CHAPTER IV
RESULT AND DISCUSSION

4.1 Abstract

In enhanced oil recovery (EOR), the decrease in foam stability through surfactant stabilized-foam technology due to the presence of crude oil and severe condition is considered to be challenging. This study aims to evaluate the effect of surfactant structures and concentration on foam generation and foam stability. Anionic surfactants, internal olefin sulfonate series (IOS), and SDBS were used in this study. The effect of alkanes and brine were also evaluated to understand the influence of oil and brine in the reservoir. In additions, mixed surfactant system with nonionic surfactant as a co-surfactant and alcohol as a co-solvent was performed to improve the foam stability. The surfactant selection was preliminary screened through out batch-shaking method. Then, the following experiment was performed by continuously purging a fixed gas flow rate through a certain amount of surfactant solution. Foam height was measured as a function of time. The results showed that the anionic surfactants gave more stable foam than the nonionic surfactant. The IOS surfactant with shorter carbon chain lengths also generated better foam stability than the higher carbon chain length IOS. The higher concentration of surfactant (above CMC) enhanced the foam stability but when the concentration reached to a certain point at a very high concentration, the foam stability tended to decrease. For the effect of alkanes, i.e. n-hexane, n-dodecane and n-hexadecane, the presence of hydrocarbon with shorter chain alkanes decreased foam stability. In fact, foam was more stable in the presence of n-hexadecane. Adding dodecanol as a co-solvent increased foam stability for IOS system when it was in contact with n-hexadecane. At elevated brine concentration, foam collapsed rapidly in the presence of brine. Using nonionic surfactant could help improve the foam stability in brine solution.

4.2 Introduction

After primary and secondary recovery of oil production, many techniques such as gas flooding, chemical injection are applied in order to extract more oil. It has been known as tertiary recovery or enhanced oil recovery (EOR). Gas flooding is widely used to recover a large amount of oil. However, there are some disadvantages of gas flooding: viscous fingering, poor areal sweep efficiency, gas channeling and gravity override. All these problems can cause a decrease in oil production. To overcome all these problems, foam has been introduced to EOR to improve the sweep efficiency. Foams have higher effective viscosity than gases. Hence, foams are capable of decreasing gas mobility (Yan *et al.*, 2006). The application of foam in the field could be CO_2 foam, steam foam or injecting foam in gas flooding (Sheng, 2013). The challenges of foam technology are the impact of oil and the conditions in reservoir on foam stability. Many researches have studied several impacts on the foam stability. Andrianov *et al.* (2012) performed foam stability test and studied the presence of alkanes and crude oil on the foam stability. They observed that alkane with lower carbon number tended to destabilize the foam stability than a long carbon chain. Vikingstad *et al.* (2005) performed a static foam test using alpha olefin sulfonate (AOS). They investigated several impacts, for examples, the effect of concentration, salt concentration, alkanes, alcohols and crude oil. They found that increasing in surfactant concentration resulted in increasing foam height. The alkane with low molecular weight destabilized the foam. Farzaneh *et al.* (2015) also studied several effects on the CO_2-foam stability. They found that anionic surfactants gave better foam stability than nonionic surfactants. There is an optimum concentration for each surfactant to give the best stability of foam. They also compared between CO_2-foam and N_2-foam which the latter gave higher foam stability. Besides, the effect of alkaline on foam stability and crude oil was studied and it was reported that the appropriate amount of alkaline could help generate more stable foam.

The purpose of this work is to study the longevity of foam generated from different surfactant system structures and concentrations. The anionic IOS surfactants series and alcohol ethoxylate surfactant were selected to evaluate. The effect of three different alkanes and high brine concentration (represent severe condition) were also investigated. To improve foam stability, co-solvent (dodecanol) and co-surfactant (nonionic surfactant) were introduced to enhance foam stability. Two approaches of foam stability measurement were performed. The first approach was shaking method; and the second approach was purging gas through the glass column. The height of foam was measured as a function of time. A good surfactant was evaluated by its ability to generate good foam that stays for a long period of time.

4.3 Experimental

4.3.1 Materials

The surfactants used in this study are C15-18 internal olefin sulfonate (C15-18 IOS), C19-23 internal olefin sulfonate (C19-23 IOS), C24-28 internal olefin sulfonate (C24-18 IOS), C16-17 alcohol alkoxy sulfate (AAS) which are obtained from Shell Chemicals; sodium dodecyl benzene sulfonate (SDBS, Sigma-Aldrich), and C13-15 alcohol ethoxylated with 8EO (AE-8EO, BASF). The solution was prepared in de-ionized water. Tensiometer (Easydyne model) was used to measure the surface tension in order to find critical micelle concentration (CMC). Dedecanol and two nonionic surfactants; alcohol ethoxylate with 5EO (Thai Ethoxylate) and TWEEN 80 (sigma-Aldrich) were used as a co-solvent and a co-surfactant. The structures of all surfactant are showed in figure 4.1.

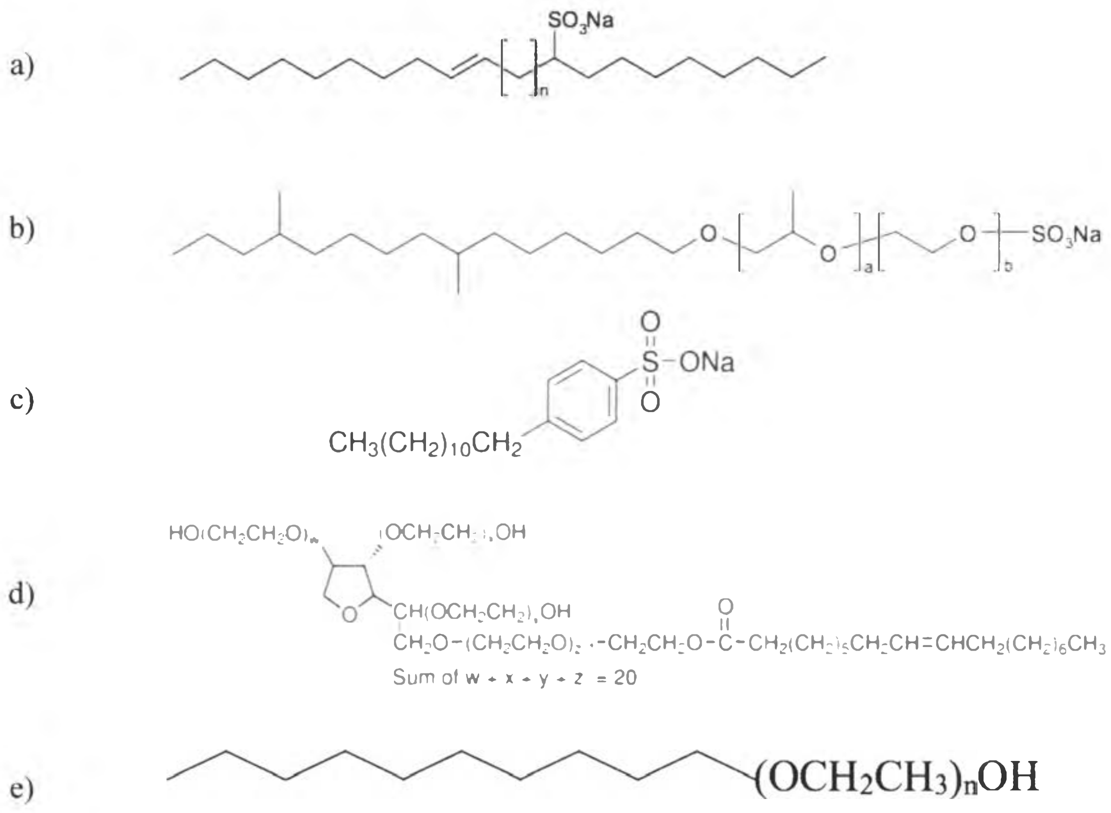

Figure 4.1 The structure of surfactant: a) Internal olefin sulfonate (Barnes *et al.*, 2008) b) Alcohol alkoxy sulfate (Barnes *et al.*, 2008) c) Sodium dodecyl benzene sulfonate d) TWEEN 80 e) Alcohol ethoxylate.

To study the effect of alkanes, three alkanes with different carbon chain lengths were used in the experiment, namely n-hexane, n-dodecane and n-hexadecane. Brine solution was prepared using NaCl and $CaCl_2$ at the weight ratio of 8:2 at 5 wt.% and 10 wt.%.

4.3.2 Experimental Approach

There were two techniques employed in this study to measure the foam stability. The first technique was a surfactant screening in order to find appropriate surfactant systems. Foam stability test was performed by shaking method (Lee *et al.*, 2014). Fifty mL of 0.5 wt.% surfactant solution was poured into a 250 mL graduated glass cylinder, then the top of the glass cylinder was sealed by a rubber cork. The solution was shaken vigorously 20 times to generate foam. The foam height was observed afterwards. The second technique was to study the effect of surfactant concentration, alkanes, brine and the addition of co-surfactant and co-solvent in the presence of alkane and brine in the systems. The experimental set up consisted of a glass chromatographic column with a diameter of 30 mm and a length of 600 mm, an air tank and a flow meter. The bottom of column was connected to a flow meter, and an air tank as showed in Figure 4.1. In the column test, 50 mL of surfactant solution was poured into the column. Then air was purged into the column at the bottom through the surfactant solution in the column to generate foam at room temperature (25±2 °C). For both techniques, foam height above the liquid phase was observed as a function of time.

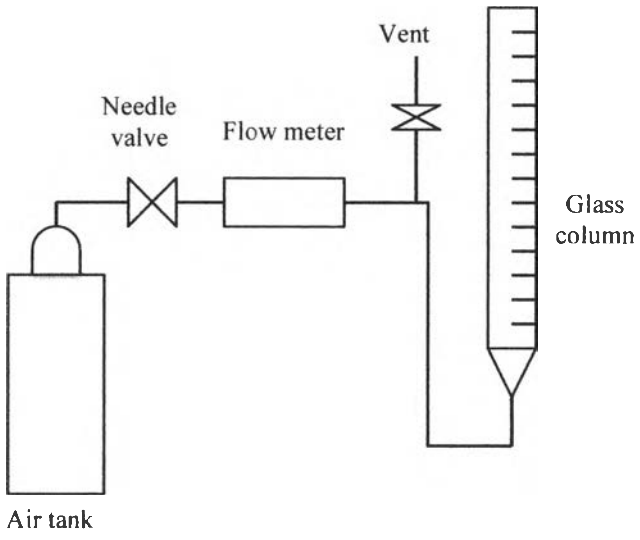

Figure 4.2 Schematic of foam column equipment.

4.4 Results and Discussion

4.4.1 The Effect of Surfactant Structure

Figure 4.3 shows the foam stability test results by the shaking method using six surfactants. The ranking from the best foam stability to the least foam stability is SDBS, C15-18 IOS, C19-23 IOS, AE-8EO, AAS and C24-28 IOS. The results indicated that anionic surfactant had better foam stability than nonionic surfactant, espicially SDBS and C15-18 IOS. To compare the effect of carbon chain length amoung C15-18 IOS, C19-23 IOS and C24-28 IOS, it was observed that the longer carbon chain length tended to decrease the foam stability. Surfactants with higher number of carbon chain length resulted in less water solubility (Farzaneh *et al.*, 2015) due to the higher tail-tail interactions causing less foam generation and poor interaction between air and water interface.

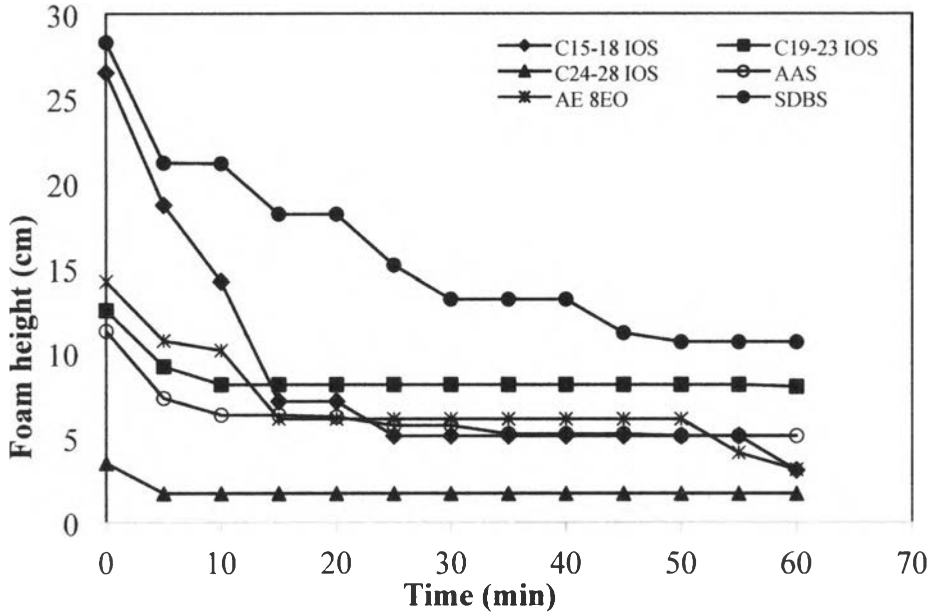

Figure 4.3 Foam stability measurement by shaking method for all surfactants.

4.4.2 The Effect of Concentration

From previous experiment, four surfactants that provided more stable foam were selected to study in the column test, namely SDBS, C15-18 IOS, C19-23 IOS and AAS. The CMC of each surfactant were measured as a reference. Table 4.1 shows the CMC of the surfactant used in this study in the absence of salt at room temperature (25±2 °C).

Table 4.1 Summary of the CMCs for all surfactants at room temperature 25±2 °C

Surfactant	**CMC (wt.%)**
C15-18 internal olefin sulphonate	0.030
C19-23 internal olefin sulphonate	0.060
C16-17 alcohol alkoxy sulphate	0.033
Sodium dodecyl benzene sulfonate	0.110

Figure 4.4 to Figure 4.7 show the results of foam stability measurement of C15-18 IOS, C19-23 IOS, AAS and SDBS, respectively. C15-18 IOS was chosen because it gave a good foam height at the beginning while C19-23 IOS had a stable foam height for long period. AAS was chosen to study because the number of extended group that might have a good foam stability when it is in contact with oil. The results indicated that the foam stability increased with the increasing in surfactant concentration; however, the foam stability started to decrease when the surfactant concentration reached a certain level at very high concentration. According to Figure 4.3, C15-18 IOS performed the best foam stability at 0.04 wt.% (1.33 times CMC) and the foam stability decreased when the surfactant concentration reached beyond this concentration (5 times CMC). For C19-23 IOS (see Figure 4.4), the foam stability increased until the surfactant concentration of 5 times CMC has reached, after that, the foam stability was lower. The decreasing in foam stability at a very high concentration could cause by the surface free energy of surfactant interaction. ASS also had the same trend but the foam had collapsed within 10 minutes for all concentrations (see Figure 4.5); therefore, AAS was not an appropriate surfactant for a good foaming agent and it was not selected for further study in this work. For SDBS system, all concentrations provided similar foam stability as shown in Figure 4.6. At higher concentration, SDBS system gave only a slight decrease in foam stability. After 120 minutes, SDBS system at 0.08 wt.% (0.75 times CMC) and 0.11 wt.% (CMC) presented the slowest rate of foam collapse as compared to other concentrations.

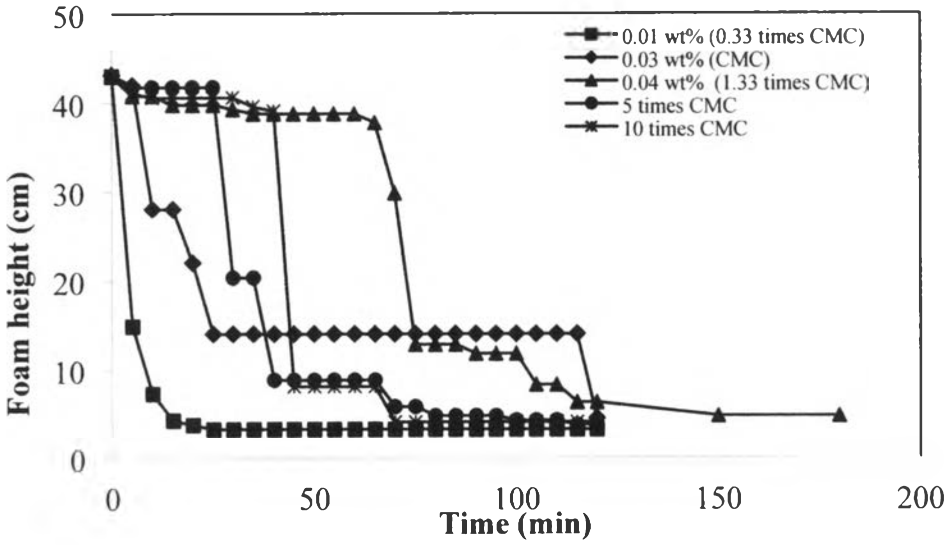

Figure 4.4 Foam stability measurement by a column test of C15-18 IOS at different concentrations.

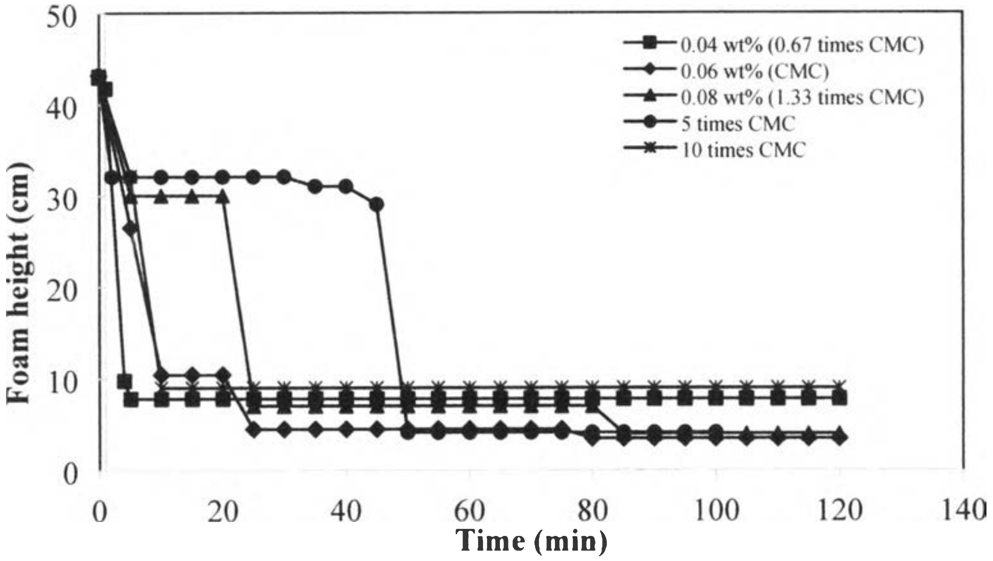

Figure 4.5 Foam stability measurement by a column test of C19-23 IOS at different concentrations.

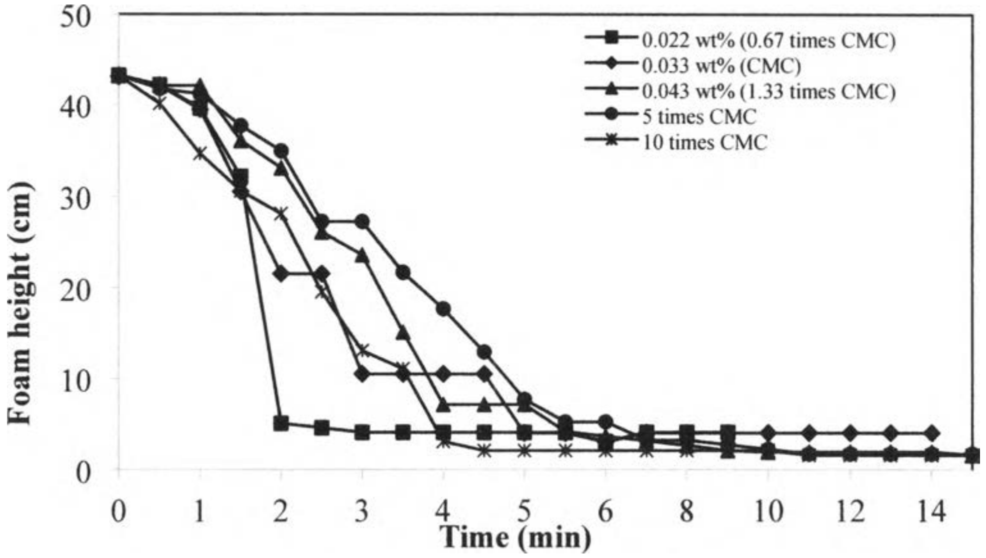

Figure 4.6 Foam stability measurement by a column test of AAS at different concentrations.

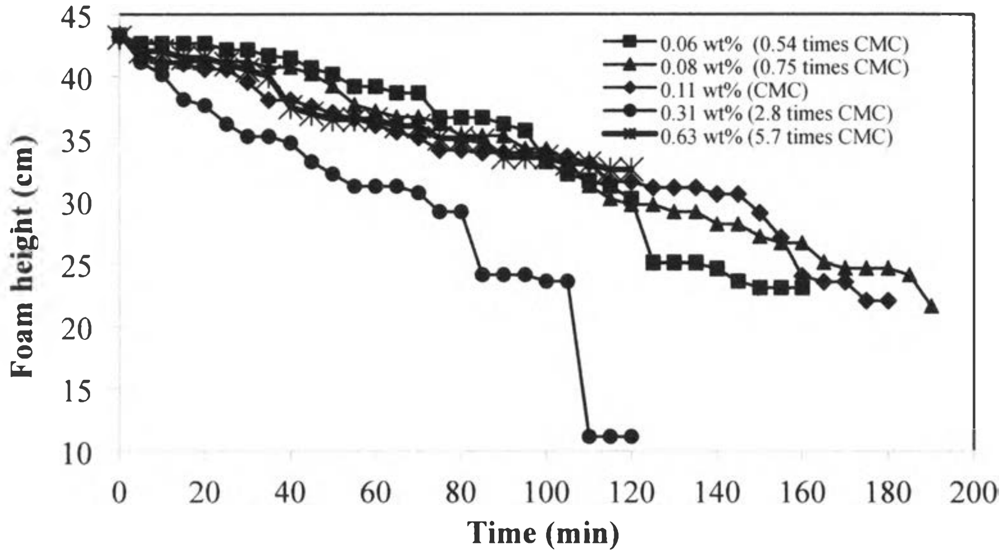

Figure 4.7 Foam stability measurement by a column test of SDBS at different concentrations.

4.4.3 The Effect of Alkanes and Brine

From previous experiment, C15-18 IOS and SDBS at the concentration that provided the best foam stability were selected to study the effects of alkane and brine. C15-18 IOS was chosen because when it was compared to C19-23 IOS, foam tended to collapse slower than C19-23 IOS at lower concentration. Three alkanes with different carbon chain length were used, namely n-hexane (C_6), n-dodecane (C_{12}) and n-hexadecane (C_{16}). 1 wt.% of alkane was added to the surfactant solution and mix-welled before performing the foam stability test. The results indicated that the addition of alkane tended to destabilize the foam. In the presence of n-hexadecane, the system showed a slight different in foam stability for C15-18 IOS but the result indicated a higher foam stability in the presence of alkanes with longer carbon chain length compared to alkanes with shorter carbon chain length for SDBS systems (see Figures 4.8 and 4.9). Alkane molecules may accumulate at the plateau border and could slow down the film drainage rate (Vikingstad *et al.*, 2005; Andrianov *et al.*, 2012; Simjoo *et al.*, 2013). According to Simjoo and coworkers (2013) destabilizing foam from short carbon chain alkane was from the higher tendency of oil to solubilize in surfactant aggregates, causing the reduction in the interaction between surfactant aggregates at the interface and, finally, causing the foam to collapse. For longer carbon chain of alkane, the tendency to solubilize in micelle is lower because of the steric effect. It is more difficult of longer carbon chain of alkane to penetrate into micelle aggregates (Vikingstad *et al.*, 2005, Simjoo *et al.*, 2013). Figure 4.10 shows the solubilization of alkane in micelles.

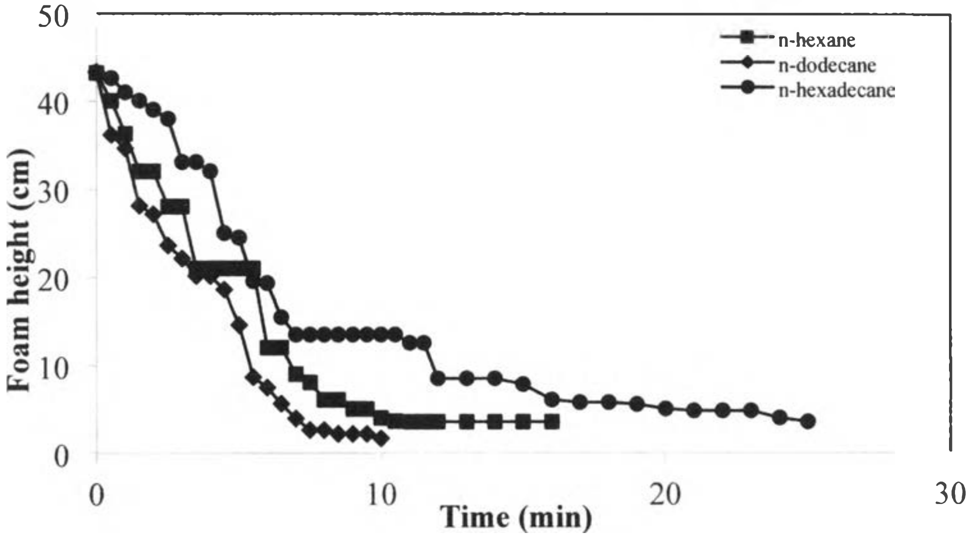

Figure 4.8 Foam stability measurement by a column test of C15-18 IOS in the presence of alkanes at C15-18 IOS concentration of 0.04 wt.%.

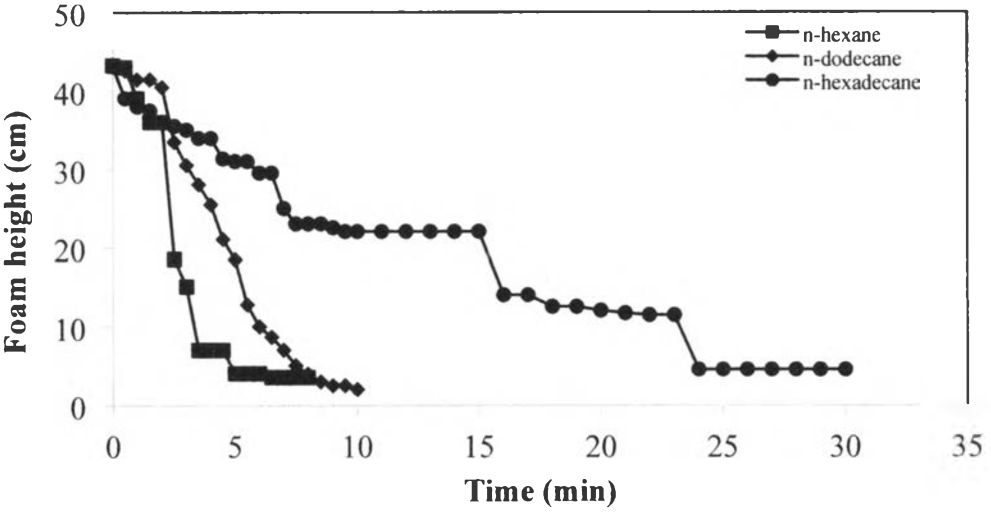

Figure 4.9 Foam stability measurement by a column test of SDBS in the presence of alkanes at SDBS concentration of 0.08 wt.%.

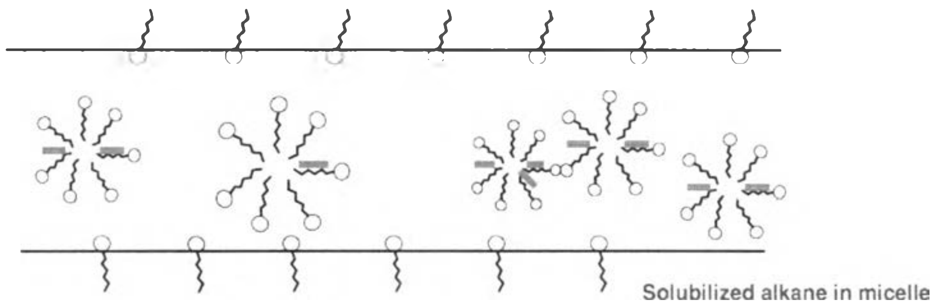

Figure 4.10 Solubilization of alkane molecule in micelles.

For the effect of brine, Figure 4.11 shows that the foam was destabilized in the presence of brine at both 5 wt.% and 10 wt.% brine concentration due to the increase in surfactant-surfactant interactions. For C15-18 IOS, foam collapsed in 20 minutes at 5 wt.% brine and in 10 minutes at 10 wt.% brine. Note that, there was surfactant precipitation occurred in the SDBS system.

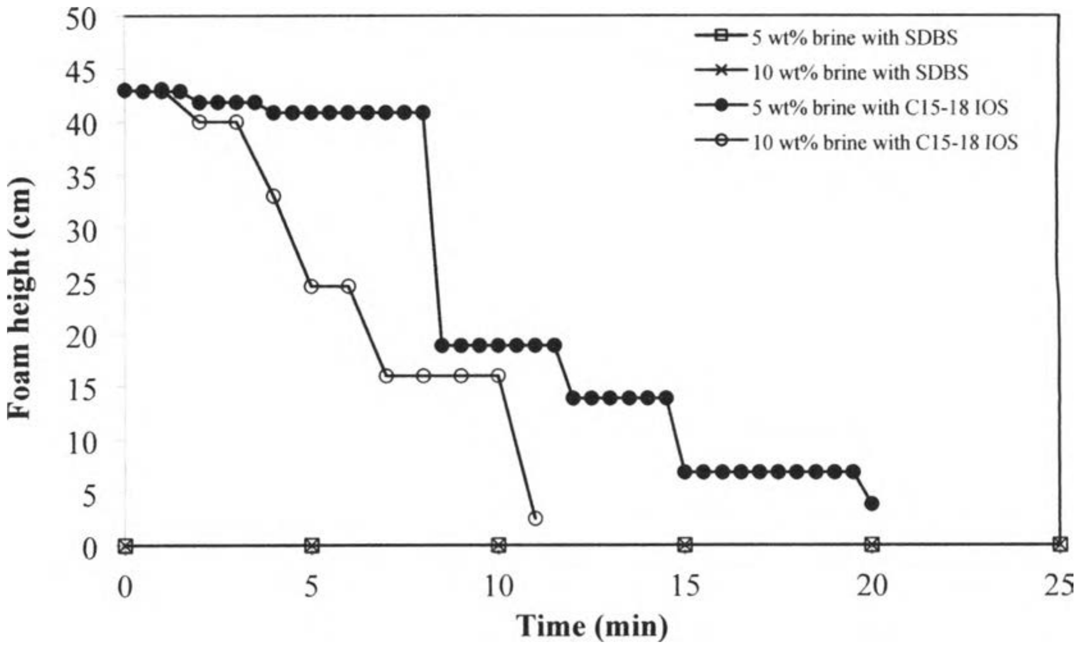

Figure 4.11 Foam stability measurement by a column test of C15-18 IOS and SDBS in 5 wt.% and 10 wt.% brine concentration. The concentrations of C15-18 IOS and SDBS were 0.04 wt.% and 0.08 wt.% respectively.

4.4.4 The Effect of Co-solvent and Co-surfactant to Foam Stability Improvement

4.4.4.1 Adding Co-solvent and Co-surfactant to Improve Foam Stability in the Presence of N-hexadecane

In order to improve the foam stability in the presence of alkanes, two nonionic surfactants, namely AE-5EO and TWEEN 80, as co-surfactant and dodecanol as co-solvent were added to the surfactant solution. Figure 4.12 and Figure 4.13 show that nonionic surfactants did not improve the foam stability whereas dodecanol remarkably showed the improvement in foam stability especially for C15-18 IOS system. Foam retained over four hours when the concentration of dodecanol increased (5 wt.% dodecanol). For SDBS system, the addition of dodecanol did not influence foam stability but the improvement was increased when dodecanol concentration increased to 0.5 wt.%. The long chain alcohol (i.e dodecanol in this case) appeared to be an effective additive for improving foam stability. Adding alcohol could help slow down the drainage rate, make a close-packing and increase surface viscosity (Rosen *et al.*, 2012).

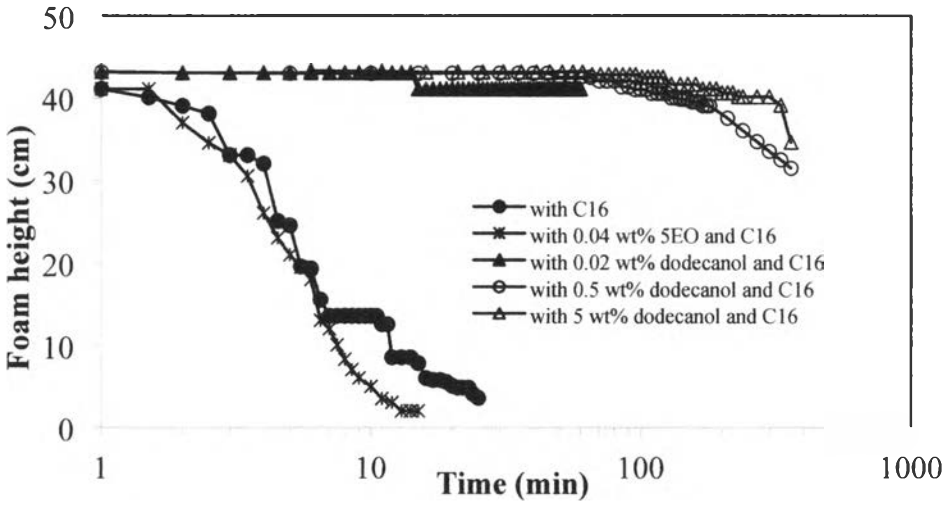

Figure 4.12 Effect of adding dodecanol and alcohol ethoxylated with 5EO (AE-5EO) on foam stability measurement of C15-18 IOS at 0.04 wt.% in the presence of n-hexadecane.

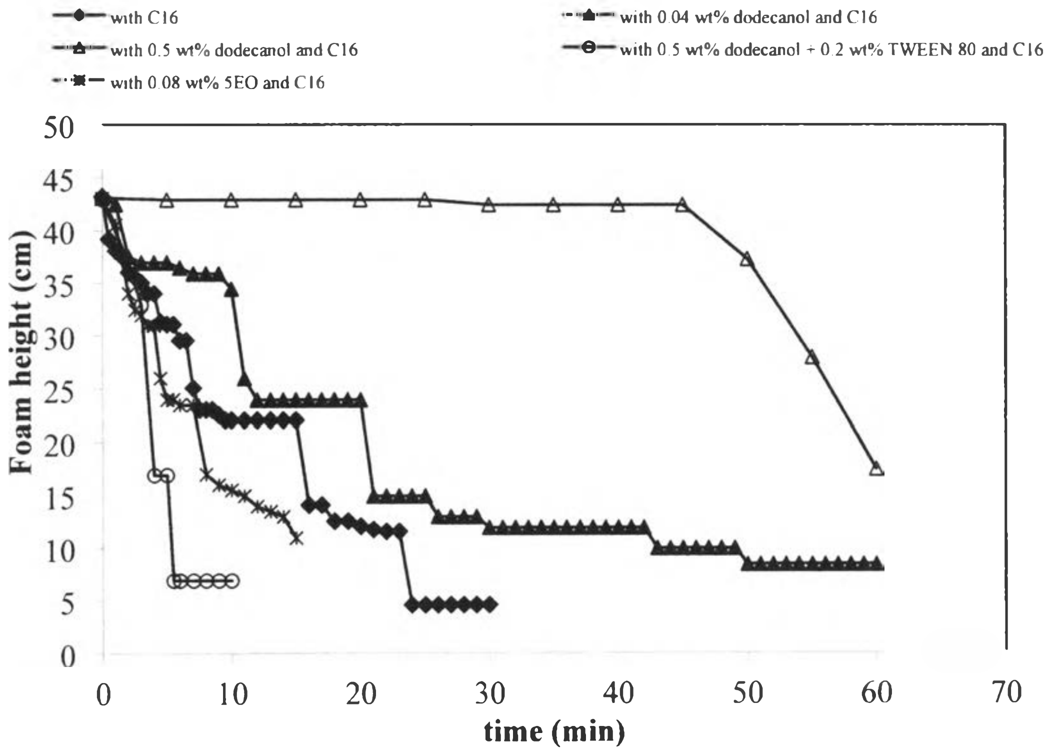

Figure 4.13 Effect of adding dodecanol, TWEEN 80 and 5EO on foam stability measurement of SDBS in the presence of n-hexadecane.

4.4.4.2 Adding Co-surfactant to Improve Foam Stability in High Brine Concentration

In this section, two nonionic surfactants namely TWEEN 80 and alcohol ethoxylated with 5EO (AE-5EO) were introduced to the C15-18 IOS system of high brine concentration. The results (see Figure 4.14 and 4.15) indicated that the presence of nonionic surfactant as a co-surfactant could enhance foam stability. For C15-18 IOS, adding 5EO gave better foam stability whereas the addition of facilitated TWEEN 80 gave the foam system improvement for SDBS system. It could be noted that adding nonionic surfactant also restrained the surfactant precipitation and helped foam generation. Increasing in concentration of nonionic surfactant in the system also help improve foam stability due to increasing surface viscosity and reducing the repulsive force between anionic surfactant molecules. The ion-dipole interaction attracts ionic heads, while the hydrocarbon parts are packed closer together by the intermolecular force (Rosen *et al.*, 2012). The differences of foam stability on the influence of brine between mixed surfactant systems with different nonionic surfactants could be due to the surfactant structure and/or synergism effect of mixed micelles.

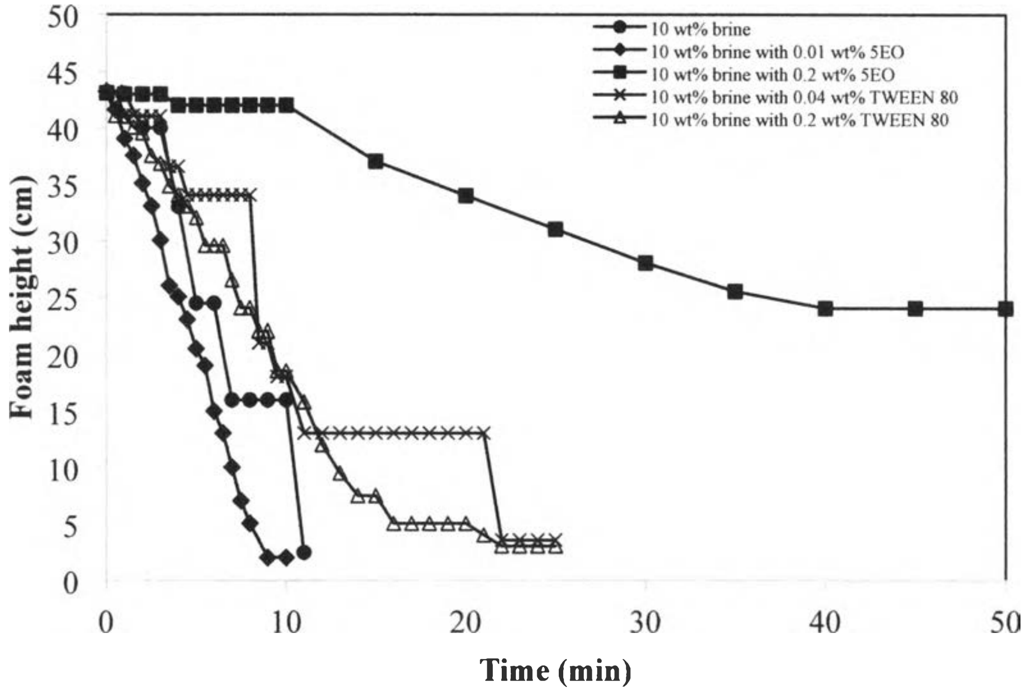

Figure 4.14 Effect of adding 5EO and TWEEN 80 on foam stability of C15-18 IOS solution in 10 wt.% brine concentration.

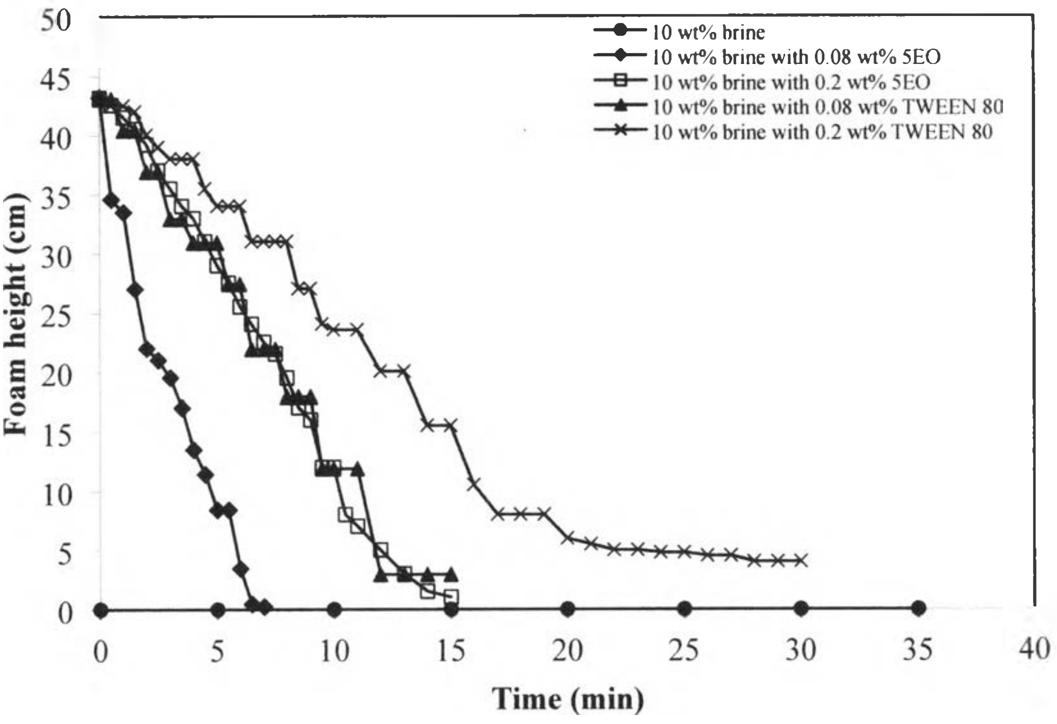

Figure 4.15 Effect of adding 5EO and TWEEN 80 on foam stability measurement of SDBS in 10 wt.% brine concentration.

4.5 References

Andrianov, A., Farajzadeh, R., Mahmoodi Nick, M., Talanana, M., and Zitha, P.L.J. (2012) Immiscible foam for enhancing oil recovery: Bulk and porous media experiments. Industrial & Engineering Chemistry Research, 51(5), 2214-2226.

Barnes, J.R., Smit, J.P., Smit, J.R., Shpakoff, P.G., Raney, K.H., and Puerto, M.C. (2008, April 19-23) Development of surfactants for chemical flooding at difficult reservoir conditions. Paper presented at The 2008 SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, U.S.A.

Farzaneh, S.A. and Sohrabi, M. (2015) Experimental investigation of CO_2-foam stability improvement by alkaline in the presence of crude oil. Chemical Engineering Research and Design, 94, 375-389.

Lee, J., Nikolov, A., and Wasan, D. (2014) Surfactant micelles containing solubilized oil decrease foam film thickness stability. Journal of colloid and interface science, 415, 18-25.

Rosen, M.J. and Kunjappu, J.T. (2012) Surfactants and Interfacial Phenomena: New Jersey: John Wiley.

Sheng, J.J. (2013) Foams and their applications in enhancing oil recovery. Enhanced Oil Recovery Field Case Studies, 251.

Simjoo, M., Rezaei, T., Andrianov, A., and Zitha, P.L.J. (2013) Foam stability in the presence of oil: Effect of surfactant concentration and oil type. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 438, 148-158.

Vikingstad, A.K., Skauge, A., Høiland, H., and Aarra, M. (2005) Foam–oil interactions analyzed by static foam tests. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 260(1), 189-198.

Yan, W., Miller, C.A., and Hirasaki, G.J. (2006) Foam sweep in fractures for enhanced oil recovery. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 282, 348-359.