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# EFFECT OF OPTIMUM SALINITY ON MICROEMULSION FORMATION TO ATTAIN ULTRALOW INTERFACIAL TENSION FOR CHEMICAL FLOODING APPLICATION

## PENGARUH SALINITAS OPTIMAL TERHADAP PEMBENTUKAN MIKROEMULSI UNTUK MENCAPAI TEGANGAN ANTAR MUKA TERENDAH DALAM APLIKASI PENDESAKAN KIMIA

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#### ABSTRAK

Terbentuknya mikroemulsi dalam larutan surfaktan mempunyai pengaruh besar terhadap keberhasilan teknik injeksi kimia pada reservoir minyak, yang merupakan salah satu metode enhanced oil recovery. Keberadaan surfaktan pada campuran air dan minyak akan membentuk larutan homogen dan tembus pandang yang dapat menurunkan tegangan antarmuka minyak dan air sehingga dapat mendorong sisa minyak yang masih terdapat di dalam reservoir. Penelitian ini membahas pengaruh salinitas dalam larutan surfaktan terhadap pembentukan mikroemulsi dan mekanismenya untuk menurunkan interfacial tension antara air formasi dan minyak dari lapangan "X" di Sumatera Tengah yang dilakukan melalui uji kompatibilitas, kelakuan fase, dan pengukuran interfacial tension di laboratorium. Hasil yang diperoleh menunjukkan bahwa pembentukan mikroemulsi sangat bergantung dari salinitas air yang terkait dengan perbedaan mekanisme kelarutan surfaktan dengan cara merubah area polar dari surfaktan. Salinitas optimum dicapai dengan menambahkan 0.65% Na<sub>2</sub>CO<sub>3</sub>, sehingga mikroemulsi terbentuk dan didapatkan kelarutan air dan minyak yang sama besar. Pada kondisi tersebut, tegangan antarmuka antara air dan minyak mencapai yang terendah yaitu sebesar 10<sup>-3</sup> dyne/cm dan berpotensi untuk meningkatkan perolehan minyak mencapai yang terendah jaitu sebesar 10<sup>-3</sup> dyne/cm dan berpotensi untuk meningkatkan perolehan minyak pada reservoar setelah tahap injeksi air dilakukan.

Kata Kunci: salinitas optimal, pembentukan mikroemulsi, injeksi kimia, EOR

#### ABSTRACT

Microemulsion formation in surfactant solution has a major influence on the success of chemical injection techniques, and is one of the enhanced oil recovery methods. Its transparent and translucent homogenous mixtures of oil and water in the presence of surfactant have an ability to displace the remaining oil in the reservoir by reducing interfacial tension between oil and water. In this study, the effect of surfactant solution salinity on the formation of microemulsion and its mechanism to reduce the interfacial tension between water and oil from "X" oil field in Central Sumatera were carried out through compatibility observation, phase behaviour test and interfacial tension measurements in a laboratory. The results showed that microemulsion formation depends on the salinity of aqueous phase associated with different surfactant solubility by altering the polar area of surfactant. The optimum salinity was obtained with the addition of 0.65% Na<sub>2</sub>CO<sub>3</sub> in which microemulsion was formed and the solubilization ratio of oil and water were equally high. At this condition the ultralow interfacial tension was around  $10^{-3}$  dyne/cm and enabled improved oil recovery in mature oil fields after waterflooding.

Keywords: optimum salinity, microemulsion formation, chemical flooding, EOR

## I. INTRODUCTION

Chemical flooding has become one of the most effective techniques to enhance oil recovery due to significant advances in chemical enhanced oil recovery (EOR) technology, and limited alternatives for additional oil recovery in many circumstances (Olaire 2014; Jang et al. 2014; Zhu 2014). It involves injection of chemicals, usually based on alkaline, surfactant, and polymer (ASP) to displace the remaining oil in the reservoir after waterflooding (Zhu et al. 2013; Olaire 2014; Battistuta 2015). Its main component plays an important role in the efficiency of the chemical method. Surfactants mainly reduce the interfacial tension between brine and oil, polymers increase the viscosity of aqueous phase and improve the volumetric sweep efficiency of the reservoirs, and alkalis reduce surfactant adsorption on the rock, thus lowering the costs and increasing the performance of the chemical EOR process (Sheng 2014).

Microemulsion formation is the most crucial factor in any type of chemical flooding using surfactants to achieve an ultralow interfacial tension (IFT) between brine and crude oil (Adkins et al. 2012) to overcome capillary pressure forces in the pores of the rock and mobilize residual oil (Kayalia et al. 2010; Bera et al. 2014a). Stable microemulsions are generated in situ from anionic surfactant with crude oil in the presence of alkalis. Different phases can exist in equilibrium depending on the salinity of the aqueous phase. Phase transition occurs from low salinity that solubilized water to high salinity that solubilized oil. In a microemulsion system with optimum salinity, a high level of solubilization capacity is achieved for both oil and water simultaneously (Jang et al. 2014; Bera & Mandal 2015), obtaining ultralow IFT and higher oil recoveries. Since microemulsion is formed at optimal salinity and generate ultralow IFT, estimating both properties is of great importance in designing economical microemulsion flooding.

In this study, we attempt to investigate the formation of microemulsion with favorable properties to reduce IFT at optimum condition to obtain effective surfactant fomulation for chemical injection. Salinity effect on microemulsion formation and its reduction on interfacial tension between water and oil were conducted through a phase behaviour test and interfacial tension measurements, as well as compatibility observation. The optimum formulation to generate microemulsion is then recommended to be applied on core flooding experiments to investigate the effectiveness of microemulsion flooding to enhanced oil recovery.

## **II. METHODOLOGY**

A novel anionic surfactant, salt (sodium carbonate), water, and crude oil, were used to investigate microemulsion formation. Polyacrylamide was used as a polymer in the surfactant polymer mixture. Crude oil was collected from "X" Oil Field (Central of Sumatera) with a viscosity of 6.7 Cp at reservoir temperature (85°C), and oil gravity of 34.17°API. Soften brine was synthetically formulated based on hard brine composition to reduce hardness interferences. The brine compositions are presented in Table 1.

## A. Phase Behaviour

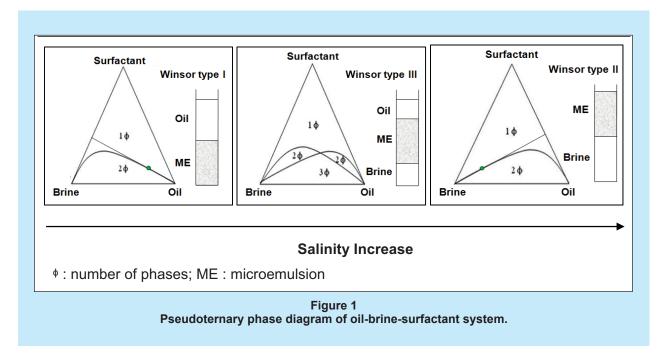
Phase behavior tests were conducted by dissolving different concentrations of surfactant in SSB at various salinities of  $Na_2CO_3$  in the range of 0.5-1%. An equal volume of surfactant solution and crude oil were added to a 5 mL glass tube and burning sealed. After mixing thoroughly, the tube was placed at reservoir temperature (85°C). When the system achieved phase equilibrium, the volume of each phase was recorded and a Winsor phase diagram was drawn with salinity on the abscissa and the equilibrium volume fraction of each phase on the ordinate.

## **B.** Compatibility

Compatibility of surfactant at various levels of salinity was determined to investigate its compatibility under optimum salinity of the microemulsion phase. A series of aqueous solutions

Table 1 Chemical composition of synthetic hard brine (SHB) and synthetic soften brine (SSB)			
Parameter	SHB	SSB	
	(mg/L)	(mg/L)	
Na⁺	1137	966	
Ca <sup>2+</sup>	25	-	
$K^{+}$	-	47.34	
Cl	1800	872.2	
SO4 <sup>2-</sup>	-	9.34	
HCO <sub>3</sub> <sup>-</sup>	-	1126.68	
TDS	2962	3022	

1. Effect of Optimum Salinity on Microemulsion Formation to Attain Ultralow Interfacial Tension for Chemical Flooding Application (Yani Faozani and Edward ML Tobing)



of surfactant-polymer (SP) were prepared by mixing optimum concentration of surfactant and 0.1% polymer solution in the presence of various concentrations of Na<sub>2</sub>CO<sub>3</sub> (0.8-1.5%) in SSB, followed by settling at 85°C for more than 7 days. Visual evaluation was conducted. Turbid or hazy solution indicated that salt concentration that had been added is beyond its solubilisation limit.

## C. Interfacial tension (IFT)

IFT between 2  $\mu$ L droplet crude oil and optimum concentration of surfactant solution without and with polymer in the presence of Na<sub>2</sub>CO<sub>3</sub> were measured using a spinning drop tensiometer TX 500, Texas. Surfactant solution with crude oil was spun at 6000 rpm and 70°C. Density difference between both liquid was used as an input to calculate IFT. Stable IFT after 10 minutes was then recorded.

## **III. RESULTS AND DISCUSSIONS**

## A. Effect of salinity on microemulsion formation

The formation of microemulsion as a function of salinity has been extensively studied by many researchers (Li et al. 2010; Liu et al. 2015). A phase behaviour test is one of the critical tools used to determine microemulsion formulation which could show ultralow IFT at an optimal salinity (Bera et al. 2012). As presented in Figure 1, three Winsor type exist in equilibrium depending on the salinity of aqueous phase. For Winsor type I or below optimum salinity, some of the crude oil dissolved in the aqueous phase, and microemulsion was formed in the aqueous phase called oil in water (O/W). Whereas in Winsor type II or above optimum salinity, some of the water dissolved in the oil phase, and microemulsion was formed in the oil phase, called water in oil (W/O). Under optimum salinity, Winsor type III occurs, and microemulsion with ultralow IFT was formed separating aqueous and oil phases. In this state, the optimum salinity is defined as the point where oil and water solubilization ratio are equally high.

Phase behaviour of surfactant solution was studied at various concentrations of surfactant in the range of 0.5 - 3%, in the presence of different salinities  $(0.40 - 0.85 \text{wt}\% \text{ Na}_2\text{CO}_3)$ . The results showed that microemulsion was formed at 2% surfactant in the presence of 0.60% - 0.70wt% Na<sub>2</sub>CO<sub>2</sub> (Figure 2) indicating this was the most effective formulation to obtain microemulsion. In this system, at lower salinity, the volume of water increases, indicating microemulsion was formed in aqueous phase, Winsor type I was formed. In contrast, at higher salinity, the volume of water decreases, and showed that microemulsion tends to form in the oil phase, and Winsor type II was formed. Transition phase between two phases, under optimum salinity, which formed clear microemulsion that separated aqueous and oil phases was observed at 0.60% - 0.70% Na<sub>2</sub>CO<sub>2</sub>, suggesting that microemulsion was formed in both phases, as described in Winsor type III. However, the tertiary diagram of this phase behaviour (Figure

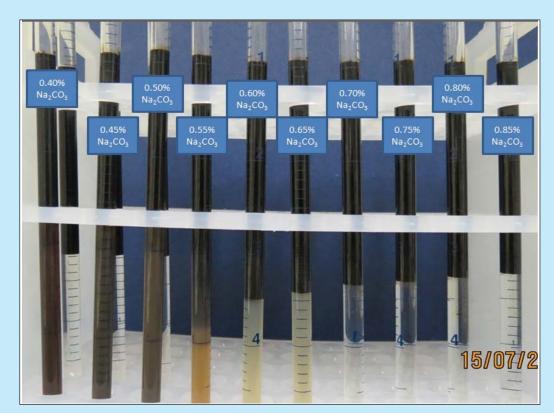
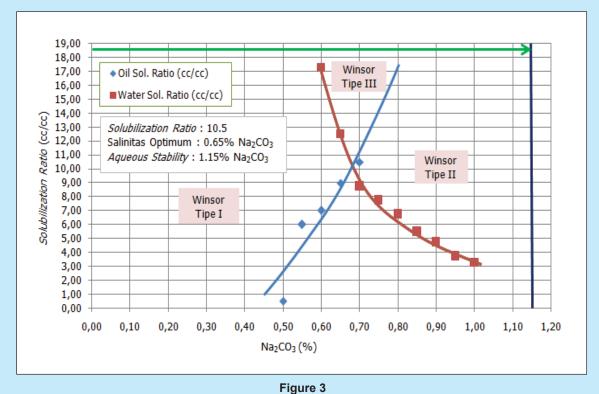


Figure 2 Phase behavior test to screen salinity optimum of microemulsion formation.



Tertiary diagram of phase behaviour test.

1. Effect of Optimum Salinity on Microemulsion Formation to Attain Ultralow Interfacial Tension for Chemical Flooding Application (Yani Faozani and Edward ML Tobing)

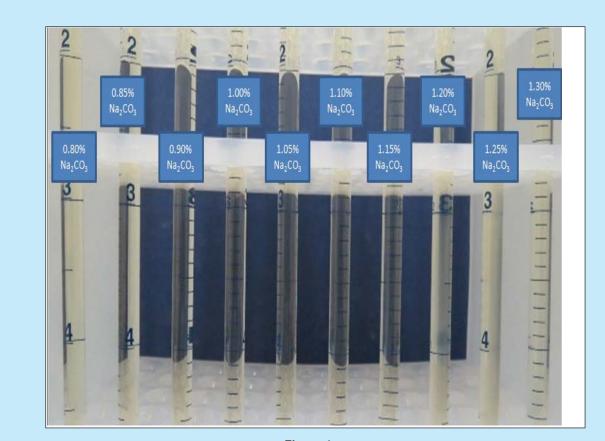


Figure 4 Compatibility of surfactant at various levels of salinity.

3) shows that optimum salinity was achieved at 0.65 wt% of  $Na_2CO_3$  with equally high value of water and a oil solubilization ratio at around 10.

High solubilization capacity of microemulsion depends on the formulation of microemulsion. Salts are responsible for the variation of solubilization capacity of microemulsion. Microemulsions show a high level of solubilization capacity toward both oil and water simultaneously. This property makes them one of the most important tools in chemical EOR. As reported by Wei et al. (2011), the water solubilization capacity increases initially with increasing Na<sub>2</sub>CO<sub>2</sub> concentration from 0.50% and reaches a maximum at 0.80% before decreasing with a further increase of Na<sub>2</sub>CO<sub>3</sub> concentration (Wei et al. 2011) and the change to solubilized oil. The addition of salt diminishes the effective polar area of the surfactant by decreasing the thickness of the electrical double layer around the polar group. In this regard, packing parameter (P) is defined as v/al, where 'v' is the effective volume of a surfactant molecule, 'a' is the effective area of its polar head and 'l' is the length of its hydrocarbon chain. As P increases, the water

T (2% Surfactant + 0.85% Na <sub>2</sub> CO <sub>3</sub> + Polym		
Polymer (ppm)	IFT (dyne/cm)	
2200	6.31E-03	
2500	7.33E-03	
2800	4.60E-03	
2900	8.74E-03	

9.17E-03

6.31E-03

3000

3100

Toble 3

solubilization capacity of microemulsion decreases, because of the two counteracting factors, a maximum value of water solubilization capacity is observed. As the concentration of salt becomes higher, the latter effect plays a dominant role, which explain the further decrease in water solubilization capacity (Bera & Mandal, 2015). Compatibility surfactant is also affected by salinity (Figure 4). Visual observation on solubility of surfactant mixed with polymer in the presence of different Na<sub>2</sub>CO<sub>3</sub> showed that at lower salinity, transparent solution was formed. At a level above the solubilisation limit, which was detected at 1.15% Na<sub>2</sub>CO<sub>3</sub>, hazy solution was observed which indicated precipitation formation. These results are in line with the phase behaviour test that gave optimal salinity at 0.65% Na<sub>2</sub>CO<sub>3</sub>, lower than its solubilisation limit.

## **B.** Relationship Between Microemulsion Formation and Interfacial Tension Reduction

To investigate the relation between microemulsion formation and ultralow IFT, measurement of IFT between surfactant solution and crude oil were conducted. Based on a phase behavior test, microemulsion was formed at 0.65% Na<sub>2</sub>CO<sub>2</sub>. However, the addition of salt has potential to decrease in the reservoir due to the contact with low salinity of SSB. The addition of a higher level of salt than its optimal salinity is then required to overcome this matter. The effect of polymer on IFT reduction was also observed since the flooding systems utilize polymer to enhance mobility control of microemulsion flooding. IFT of 2% surfactant solution with 0.85% Na<sub>2</sub>CO<sub>3</sub> was then measured in the presence of 2200 – 3100 ppm polymer (Table 2). The results showed that IFT between surfactant solution and crude oil were measured to be around 10-3 dyne/ cm, which showed that in the microemulsion phase, the ultralow IFT was achieved to recover the trapped oil with increasing capillary number, and it was not affected by adding polymer until 3100 ppm. It is well known that ultralow IFT plays an important role in oil recovery processes. The reasons for ultralow IFT have been extensively investigated (Bera & Mandal, 2010). The ultralow IFT are associated with phase behaviour at plait point. At the plait point of liquid/ liquid system, two phases become indistinguishable and IFT between the two equilibrium phases goes to zero. The microemulsion systems exhibit ultralow IFT over wide ranges of salinities, surfactant concentrations and temperatures, suggesting that a critical phenomenon is involved.

The relative solubility of surfactant in oil and water vary significantly with a change in the salinity of the aqueous phase. At low salt concentration, most of the surfactant molecules stay in the aqueous phase, while at high salt concentration, the surfactant molecules preferentially dissolve into the oil phase. An equal distribution of surfactant in both oil and water phase is observed at a particular salinity, called optimal salinity, which produces the lowest IFT. The solubility of surfactant molecules in aqueous medium is reduced by salt. However, at a certain concentration of surfactant, the presence of salt up to a certain concentration may promote the surfactant migration toward the interfacial layer from the bulk phase, generating a substantial decrease in the IFT between oil and water (Bera et al, 2014b; Bera et al., 2014c). Therefore, the IFT decreases with increasing salinity up to a certain salt concentration and then increases. This salt concentration is generally known as optimal salinity.

#### **IV. CONCLUSIONS**

Microemulsion formation is the key factor in any type of chemical flooding utilizing surfactant to attain an ultralow IFT and mobilize the trapped oil in the reservoir. Salinity has a great effect on microemulsion formation due to the different mechanism of solubility by altering the polar area of the surfactant. Under microemulsion state, solubility of surfactant towards water and oil is equally high that generate a substantial decrease in IFT. The results of this study showed that, microemulsion was formed in the presence of 0.65% Na<sub>2</sub>CO<sub>3</sub> which has the ability to reduce the interfacial tension between water and oil to the level of 10<sup>-3</sup> dyne/cm. However, to investigate performance of surfactant formulation to produce microemulsion in the reservoir condition, core flooding experiments using representative core will be required.

#### LIST OF SYMBOLS

- IFT = Interfacial tension, dyne/cm
- SHB = Synthetic Hard Brine
- SSB = Synthetic Soft Brine

#### REFERENCES

- Adkins S, Arachchilage GP, Solairaj GP, Weerasooriya U, Pope GA. 2012. Development of thermally and chemically stable large-hydrophobe alkoxy carboxilate surfactants. In: SPE Improved Oil Recovery Sympasium, Tulsa, Paper SPE 154256-MS.
- **Battistutta E.** 2015. Alkaline-surfactant-polymer (ASP) flooding of crude oil at under-optimum salinity conditions. In: SPE Enhanced Oil Recovery Conference, Kuala Lumpur SPE 174666-MS.
- Bera A, Ojha K, Mandal A, Kumar T. 2012. Phase behaviour and physicochemical properties of (sodium dodecyl sulfate + brine + propan-1-ol + heptane) microemulsions. J. Chem Eng Data 57:1000-1006.

- Bera A, Kumar T, Mandal A. 2014a. Physicochemical characterization of anionic and cationic microemulsions: water solubilization, particle size distribution, surface tension and structural parameters. J. Chem Eng Data 59:2490-2498.
- Bera A, Kumar T, Mandal A. 2014b. Screening of microemulsion properties for application in enhanced oil recovery. Fuel 121:198-207.
- Bera A, Mandal A, Guha BB. 2014c. Effect of synergism of surfactant and salt mixture on interfacial tension reduction between crude oil and water in enhanced oil recovery. J. Chem Eng. Data 59:89-96.
- Bera A, Mandal A. 2015. Microemulsions: a novel approach to enhanced oil recovery: a review. J. Petrol Explor Prod Technol 5:255-268.
- Jang SH, Liyanage PT, Lu J, Kim DH, Arachchilage GWPP, Britton C, Weerasooriya U, Pope GA. 2014. Microemulsion phase behaviour measurements using live oils at high temperature and pressure. In: Improved oil recovery symposium, Tulsa, Paper SPE 169169-MS.
- **Kayalia IH, Liub S, Miller CA**. 2010. Microemulsions containing mixtures of propoxylated sulfates with slightly branched hydrocarbon chains and cationic surfactants with short hydrophobes or PO chains. Colloids Surf A 354:246-251.
- Li X, He G, Zheng W, Xiaou G. 2010. Study on conductivity property and microstucture of

TritonX-100/alkanol/*n*-heptane/water microemulsion. Colloids Surf A 360:150-158.

- Liu H, Yuan Y, Ding C, Chen S, Qi X. 2015. Effect of electrolytes and correlations for salinities at the optimum formulation of sodium dodecyl benzene sulfonate microemulsions. J. Surfact Deterg 18:569-578.
- **Olaire A.A.** 2014. Review of ASP EOR (alkaline, surfactant, polymer enhanced oil recovery) technology in the petroleum industry: prospects and challenges. Energy 77:963-982.
- Sheng, J.J. 2014. A comprehensive review of alkalinesurfactant-polymer (ASP) flooding. SPE Western Regional & AAPG Pacific Section meeting SPE 165358-MS.
- Wei J, Huang G, Yu H, An C. 2011. Efficiency of single and mixed Gemini/conventional micelles on solubilization of phenanthrene. Chem Eng J 168:201-207.
- Zhu Y, Hou Q, Jian G, Ma D, Wang Z. 2013. Current development and application of chemical combination flooding technique. J. Petrol Explor & Develop 40:96-103.
- **Zhu Y.** 2014. Studies on ASP flooding formulation based on alkylbenzene sulfonate surfactants. In: SPE Asia Pacific Oil & Gas Conference, Adelaide, SPE 171433-MS.