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Potential of Polymeric Surfactant in Stabilizing Carbon Dioxide Foam for Enhanced Oil Recovery

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This study investigates the stability of carbon dioxide (CO_2) foam generated from water, gas and formulation of Alpha-Olefin Sulfonate (AOS), Betaines and different types of polymeric surfactant. The effects of different types of crude oil on foam stability were also analyzed. It was found that a higher concentration of surfactant provided more stable foam while a finer texture of foam bubbles were observed with addition of Betaines. The addition of Poly(ethylene glycol) dimethyl ether showed the best result as the foam did not degenerate as rapidly as the other polymeric surfactants. The presence of crude oil also affected the foam stability as it went into a steep decline.

1. Introduction

There are practical issues regarding the water alternating gas (WAG) technique; increasing gas mobility and reducing sweep efficiency. With that, introducing foam into the reservoir can reduce gas mobility, thus mitigating gravity override and fingering. According to Sydansk and Romero-Zerón (2011), foam is a metastable dispersion of a relatively big amount of gas in a continuous liquid phase that constitutes a relatively quite small amount of the foam. In simpler words, foam is defined as a dispersion of gas bubbles in liquid. In a porous medium with foam, the gas phase is blocked by a liquid film called lamellae. Although foams are thermodynamically unstable, surfactants can stabilize the liquid films (Li, 2006). Besides its role as a foaming agent in CO_2 foam flooding, surfactant can also be applied in surfactant flooding to reduce interfacial tension (IFT), thus allowing emulsification and displacement of the trapped oil in the reservoir. Hamidi et al. (2015) have investigated the potential of ultrasonic stimulation in the integrated ultrasound-surfactant flooding process in order to remain low IFT and reduce the surfactant consumption, while Honarvar et al. (2017) have found that increasing temperature and pressure had a positive impact on reducing the IFT between carbonated brines and oil. Foam generation can be defined as the creation of effective foam of high mobility of gas in the porous medium at a condition of high gas mobility. In other words, foam generation is a condition where the rate of lamellae creation greatly exceeds the rate of lamellae destruction (Chui, 2014). There are three mechanisms identified under foam generation, which are snap-off, leave behind as well as lamella distribution (Tanzil et al., 2002). Snap-off and lamellae distribution will generate a strong-foam, while the leave behind mechanism usually generates a weak-foam. There are two mechanisms related to degeneration phase, namely capillary suction, which is the primary mechanism for lamellae breakage and the other one is gas diffusion (Kovscek and Radke, 1994). Polymer flooding is the most popular chemical enhanced oil recovery (EOR). Common water-based polymers such as polyacrylamide (PAM) and xanthan are proven to increase the viscosity of water and eventually assist in improving the sweep efficiency of waterfloods (Donaldson et al., 1989). This EOR process could be monitored using streaming potential measurement with electrodes permanently installed downhole (Mohd et al., 2017b), which is also potential to monitor alkaline-surfactant-polymer (ASP) flooding (Mohd et al., 2017a). Besides its potential application in EOR, polymer provides a significant contribution to polymer electrolytes, which is a mixture of organic polymer and inorganic salt. This study includes the use of polymer based electrolytes such as cellulose acetate (Abidin et al., 2014), poly(ethylene oxide) (Chan and Kammer, 2014) on impedance spectroscopy (Chan and Kammer, 2016) as

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well as biopolymer based electrolytes such as a blend of kappa-carrageenan and cellulose derivatives (Rudhziah et al., 2015). In this foam stability study, the idea of using polymeric surfactants and not the conventional surfactants to produce stable foams is due to a stronger adsorption at the air-water interface. This idea has originated from the wide use of protein stabilizing food emulsion and foams (Hide, 2004). Polymeric surfactant has the ability to possess both the behavior of a polymer and surfactant, which is also useful in many disperse systems. They are mainly applied in the preparation of oil-in-water (O/W) and water-in-oil (W/O) emulsion dispersions. The most convenient polymeric surfactants are those of the block and graft copolymer type. A block copolymer is a linear arrangement of blocks of variable monomer composition (Tadros, 2009). Understanding the adsorption and conformation of polymeric surfactants at interfaces is the key to knowing how these molecules act as stabilizers. Most of the basic ideas on adsorption and conformation of polymers have been developed for the solid/liquid interface (Chui, 2014). Thus, the purpose of this paper is to gain a better insight into the stability of foam with varying surfactant concentration and crude oil introduced into the column. In addition to polymeric surfactant, this paper also aims to analyze the reasons behind the thinning of lamellae and the stabilization of foam.

2. Methodology

2.1 Materials

Alpha-Olefin Sulfonate (AOS), obtained from Chem Laboratory has been chosen compared to other commercial surfactants for this study due to its higher longevity in the presence of oil (Bhide et al., 2005). Three different polymeric surfactants are used in this study, namely Lignosulfonic Acid, Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) and Poly(ethylene glycol) dimethyl ether, denoted as LS, PEGB and PEGDME, respectively. They have been purchased from Sigma-Aldrich. Betaines, the foam booster has also been obtained from Sigma-Aldrich and can be used to stabilize the foam in the presence of crude oil (Chui, 2014; Simjoo et al., 2013). Betaines are stored in a refrigerator at a temperature of 8 ^{o}C in order to maintain its structure. In this study, the formulation was prepared in distilled water and surfactant concentrations were based on the active content. The concentrations were 0.10 wt%, 0.25 wt% and 0.50 wt%, similar to that investigated by many researchers in foam flooding. Crude oils were obtained from two different fields in Malaysia, named as Crude Oil A (from a field in Sarawak) and Crude Oil B (from offshore Peninsular Malaysia) with API gravity of 59.6^{o} and 44.8^{o}, respectively. Lastly, carbon dioxide (CO_2) was used since it is available in abundance in most of the reservoirs in Malaysia and it is therefore more economical to reuse the gas produced.

2.2 Foam generator testing rig

The foam was developed using a foam generator testing rig as illustrated in Figure 1. The experimental set up consists of an observation cell (foam column) made of glass with a length of 60.0 cm, a gas and injection solution inlet, a valve as well as a drainage outlet. Generally, CO_2 was blown at a constant rate of 10 ml/min from the bottom of the column through 100 ml of the formulation. The gas was continuously injected until the reaction leads to the generation of foam that filled the glass column (Donaldson et al., 1989). Then, the gas valve was immediately shut off to avoid any backflow during the foam stability test. The experiment was conducted for one hour by taking the foam's height at every five minutes interval in order to analyze the stability of the foam. Finally, the solution was drained once the experiment was completed for other experiments with a different parameter.

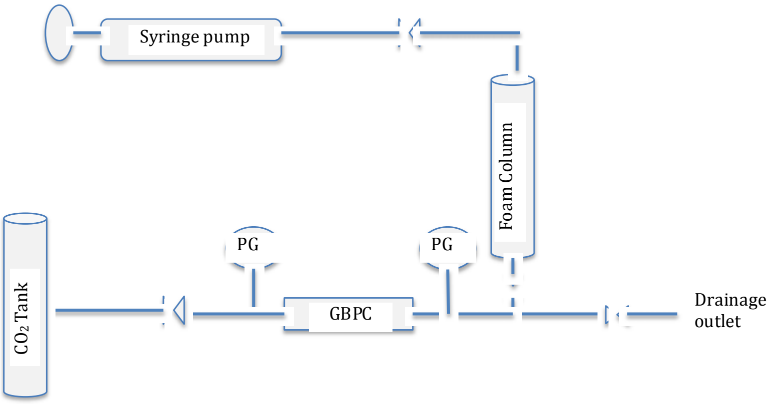

Figure 1: Schematic diagram of foam generator testing rig with Glass Bead Pack Column (GBPC)

2.3 Foam stability test

In order to investigate the effects of surfactant type and the presence of oil on foam stability, a series of experiment have been conducted and summarized in Table 1. Foam decay was monitored by imaging the foam in the columns at different times. The foam stability test was conducted at room temperature by recording the height of the foam as a function of time. For the first experiment, the stability of the foam was tested by using AOS at different concentrations of 0.10 wt%, 0.25 wt% and 0.50 wt%. Foam was generated by sparging CO_2 through the column. After the best concentration was selected, Betaines was added to observe the structure of the foam. Next, preparation of the formulation with different polymeric surfactants was conducted. Injection of CO_2 was made continuously in order to create foam with the prepared formulation. The gas injection was then shut off once the desired foam height was achieved. The time taken for the foam to degenerate after 60 minutes was recorded and further analyzed. Lastly, crude oil was added to analyze foam stability with the best polymeric surfactant as determined by previous experiments.

Table 1: Summary of experimental formulation for stability test

Experiment	Foam formulation	Polymeric surfactant	Crude oil	Concentration of formulation (wt%)
1	AOS	-	-	0.10, 0.25, 0.50
2	AOS, Betaines	-	-	0.50
3	AOS, Betaines	LS, PEGB, PEGDME	-	0.50
4	AOS, Betaines	PEGDME	Crude A, crude B	0.50

3. Results and discussion

3.1 Effect of surfactant concentration on foam stability

One of the obstacles for the wide use of foam in the field is the cost of surfactants. If strong foam could be created at a lower surfactant concentration (Kovscek, 1994), the cost in using it could be greatly reduced. Overall, the AOS foam could be characterized as smaller fine bubbles with a uniform bubble size distribution. Once the injection of gas was stopped the foam entered the decay regime after a period of time (Bhide et al., 2005). Figure 2 represents the inverse relationship of foam height as a function of time. In this experiment, three different AOS concentrations were used to distinguish the foam's longevity.

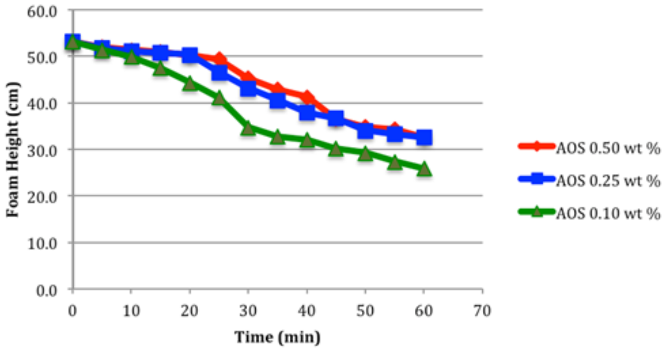

Figure 2: Foam height versus time with different AOS concentration

All three line graphs started at a foam height of 53.1 cm but as time passed, stability of the foam could only be identified at the end of 60 minutes. This clearly shows that AOS with 0.50 wt% exhibited the best foam stability with a height of 32.6 cm at 60 minutes. This was followed by 0.25 wt% with a height of nearly 32.5 cm at 60 minutes and 0.10 wt% with a height of 24.9 cm. There was a rapid change in foam height for AOS at 0.10 wt%. The bubble coalesce was more significant in surfactant concentration of 0.10 wt%, resulting in faster collapse of the foam column. The decay of AOS foam was followed by coalescing bubbles at the top of the column leading to a local change in the foam texture similar to what happened for 0.1 wt% AOS. Theoretically, trapped gas saturation depends on surfactant concentration. The higher the concentration of AOS used, the higher the stability of the foam as many new bubble trains would be created (Mohd et al., 2014). The films were stabilized by surfactants adsorbed at the gas-liquid interface, which were generally very thin. In addition, the destruction of lamellae was governed by the combined effect of attractive and repulsive forces within the lamellae. This is represented by the disjoining pressure isotherm (Kovscek and Radke, 1994), a pressure defined as the additional pressure exerted when the films are thinner. The electrical double-layer produced by the adsorption of ionic surfactants was responsible for the repulsive forces that stabilized the thin film.

3.2 Effect of Betaines in the formulation

Thicker and finer foam was observed with the addition of Betaines in the formulation as shown in Figure 3. Finer bubbles lead to a longer stability of the foam since the capillary end effect causes foam generation near the exit by the snap-off mechanism, trapping some of the air from the foam washed in the preceding sections near the exit, and resulting in a longer time to destabilize (Chui, 2014).

3.3 Effect of polymeric surfactant on foam stability

PEGB is a type of EO/PO block copolymers in which the active surface material properties are dependent on the hydrophilic (EO)/hydrophobic (PO) ratio. A higher EO content gives better O/W stabilizers (Hide, 2004). In Figure 5 however, the PEGB foam collapsed rapidly until no foam bubbles were visible to the eye as shown in Figure 4.

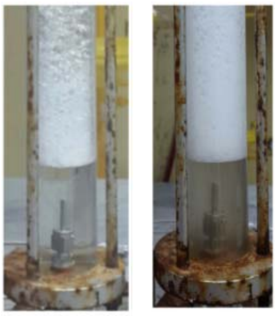
(a) (b)

Figure 3: Foam (a) without Betaines; (b) with Betaines

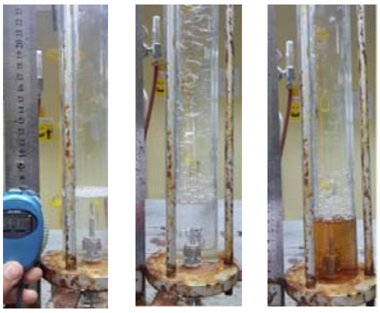
(a) (b) (c)

Figure 4: (a) Foam collapse completely at about 5 minutes for PEGB; and foam height at 60 minutes for (b) PEGDME and (c) LS

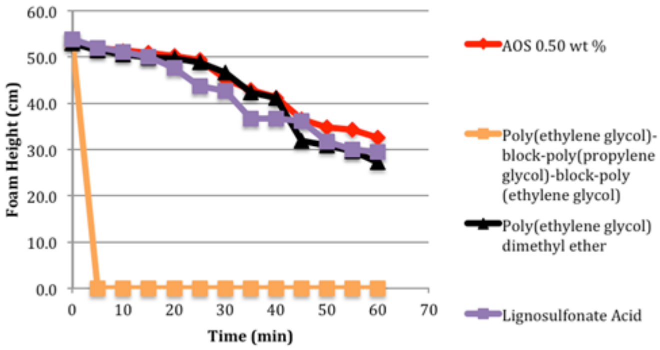

Figure 5: Foam height versus time with different polymeric surfactant

3.4 Effects of crude oil on foam stability

This section aims to examine the destruction mechanism on AOS-stabilized foam when oil is present. The description of both types of crude oil used is summarized in Table 2. Generally, polymeric surfactants exhibit little foam tolerance in the presence of any type of crude oil. It reduces foam gradient, thus resulting in the significant reduction of foam stability (Shen et al., 2006). Figure 8 illustrates the time taken against foam height. It is clearly seen that the foam collapsed rapidly throughout the 60 minutes when oil was injected through the glass column containing foam. This is indicated by a sharp decline which started at 10 minutes. Figure 7 shows several gaps between the foam bubbles at 10 minutes. In accordance with the surfactant screening study, the AOS foam exhibited the largest oil-tolerance leading to faster foam decay in the presence of oil. Larger bubble coalescence for foam in the presence of oil is consistent with studies on the stability of single foam films in the presence of oil. As shown in Figures 6 and 7, foam in the presence of oil required a slightly longer sparging time to fill the column and could not fill the column completely. The foam stability was sensitive to the oil phase if the oil could enter the gas/water interface. There was critical oil saturation; below which the foam behavior was not affected dramatically even in the presence of oils, but above which the foam collapsed abruptly (Simjoo et al., 2013). According to Schramm (1994), foam destabilization by an oil phase may be due to the oil being spontaneously spread on foam lamellae thus displacing the foam stabilizing interface. The other reason is that oil may emulsify the stabilizing interface. In terms of the amount of air taken to fill the column with foam, Crude Oil B took a longer time which could probably be due to the intrinsic stability of the foam films. Apart from that, the cause could be due to the dynamic effects of the foam films during the generation of foam (Schramm, 1994). With respect to API gravity, Crude Oil A does possess lighter properties compared to Crude Oil B although there is no literature to justify that it may have an effect on foam stability.

Table 2: Summary of rheological measurement

Type of crude oil	SG @15 °C	API Gravity (°)	Foam Height at 0 min (cm)	Foam Height at 60 min (cm)
Crude Oil A	0.740	59.6	45.5	2.4
Crude Oil B	0.802	44.8	39.0	0.4

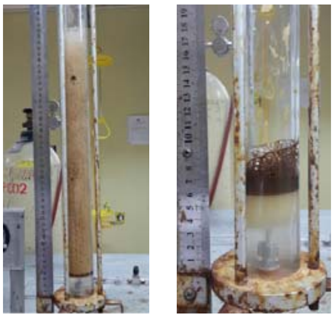
(a) (b)

Figure 6: Foam image with Crude Oil A at (a) 0 minute and (b) 60 minutes.

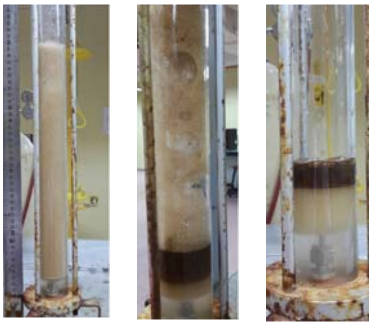
(a) (b) (c)

Figure 7: Foam image with Crude Oil B at (a) 0 min; (b) 10 min and (c) 60 min.

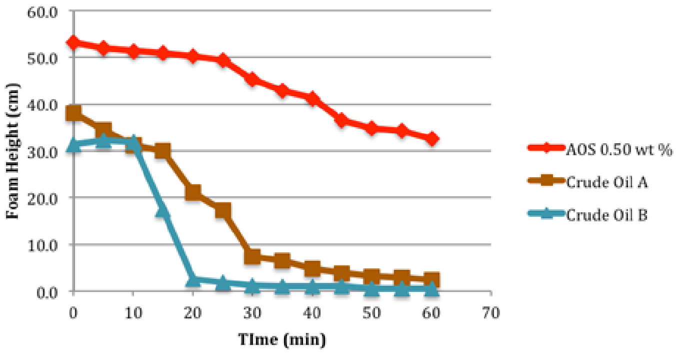

Figure 8: Foam height versus time with different crude oil

4. Conclusion

In summary, this paper demonstrates the principle of using polymeric surfactant to provide higher foam stability. However, the manipulated variable of polymeric surfactant needs to be developed for particular field conditions. It was found that 0.5 wt% AOS provided the most stable foam compared to other concentrations. Thus, a higher concentration of AOS resulted in a longer time for foam to degenerate. Besides that, thicker and finer foam was observed with the addition of Betaines in the formulation. Thus, thinning of lamellae occurred later and helped in enhancing longevity of foam stability. The addition of polymeric surfactant in the formulation further enhanced foam stability. It was found that PEGDME demonstrated the best polymeric surfactant added into the formulation. Other than that, foam tolerance for crude oil was the lowest as rapid changes occurred in foam height, yet Crude Oil A with a higher API gravity was proven to maintain longer foam stability.

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References

Abidin S.Z.Z., Yahya M.Z.A., Hassan O.H., Ali A.M.M., 2014, Conduction Mechanism of Lithium Bis(oxalato)borate–cellulose Acetate Polymer Gel Electrolytes, Ionics, 20(12), 1671–1680.

Bhide V., Hirasaki G., Miller C., Puerto M., Robb I., Norman L., 2005, Foams for Controlling Water Production, SPE International Symposium on Oilfield Chemistry, Texas, U.S.A.

Chan C.H., Kammer H.W., 2014, Polymer Electrolytes-Relaxation and Transport Properties, Ionics, 21(4), 927–934.

Chan C.H., Kammer H.W., 2016, On Dielectrics of Polymer Electrolytes Studied by Impedance Spectroscopy, Ionics, 1–9.

Chui L., 2014, Application of Foam for Mobility Control in Enhanced Oil Recovery (EOR) Process, PhD Thesis, Rice University.

Donaldson E., Chilingar G., Yen, T., 1989, Enhanced Oil Recovery. Amsterdam: Elsevier.

Hamidi H., Mohammadian E., Rafati R., Azdarpour A., Ing J., 2015, The Effect of Ultrasonic Waves on the Phase Behavior of a Surfactant-Brine-Oil System, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 482, 27–33.

Hide V.B., 2004, Developing Stable Foams from Polymeric Surfactants for Water Production Control, PhD Thesis, Rice University.

Honarvar B., Azdarpour A., Karimi M., Rahimi A., Karaei M.A., Hamidi H., Mohammadian E., 2017, Experimental Investigation of Interfacial Tension Measurement and Oil Recovery by Carbonated Water Injection: A Case Study Using Core Samples from an Iranian Carbonate Oil Reservoir, Energy and Fuels, 31(3), 2740–2748.

Kovscek, A., 1994, Foam Displacement in Porous Media: Experiment and Mechanistic Prediction by the Population Balance Method, PhD Thesis, University of California, Berkeley.

Kovscek, A.R., Radke, C.J., 1994, Fundamentals of Foam Transport in Porous Media, Foams: Fundamentals and Applications in the Petroleum Industry, 3, 115-163.

Li, Q., 2006, Foam Generation and Propagation in Homogeneous and Heterogeneous Porous Media, PhD Thesis, University of Texas at Austin.

Mohd T.A.T., Jaafar M.Z., Rasol A.A.A., Ali J., 2017, Review: A New Prospect of Streaming Potential Measurement in Alkaline-Surfactant-Polymer Flooding, Chemical Engineering Transactions, 56, 1183-1188.

Mohd T.A.T., Jaafar M.Z., Rasol A.A.A., Hamid M.F., 2017, Measurement of Streaming Potential in Downhole Application: An Insight for Enhanced Oil Recovery Monitoring, 03002.

Mohd T.A.T., Muhayyidin A.H.M., Ghazali N.A., Shahruddin M.Z., Alias N., Arina S., Ismail S.N., Ramlee N.A., 2014, Carbon Dioxide (CO_2) Foam Stability Dependence on Nanoparticle Concentration for Enhanced Oil Recovery (EOR), Applied Mechanics and Materials, 548-549, 1876-1880.

Rudhziah S., Ahmad A., Ahmad I., Mohamed N.S., 2015, Biopolymer Electrolytes Based On Blend of Kappa-Carrageenan and Cellulose Derivatives for Potential Application in Dye Sensitized Solar Cell, Electrochimica Acta, 175, 162–168.

Schramm L., 1994, Foams. Washington, DC: American Chemical Society.

Shen C., Nguyen Q., Rossen W., 2006, Does Polymer Stabilize Foam in Porous Media?, SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma.

Simjoo M., Rezaei T., Andrianov A., Zitha P., 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.

Sydansk R., Romero-Zerón L., 2011, Reservoir Conformance Improvement, Society of Petroleum Engineers.

Tadros T., 2009, Polymeric Surfactants in Disperse Systems, Advances in Colloid and Interface Science, 147-148, 281-299.

Tanzil D., Hirasaki G., Miller C., 2002, Conditions for Foam Generation in Homogeneous Porous Media, SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma.