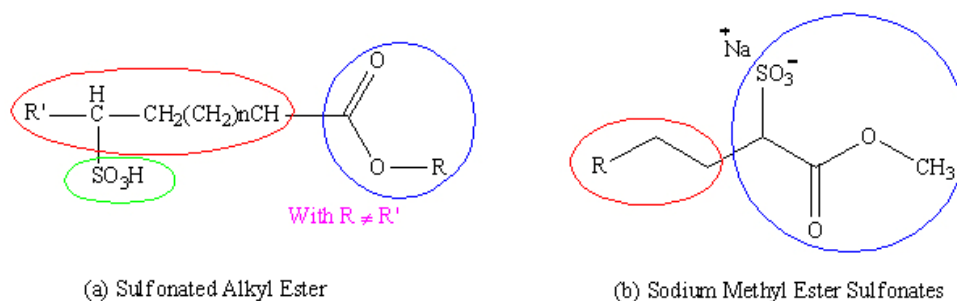


Figure 2. Difference between the chemical structures of sulfonated alkyl ester (a) and methyl ester sulfonate (b) surfactant

By having a side groups (branch) at the hydrophobic groups, surfactant will have a better wetting (penetrating) effect than those hydrophobic groups without side chains (Fujimoto, 1985). And by attaching the sulfonate group as a branch or a side group, the sulfonated alkyl ester surfactant molecules will have a wider coverage of surface area. It is because the structure of SAE molecules is bulky, therefore it would make a spacious area between the molecules itself and would make its interaction to water and oil at its interface becomes more effective. It can be seen on Figure 3a, the sulfonated alkyl ester surfactant molecules have a wider space between themselves than the unbranched surfactants (Figure 3b) (Miller & Neogi, 1985).

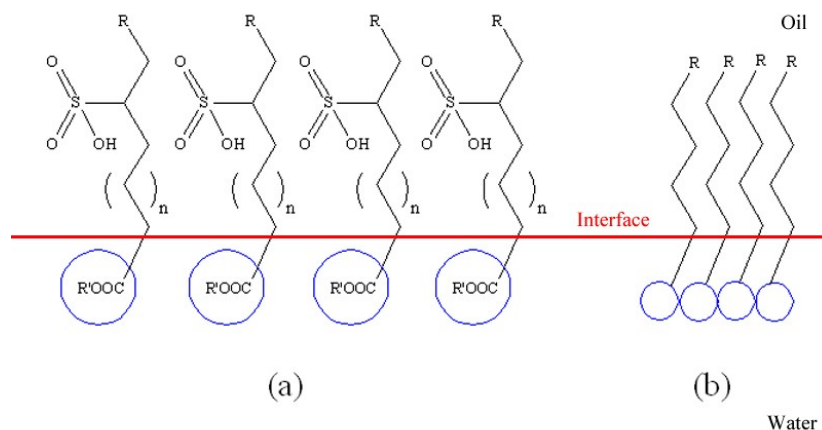


Figure 3. Sketch of the arrangement of sulfonated alkyl ester surfactant molecules (a) and the unbranched surfactant molecules (b) at the interface of oil and water

On the other side, a surfactant from the ester groups has a good resistance to divalent ion unlike the sulfonate groups and it has a low CMC. By combining these advantages from both sulfonate and ester group surfactant, the sulfonated alkyl ester (SAE) surfactant is expected to be worked well on different types of oil (light to heavy oil) and in a fairly wide range of salinity contains monovalent and divalent ions.

Therefore, in this study, the sulfonated alkyl ester (SAE) surfactant was tested for its compatibility in both light and heavy oil characteristics to lower the interfacial tension in a wide range of brine salinity and variation of monovalent and divalent ions.

2. Method

2.1 Surfactant

The sulfonated alkyl ester surfactant was synthesized and characterized at Bioorganic and Organic Synthesis Laboratory–Chemistry Study Program, Institute Technology Bandung.

2.2 Oil Samples and Brine

The sulfonated alkyl ester surfactant was tested for its compatibility with light oil and heavy oil from two different oil fields.

Table 1. Characteristics of oil samples

Characteristics	Light Oil Sample	Heavy Oil Sample
SARA		
<i>Saturated (%)</i>	61.2	52.7
<i>Aromatics (%)</i>	33.12	32.4
<i>Resins (%)</i>	4.82	0.0
<i>Asphaltenes (%)</i>	0.84	2.9
EACN (Equivalent Alkane Carbon Number)	8.7	12.8
Viscosity (cP) at 68 °C	2.32	51.9
API Gravity	42.2	16.8

2.3 Aqueous Stability

This measurement was conducted to analyze the ability of this surfactant to dissolve in both monovalent and mixtures of monovalent and divalent ions solutions. Variations in the concentration of surfactant tested were ranged between 0.4–2 %w/w was dissolved in a variation of monovalent ion in the concentration of 10,000; 30,000; 50,000; 100,000 and 200,000 ppm. This surfactant was also tested for its ability to dissolve in the existence of calcium chloride as the source of divalent ion with a variation of the concentrations from 50 to 750 ppm.

2.4 Aqueous Stability

This measurement was conducted to determine the sulfonated alkyl ester surfactant ability to lower the interfacial tension and to determine its CMC in oil samples using Tensiometer TX-500D at 68 ± 0.5 °C with 6000 rpm of rotation for 30 minutes. Salinity scan was performed by measuring the decrease in the value of the interfacial tension due to the changes in the type and concentration of salts, either monovalent or divalent salt. Variation in the concentration of surfactant tested was ranged between 0.4–2 %w/w. As for the salt used in this test are sodium chloride with variation in the concentration of 10,000; 30,000; 50,000; 100,000 and 200,000 ppm. The surfactant was also tested for its compatibility with the mixtures of salts containing monovalent and divalent ions at the optimum salinity of the monovalent ion salt. Calcium chloride was used as the source of divalent ion with a variation of the concentrations from 50 to 750 ppm.

3. Results

3.1 Sulfonated Alkyl Ester (SAE) Surfactant Performance in Monovalent Ion Solutions

The sulfonated alkyl ester (SAE) surfactant has been tested for its performance in a monovalent solution. Sodium chloride was used for monovalent ion solution in the concentration range between 10,000 to 200,000 ppm. It can be seen on Table 2 that this surfactant can dissolve in a wide range of concentration and sodium chloride concentration.

Table 2. Aqueous stability test for the sulfonated alkyl ester (SAE) surfactant in a different concentration of sodium chloride solutions

[SAE] % w/w	Aqueous stability at concentration of NaCl (ppm)				
	10,000	30,000	50,000	100,000	200,000
0.4	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve
0.6	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve
0.8	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve
1.0	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve
1.2	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve
1.5	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve
2.0	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve

At interfacial tension measurement with light oil, the SAE surfactant shows a lower interfacial tension in a high concentration of sodium chloride. It can be seen in Figure 4 that the sulfonated alkyl ester surfactant reaches a low interfacial tension ($\approx 10^{-3}$ mN/m) at salinity of 100,000 ppm sodium chloride. At lower salinity, the sulfonated alkyl ester hydrophilic group has a stronger interaction with water than the interaction between sodium chloride with water. The sulfonated alkyl ester hydrophobic group interaction with oil also cannot balance its hydrophilic interaction with water. As the result, the interfacial tension of this surfactant at low salinity could not achieve a low interfacial tension.

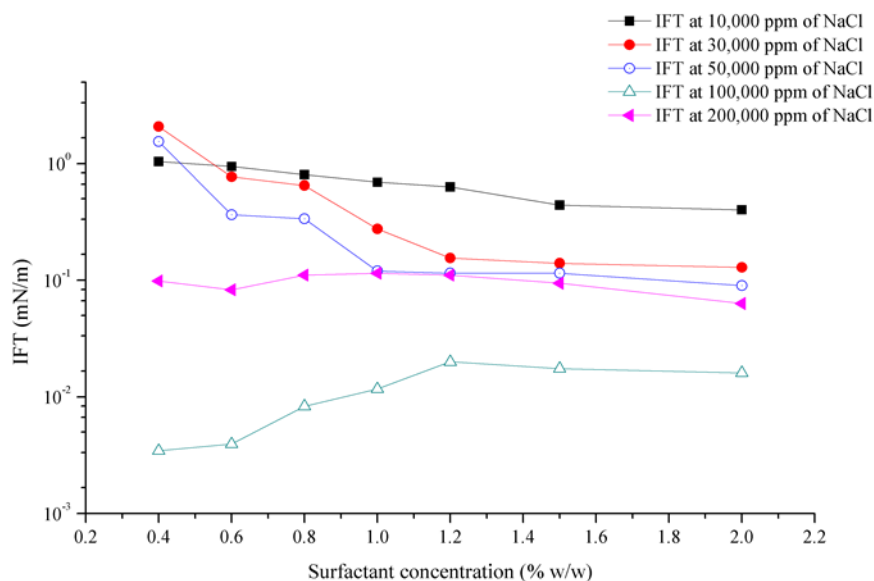


Figure 4. Interfacial tension measurements data of various concentrations of sulfonated alkyl ester dissolved in various concentrations of sodium chloride applied to the light oil sample

The interfacial tension measurement of sulfonated alkyl ester in a different concentration of surfactant and sodium chloride concentration decreased with increasing concentration of surfactant. The SAE surfactant reaches a low interfacial tension at concentration of 100,000 ppm sodium chloride. The lowest interfacial tension is reached at surfactant concentration of 0.4 %wt and increase significantly after the concentration of surfactant 0.8 %wt. At this point, it can be said that the sulfonated alkyl ester surfactant has reached its micelle concentration.

But along with the increase of sodium chloride concentration, the interaction of the hydrophilic group with water can be reduced. The interaction between sodium chloride and water is an ionic-dipole and it is stronger than the interaction between the hydrophilic group and water which is a dipole-dipole interactions (hydrogen interaction) (Atkins & De Paula, 2006). It can be seen on Figure 4 that the CMC decreases along with the increasing of sodium chloride concentration. But there is no significant change in the interfacial tension value when the concentration of sodium chloride is 200,000 ppm.

Different results of interfacial tension measurement were given by sulfonated alkyl ester (SAE) surfactant when it was applied to a heavy oil sample. It can be seen that sulfonated alkyl ester surfactant has a wider range of concentration that gives a low interfacial tension ($\approx 10^{-3}$ mN/m). Figure 5 show that SAE surfactant gives a low interfacial tension value at a surfactant concentration of 1.2 and 1.5 %wt with 10,000 ppm of sodium chloride. A wider range concentration at low IFT is given by the SAE surfactant when the concentration of sodium chloride increased to 30,000; 50,000 and 100,000 ppm. The widest range of sulfonated alkyl ester surfactant concentration is reached when the concentration of sodium chloride at 30,000 ppm. The SAE surfactant gives a low interfacial tension values in a range concentration between 0.4 to 1.5 %wt, it also gives an ultra-low interfacial tension ($\approx 10^{-4}$ mN/m) at concentration of 0.4; 0.8 and 1.2 %wt.

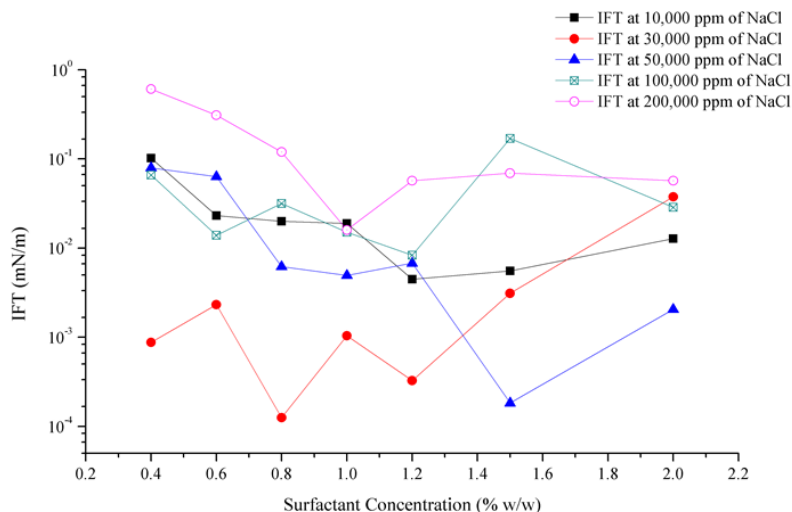


Figure 5. Interfacial tension measurements data of various concentrations of sulfonated alkyl ester dissolved in various concentrations of sodium chloride applied to the heavy oil sample

3.2 Sulfonated Alkyl Ester (SAE) Surfactant Performance in a Mixture of Monovalent and Divalent Ions Solution

The sulfonated alkyl ester (SAE) surfactant was also tested by using a mixture of monovalent and divalent ions solution. Calcium chloride was used as a divalent ion and added to each optimum concentration of sodium chloride, either in light and heavy oil, in a different concentration.

The optimum sodium chloride concentration for light oil sample reached at 100,000 ppm with a concentration of surfactant at 0.4 %wt. A variation in concentrations of calcium chloride was added to its optimum condition for light oil with a concentration range between 50 to 400 ppm (Table 3). The mixture of sulfonated alkyl ester surfactant (0.4 %wt), sodium chloride (100,000 ppm) and calcium chloride (> 400 ppm) formed a two phase solution. It can be said that the optimum of calcium chloride in optimum condition for light oil is 400 ppm, because the concentration of sodium chloride in solution system is already very high. This will cause the solubility of the sulfonated alkyl ester surfactant in the solution system will decrease.

Table 3. Aqueous stability test for the sulfonated alkyl ester (SAE) surfactant in 100,000 ppm NaCl added with various concentrations of calcium chloride for light oil

[SAE] wt %	Aqueous stability with an addition of CaCl ₂ (ppm) to 100,000 ppm of NaCl				
	50	100	200	300	400
0.4	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve

Different results were given if calcium chloride is added to the optimum conditions for heavy oil. It can be seen in Table 4 that the mixture of SAE surfactant (0.8 %wt), sodium chloride (30,000 ppm) and calcium chloride give a wider range that still form a one phase solution. The maximum concentration of calcium chloride reached at 750 ppm. After this concentration, the solution system will form two phase.

Table 4. Aqueous stability test for the sulfonated alkyl ester (SAE) surfactant in 100,000 ppm NaCl added with various concentrations of calcium chloride for heavy oil

[SAE] wt %	Aqueous stability with an addition of CaCl ₂ (ppm) to 30,000 ppm of NaCl				
	50	100	250	500	750
0.8	Dissolve	Dissolve	Dissolve	Dissolve	Dissolve

The existence of divalent ions greatly affects the solubility of the surfactant in water and also other measurement

parameters. Therefore it is important if the surfactant can work well despite with the existence of divalent ions. Even in a low concentration of SAE surfactant, it still can dissolve in the concentration range of sodium chloride and calcium chloride quite wide.

But despite the sulfonated alkyl ester surfactant can dissolve well in a solution system with a high concentration of sodium chloride and calcium chloride, there is a significant increase in the IFT measurement results by using a light oil sample. It can be seen in Figure 6 that even in an addition of calcium chloride at 50 ppm, the interfacial tension value increase from 3.46×10^{-3} mN/m to 1.97×10^{-1} mN/m.

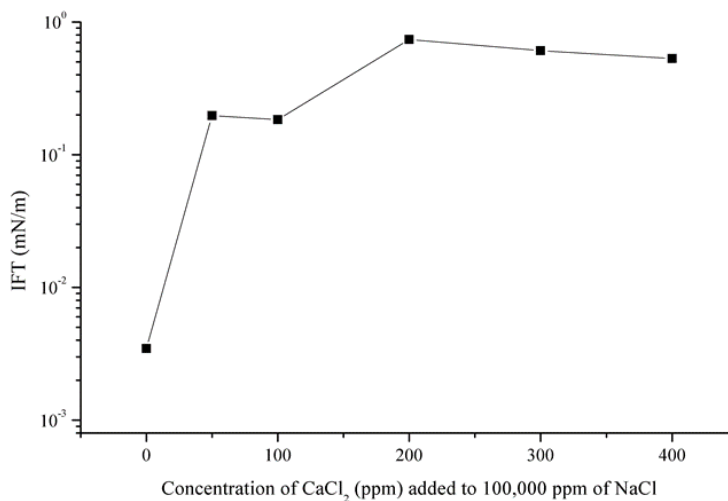


Figure 6. Interfacial tension measurement result with variations of calcium chloride concentration added to 100,000 ppm of sodium chloride for light oil

It is different when calcium chloride was added to the optimum condition for heavy oil. In its optimum condition for heavy oil, the sulfonated alkyl ester surfactant is more resistant to an addition of divalent ion, even in a high concentration. In Figure 7, it can be seen that the interfacial tension value is relatively stable in a wide range of calcium chloride concentration and still in a range of low interfacial tension ($\approx 10^{-3}$ mN/m).

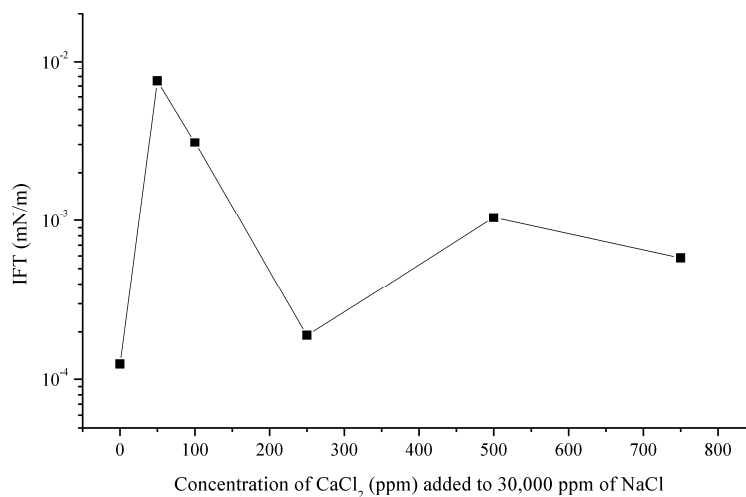


Figure 7. Interfacial tension measurement result with variations of calcium chloride concentration added to 30,000 ppm of sodium chloride for heavy oil

3.3 Effect of Oil Compositions on the Performance of SAE Surfactant to Reduce Oil-Water Interfacial Tensions

For displacement of oil in the pores by surfactant, a low interfacial tension ($\approx 10^{-3}$ mN/m) between water and oil

is generally required (Rosen, 2004). When the balance between hydrophilic and hydrophobic groups of the surfactant in the particular system (ex: water-oil system) is reached, a low interfacial tension value will be given by surfactant (Rosen, 2004; Witthayapanyanon, Acosta, Harwell, & Sabatini, 2006).

The balance of this interaction is described by the Winsor ratio (R). The Winsor ratio is convenient for relating changes in the hydrophilic solvent (W), the hydrophobic solvent (O), and the surfactant (C) to interfacial tensions and phase volumes and for the explaining them in terms of the molecular interactions involved (Bourrel, Verzaro, & Chambu, 1987; Rosen, 2004). The Winsor ratio described in an equation,

$$R = \frac{A_{CO} - A_{OO} - A_{HB}}{A_{CW} - A_{WW} - A_{HL}} \tag{1}$$

A_{CO} and A_{CW} are the interaction strengths per unit area of interface of C with oil and water, respectively, promoting solubilization of the other liquid phase; A_{OO} and A_{WW} are the respective self-interaction strengths of the solvent molecule in oil and water, respectively, opposing solubilization into them; A_{HB} and A_{HL} are the strengths of the self-interactions between the lipophilic and hydrophilic portions, respectively, of the surfactant molecules, also opposing solubilization. The lowest interfacial tensions will be reached when the Winsor ratio $R \cong 1$.

The effect of oil composition to interfacial tensions for this surfactant can be explained by using equation above. The sulfonated alkyl ester has a carbon chains on its hydrophobic groups greater than 12 with sulfonate group attached as a side chain. And for the EACN value for light oil and heavy oil samples are 8.7 and 12.8, respectively.

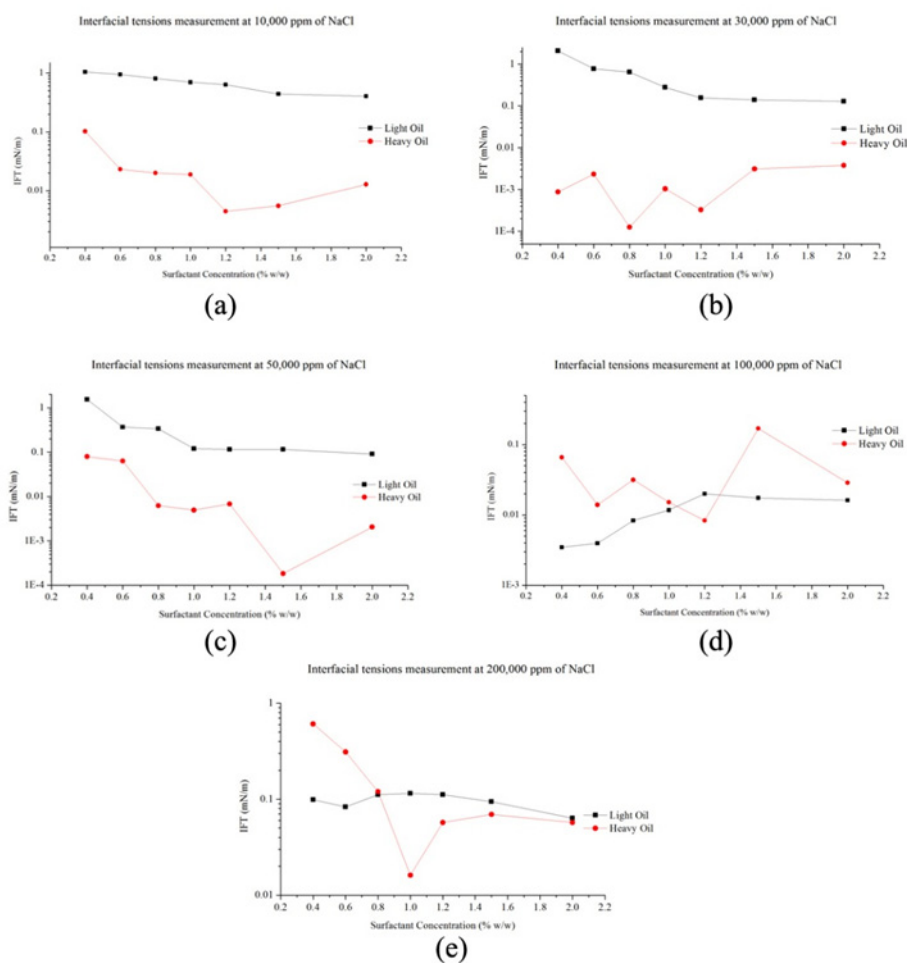


Figure 8. Interfacial tension measurements for light oil and heavy oil samples in particular sodium chloride concentrations

It can be seen in Figure 8 that the sulfonated alkyl ester works more effective when using a heavy oil sample in resulting a low interfacial tension values. In the range of sodium chloride concentrations from 10,000 to 50,000 ppm, the interfacial tensions value by using a light oil sample constantly above the interfacial tension value by using a heavy oil sample. It can be said that the interaction strengths per unit area of interface (A_{CO}) between the SAE surfactant with heavy oil is greater than light oil. This is also suitable with the EACN value for each oil sample and the hydrophobic length of SAE surfactant. The EACN value of heavy oil is greater than light oil samples which cause the interaction between the hydrophobic groups of SAE surfactant with heavy oil is stronger.

For the light oil case, the SAE surfactant can reach a low interfacial tension when the concentration of sodium chloride is 100,000 ppm (Figure 8d). When the sodium chloride concentration is lower than 100,000 ppm, the interaction strengths per unit area of interface between the SAE surfactant hydrophilic groups (A_{CW}) with water is still strong and it makes the Winsor ratio $R \ll 1$ because A_{CO} also not strong enough to balance the strength of it. But when the existence of sodium chloride is greater in the system, it will cause the decreasing of interaction between hydrophilic groups of SAE surfactant with water. The decreasing of this interaction strength will balance the Winsor ratio (R) and gives a low interfacial tension for light oil. But the decreasing of this interaction strength (A_{CW}) gives a different effect for heavy oil sample. The EACN value of heavy oil is higher than light oil, it makes the A_{CO} gives a higher contribution than A_{CW} and it results the Winsor ratio $R \gg 1$. As the results, the decreasing interfacial tensions when using a heavy oil with a high concentration of sodium chloride is not as low as when the concentration of sodium chloride is low.

In the light oil sample used, there is an amount of resins in its composition (Table 1). Resins are components with a highly polar end group and long alkane tails, which can be considered as a “large surfactant”. It can be a disadvantage if surfactant is applied to oil with resin content, because these molecules are often surface active (Buijse, Prelicz, Barnes, & Cosmo, 2010).

Conclusions

The sulfonated alkyl ester surfactant has been analyze for its performance in a wide range of salinity by using monovalent and mixture of monovalent and divalent ions solutions. It gives a good performance in both of solubility and interfacial tension measurement by using light and heavy oil samples. The sulfonated alkyl ester surfactant works well in a high salinity of monovalent ion (100,000 ppm) and gives a low interfacial tension. A better results given by the sulfonated alkyl ester surfactant when tested using heavy oil sample. It gives a wider range of concentration of surfactant and monovalent ions that gives a low interfacial tension value. But the SAE surfactant seems to be limited in its application to reduce the interfacial tensions for type of oil with resins content. Further studies to analyze this limitation remain to be done.

References

- Atkins, P., & De Paula, J. (2006). *Physical Chemistry 8th Edition*. New York: W. H. Freeman & Company.
- Barnes, J. R., Dirkzwager, H., Smit, J. R., Smit, J. P., On, A., Navarrete, R. C., ... Buijse, M. A. (2010). Application of Internal Olefin Sulfonates and Other Surfactants to EOR. Part 1: Structure-Performance Relationship for Selection at Different Reservoir Conditions. *SPE*(129766). <http://dx.doi.org/10.2118/129766-MS>
- Bourrel, M., Verzaro, F., & Chambu, C. (1987). Effect of Oil Type on Solubilization by Amphiphiles. *Society of Petroleum Engineers*, 2(01). <http://dx.doi.org/10.2118/12674-PA>
- Buijse, M. A., Prelicz, R. M., Barnes, J. R., & Cosmo, C. (2010). Application of Internal Olefin Sulfonates and Other Surfactants to EOR Part 2: The Design and Execution of an ASP Field Test. *Society of Petroleum Engineers*(129769). <http://dx.doi.org/10.2118/129769-MS>
- Farn, R. J. (2006). *Chemistry and Technology of Surfactants*. Oxford: Blackwell.
- Fujimoto, T. (1985). *New Introducing to Surface Active Agents*. Kyoto, Japan: Sanyo Chemical Industries, Ltd.
- M., B., & C., C. (1983). The Rules for Achieving High Solubilization of Brine and Oil by Amphiphilic Molecules. *Society of Petroleum Engineers Journal*, 327-338. <http://dx.doi.org/10.2118/10676-PA>
- Majidaie, S., Mushtaq, M., Tan, I. M., Demiral, B., & Lee, S. Y. (2012). Non-Petrochemical Surfactant for Enhanced Oil Recovery. *SPE* (153493). <http://dx.doi.org/10.2118/153493-MS>
- Miller, C. A., & Neogi, P. (1985). *Interfacial Phenomena: Equilibrium and Dynamic Effects*. New York : Marcel Dekker, Inc.

- Muherei, M. A., & Junin, R. (2008). Mixing Effect of Anionic and Nonionic Surfactants on Micellization. *Modern Applied Science*, 2(3). Retrieved from <http://ccsenet.org/journal/index.php/mas/article/view/2503/2368>
- Puerto, M., Hirasaki J., G., Miller, C. A., & Barnes, J. R. (2011). Surfactant Systems for EOR in High-Temperature, High-Salinity Environments. *SPE*, 129675. <http://dx.doi.org/10.2118/129675-MS>
- Rosen, M. J. (2004). *Surfactants and Interfacial Phenomena, 3rd Edition*. New Jersey: John Wiley & Sons, Inc.
- Salanger, J. L. (2002). *Surfactants: Types and Uses*. Mérida.
- Witthayapanyanon, A., Acosta, E., Harwell, J., & Sabatini, D. (2006). Formulation of Ultralow Interfacial Tension Systems Using Extended Surfactants. *Journal of Surfactants and Detergents*, 9. <http://dx.doi.org/10.1007/s11743-006-5011-2>

Copyrights

Copyright for this article is retained by the author(s), with first publication rights granted to the journal.

This is an open-access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).