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Insights into CO_2 Foaming Behavior of Ethoxylated Amines

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Abstract: Switchable ethoxylated amine surfactants are readily soluble in CO_2 and high-saline brines. The objective of the current work is to maximize the foamability and stability of CO_2 foam at 150 °F (65 °C) through adjustments in the surfactant concentration, pH, and brine salinity. From the results, the authors recommend potential applications of Ethomeen C12 (EC12) for CO_2 foam in the oil/gas industry. Foam stability tests helped determine the optimum parameters for CO_2 foam stability at 77 °F (25 °C) and 150 °F (65 °C). The surface tension of EC12 as a function of concentration was evaluated using a drop-shape analyzer. Maximum foam stability was observed for a solution comprising of 1.5 wt% EC12, 25 wt% NaCl, and pH 6.5 at 150 °F (65 °C). The interactions with the salts allowed closer packing of the surfactant molecules at the lamellae and strengthening the foam. At a pH of 2.5, the absence of salt led to poor foam stability. However, at the same pH and in the presence of sodium chloride, the foam was stable for longer periods of time due to the salt influence. The surface tension gradients had a direct relationship to foam stability. There was a strong resistance to foam degradation when multivalent ions were present with the surfactant.

Keywords: foam; interfacial properties; saline brine

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1. Introduction

CO_2 injection has proved to be an effective enhanced oil recovery (EOR) method and is applied extensively in various oil fields around the world. CO_2 flooding enhances oil recovery mainly through gas drive, oil swelling, interfacial tension (IFT) reduction, and oil viscosity reduction [1]. The major limitations of CO_2 EOR are conformance issues, mobility control, and displacement front instability. These problems are especially severe in formations with a high degree of heterogeneity and varying wettability. To combat these issues, foam was introduced to assist CO_2 EOR. In foam-assisted CO_2 EOR, the mobility of CO_2 is reduced by increasing the apparent viscosity of the gas phase, stabilizing the displacement process and increasing the sweep efficiency. Moreover, through the formation of foam in high permeability zones/layers, the technique achieves conformance control for CO_2 EOR [2,3]. Gravity segregation, another problem of CO_2 EOR, is also alleviated when foam is applied by shifting the viscous/gravitational force competition [4]. The presence of foam may also help reduce the capillary forces and residual oil saturation.

In a CO_2 foam system, CO_2 exists in the gaseous phase within the bubbles dispersed in the liquid/brine phase. Most of the liquid phase, however, is not stored in these lamellae films; rather, they stay within the networks of the plateau borders (PB), where the films meet. The volumetric ratio of the gas phase to that of the liquid phase is often referred to as foam quality. Low-quality foam is also known as wet foam, while the high-quality foam is also called dry foam [5]. Foam quality promotes the stability of liquid films, which translates to the stability of the entire foam system [6]. A remaining concern is that high volumetric gas fraction causes the lamellae films to be thinly spread, generating high capillary pressure. This makes the dry foam more prone to faster destabilization because of lamellae drainage [7].

For many surfactants, an increase in salinity negatively affects foam stability. Increasing the salinity leads to a compression of the electrical double layer and lowers the maximum disjoining pressure in foam films, which destabilizes the foam [8,9]. In high-salinity environments, the process of foam coalescence starts earlier, and foam collapses at a faster rate. Several authors have investigated the use of alpha-olefin sulfonate (AOS) with additives such as SiO_2 nanoparticles and cocamidopropyl betaine (cocobetaine) viscoelastic surfactant for CO_2 EOR application but only for solutions with salinity up to 8 wt% NaCl [10,11]. These researchers further identified an insolubility threshold at salinity greater than 8 wt%. Therefore, high-salinity brines for anionic and nonionic surfactants are undesirable due to detrimental interactions between the salt ions and the surfactant [12]. Formation water and the EOR fluid can mix in the reservoir causing high-salinity conditions for the surfactant.

Switchable ethoxylated amines have been found to be effective CO_2 foaming agents that are also soluble in CO_2 [13]. A switchable ethoxylated amine is capable of converting reversibly between its nonionic and cationic forms. A solution/environment pH threshold triggers this conversion, which, for Ethomeen C12 is a pH between 4 and 5 [14]. At the original pH greater than 9, the surfactant is in its nonionic form. In the presence of H^+, the amine headgroup is protonated, and Ethomeen C12 assumes its cationic form. When assuming its nonionic form, Ethomeen C12 has limited solubility in water; however, when protonated at pH 4, Ethomeen C12 is highly soluble in water, even at 266 °F (130 °C) [14]. Moreover, under its cationic form, Ethomeen C12 exhibits low adsorption on carbonates due to the electrostatic repulsion between the protonated head and the positively charged carbonate surface. Literature showed that Ethomeen C12 has a cloud-point of approximately 176 °F (80 °C) and 248 °F (120 °C) at pH 6.5 and pH < 5.5, respectively [13]. In a sandpack, the authors found that the apparent viscosity of the foam generated at 248 °F (120 °C) reached its maximum at 90% foam quality.

The excess surface concentration is derived from the Gibbs isotherm and is given by Equation (1) [15]:

$$\Gamma = -\frac{1}{RT}\left(\frac{\delta\gamma}{\delta \ln C_{surf}}\right)_{T,P} \tag{1}$$

where Γ is the surface excess concentration, R is the universal gas constant, T is absolute temperature, and the $\frac{\delta\gamma}{\delta \ln C_{surf}}$ term represents the rate of change of the surface tension with surfactant concentration. This term is calculated from the slope of the surface tension versus surfactant concentration plot. The slope is related to Gibbs elasticity, which is used to study the foam stability. The rate of change of the surface tension with the surfactant concentration indicated how rapidly the surface tension gradients develop [16]. The surface tension gradients induce a flow of liquids from low to high surface tension regions, which is known as the Marangoni effect [17]. A high surface tension gradient effectively heals the thinning foam bubble and provides stability [18]. In general, the solution needs a high surface tension gradient to sufficiently enable the bubble film to withstand stress [19,20]. The Gibbs elasticity, describing the elasticity of the foam film, is expressed as Equation (2).

$$E = 2A\frac{\delta\gamma}{\delta A} = 2A\frac{\delta\gamma}{\delta C_{surf}}\frac{\delta C_{surf}}{\delta A} \tag{2}$$

For foam systems, the Gibbs elasticity is more impactful than the absolute values of surface tension or the CMC. To the knowledge of the authors, there exists no work in literature to evaluate the surface tension gradient of the ethoxylated amine surfactant in the presence of CO_2. This investigation can help in understanding the foam stability of the surfactant at various concentrations, pH, and brine salinity, and composition through surface tension measurements.

Switchable ethoxylated amine surfactants are suitable for applications in carbonate reservoirs, because of their capability to assume cationic form when protonated, resulting in low adsorption onto the rock surface under the appropriate pH condition. There are other commercially available cationic surfactants that also exhibit low adsorption onto carbonate rock surface [21]. However, most of these cationic surfactants have poor solubility in CO_2 [13] and can oil-wet formation rocks [22]. Switchable ethoxylated amine surfactants, on the other hand, have excellent solubility in CO_2 when assuming their nonionic form [15]. This high CO_2 solubility enables injection along with the CO_2 phase during EOR operations, which proved more beneficial and effective than the traditional injection scheme [4]. Another common benefit shared by both the switchable ethoxylated amine and nonionic ethoxylated surfactants is high salinity tolerance [12]. Ethomeen C12 foam was investigated for its apparent viscosity through coreflood studies at different foam qualities, salinity, and temperature [14]. The coreflood studies indicated the dissolution of carbonate minerals, and the authors recommended to use sufficient divalent ions to suppress the damage. However, the switchable surfactant needs to be evaluated and optimized for its foam stability. Ethomeen C12 is an interesting and promising surfactant with a wide range of applicability that deserves closer attention. There is limited work on the stability behavior of generated foam over different surfactant concentrations, pH, and brine salinity, and composition. The effects of these factors on the surfactant solution/CO_2 interfacial properties at 150 °F (65 °C) have not been discussed. The objectives of this work include:

1. Investigate the CO_2 foaming properties of EC12, such as initial foamability and foam stability at different surfactant concentrations, initial pH, and brine salinity and composition.
2. Evaluate the surface tension of EC12 as a function of surfactant concentration in the presence of CO_2 at 150 °F (65 °C) using the pendant drop method.
3. Calculate the CMC and surface tension gradients from the surface tension versus surfactant concentration plot. The surface tension gradients were used to understand the foaming properties of EC12.

The current work uses bottle foam tests, high-pressure chamber foam tests, and drop shape analysis to investigate the surfactant solution for maximum foam stability. The following sections describe the materials, experimental tests and procedure, results and discussion, conclusions, and recommendations in that order.

2. Materials

The switchable ethoxylated amine surfactant, Ethomeen C12 or coco bis(2-hydroxyethyl) amine (95%), was obtained as a gift from Nouryon and was used as received. It is a tertiary amine ethoxylate and its chemical structure is presented in Figure 1. The surfactant activity and hydrophile-lipophile balance (HLB) were 90 wt% and 12.2, respectively, according to the manufacturer. The molecular weight of the surfactant was 270 g/mol. The density and viscosity of the surfactant were 0.9 g/cm^3 and 120 cP, respectively. The surfactant solutions were prepared with a salinity of 0–25 wt% sodium chloride and a surfactant concentration of 0.0001–2 wt% using deionized water with a resistivity of 18.2 MΩ-cm at room temperature. The ionic strength of the solution ranged from 0.855 to 4.535 mol/L. The surfactant was prepared by adding a measured volume of EC12 into the brine solution drop-by-drop while the solution was being stirred. The surfactant is water-soluble at pH < 6.7. To achieve complete solubility, the initial solution pH was adjusted using HCl (procured from the Texas A&M Biochemistry and Biophysics Stockroom). The initial solution pH was either 6.5 or 2.5 to investigate the foaming properties for acidizing, fracturing, and EOR related applications. CO_2 gas (from Airgas, College Station) with a purity of 99.9 mol% was used.

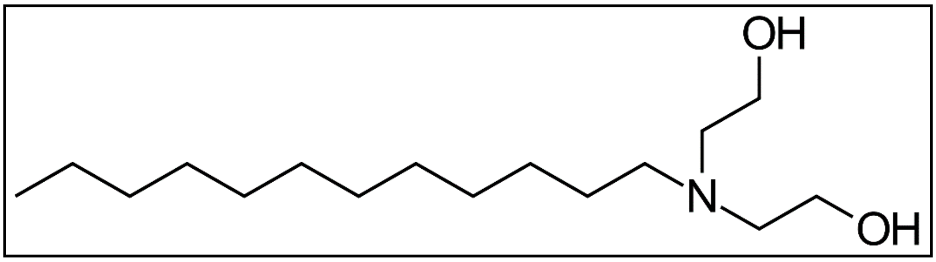

Figure 1. Chemical structure of the surfactant used in this study. The hydrophobic tail contains 12 carbon atoms.

3. Experimental Tests and Procedures

3.1. Bottle Foam Test

The foamability of various surfactant solutions at ambient conditions was investigated in glass vials. The vials were rinsed several times with acetone and deionized water before starting the experiment. To generate the foam, 5 cm^3 of the surfactant solution was transferred into a 20 cm^3 vial. The vial was then shaken at ambient conditions for one minute and then allowed to sit while the timer started. The foam height inside the vial was recorded at regular intervals of time to determine the decay profile of the surfactant solutions. Each experiment was repeated at least three times to ensure repeatability and the error was less than 5%.

Two parameters were measured through the bottle tests. The height of the initial foam after shaking the bottle is denoted as foamability. The foam half-life, which is the time taken for the foam to reach half of its initial height, indicated the foam stability of the surfactant solution.

3.2. High-Pressure Foam Test

A high-pressure view chamber (HPVC) was utilized to study the foam stability under pressure. Figure 2 shows the schematic diagram of the setup. The view chamber is constructed in stainless steel with a full-length glass window. A glass tube was placed inside the chamber with a metal plate at the bottom to allow sparging of the gas into the surfactant solution and create a foam column. 30 cm^3 of the surfactant solution was placed inside the chamber and then pressurized using CO_2 to a maximum of 500 psi (34.5 bar) and heated to 150 °F (65 °C). Sufficient time was given to allow the chamber to be heated to 150 °F (65 °C) and achieve thermal equilibrium with the surfactant solution. The foam was created by sparging CO_2 from the fixed volume gas accumulator into the bottom of the chamber at a pressure of 550 psi (38 bar). A camera setup helped record the foam decay over time. The chamber was evacuated and cleaned with deionized water at the end of the experiment. Each experiment was repeated at least three times to ensure repeatability and the error was less than 5%.

3.3. Surface Tension Study

The interfacial properties such as surface tension, CMC, and surface tension gradients of EC12 were evaluated at different surfactant concentrations, pH, and brine salinity and composition using the pendant drop method with computer-aided image processing. A system containing the view chamber, light source, camera, video frame digitizer board, and software was utilized. A schematic diagram of the setup is shown in Figure 3.

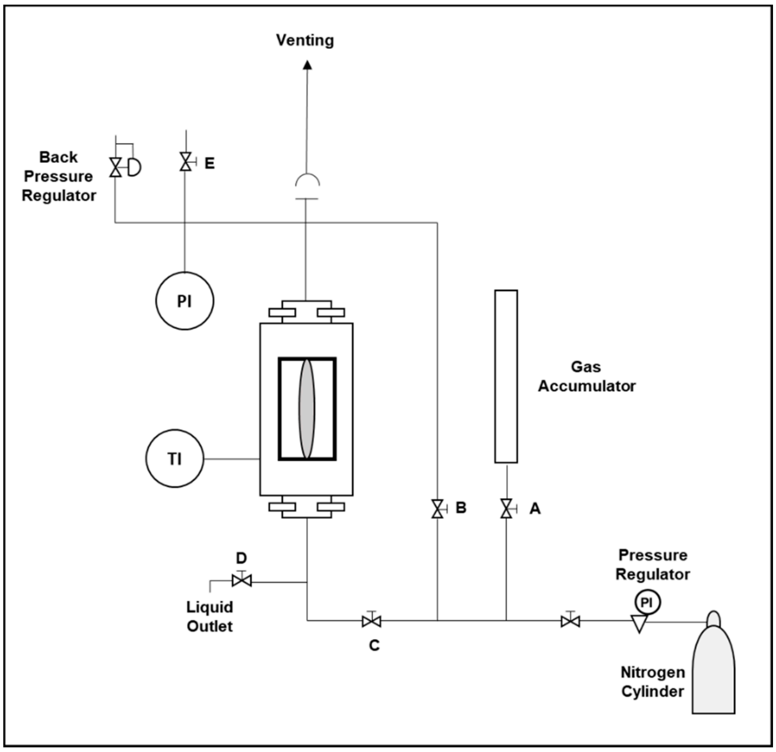

Figure 2. Schematic diagram of the high-pressure view chamber setup for the foam stability test. A and B are ball valves; C, D, and E are needle valves. PI and TI represent pressure gauge and thermocouple, respectively.

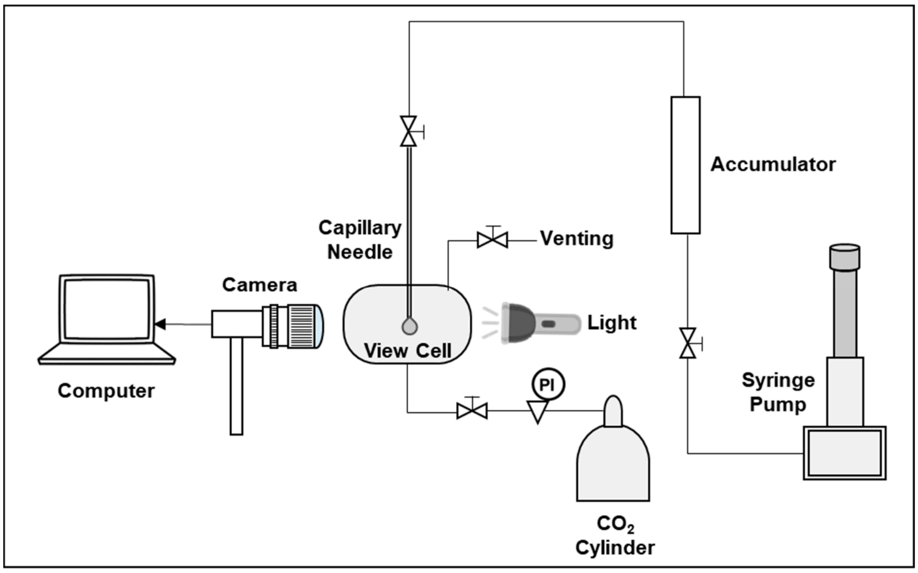

Figure 3. Schematic diagram of the drop shape analyzer setup.

The fundamentals and nuances of setting up and using the pendant drop method with computer-aided processing were described in the literature to accurately measure the surface tension at elevated temperature and pressure conditions [23,24]. The prepared surfactant solution was loaded into the accumulator. The view chamber was filled with CO_2 and brought to the desired temperature and pressure conditions. A drop of surfactant solution was injected from the top to allow the formation of a liquid droplet. This droplet was then allowed to stay for 120 min to achieve thermal and chemical equilibrium. Dispersions containing surfactants usually exhibited a decrease in the equilibrium surface tension because of surfactant adsorption at the interface [25]. Minimization of the surface Gibbs free energy was usually the main driving force for adsorption. The transient surface tension, also known as the dynamic surface tension (DST), was different from the equilibrium surface tension. It could take hours to establish the equilibrium adsorbed surfactant density. In this study, the change in surface tension was monitored over time, and the equilibrium was established in 1.5 and 1 h at 77 °F (25 °C) and 150 °F (65 °C), respectively (Figure 4). All surface tension measurements were conducted at a pressure of 500 psi (34.5 bar). All the recorded values for the surface tension study were at equilibrium.

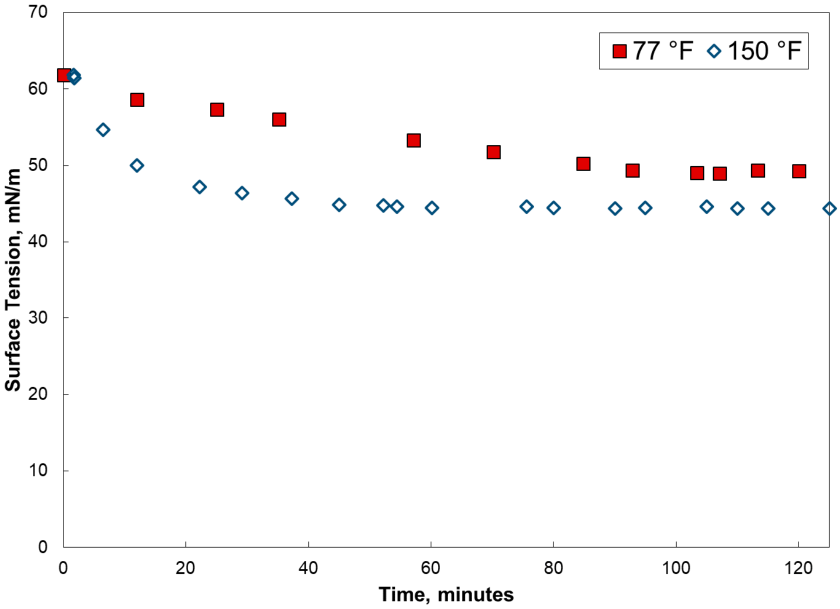

Figure 4. Time to reach equilibrium surface tension of surfactant-CO_2 system. The surfactant concentration was 0.0005 wt%. The salinity and pH of the solution were 25 wt% NaCl and 6.5, respectively.

4. Results and Discussion

4.1. Bottle Foam Tests at Ambient Conditions

Optimizing the surfactant parameters such as surfactant concentration, pH, and brine salinity and composition for maximum foamability and foam stability is important. Bottle tests provided an initial screening for these parameters and demonstrated an idea of the surfactant's performance as a foaming agent. Surfactant solutions were prepared at a concentration ranging from 0.1 to 1 wt% to investigate the effect of surfactant concentration on the initial foamability and foam stability at ambient conditions. 5 cm^3 of the solution was placed in a 20 cm^3 glass vial and shaken for a period of one minute. The initial foam height was recorded as the initial foamability. The decay of the foam was observed at regular time intervals.

At 5 wt% NaCl, the initial foamability increased as surfactant concentration increased from 0.1 to 0.5 wt% (Figure 5). A concentration of 1 wt% surfactant showed a decrease in the initial foamability. However, this trend of increasing initial foamability with the increase in surfactant concentration diminished at NaCl concentrations greater than 15 wt%. Figure 6 presents the initial foamability of the surfactant solutions at 20 wt% NaCl. The figure shows a similar initial foamability for 0.1, 0.25, and 0.5 wt% surfactants and a decrease in the initial foamability for 1 wt% surfactant.

Ethomeen C12 is either cationic or nonionic, influenced by the solution pH. As the pH is lowered, the lone pair of electrons on the nitrogen atom is lost, and the surfactant becomes positively charged. It is cationic below pH 4.5 [14]. The initial pH of the solution is important when evaluating such surfactants for foam CO_2 injection. The present paper studies the initial foamability of the surfactant solution at a pH of 6.5 and 2.5. Figure 7 demonstrates the effect of the initial pH on the initial foamability of the surfactant solution. A solution with pH 2.5 has a better initial foam than pH 6.5. There is evidence of bigger bubble sizes in solutions with pH 2.5. The larger bubbles within the low-pH foam lead to poor foam stability, as will be discussed later.

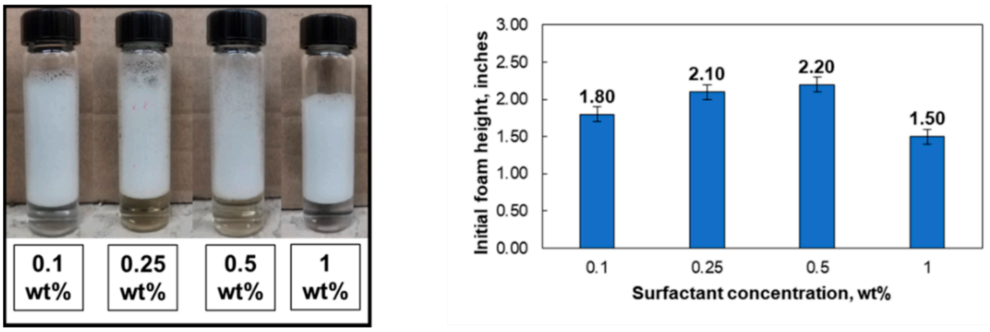

Figure 5. Effect of surfactant concentration on the initial foamability at 5 wt% NaCl, pH 6.5, and 77 °F (25 °C).

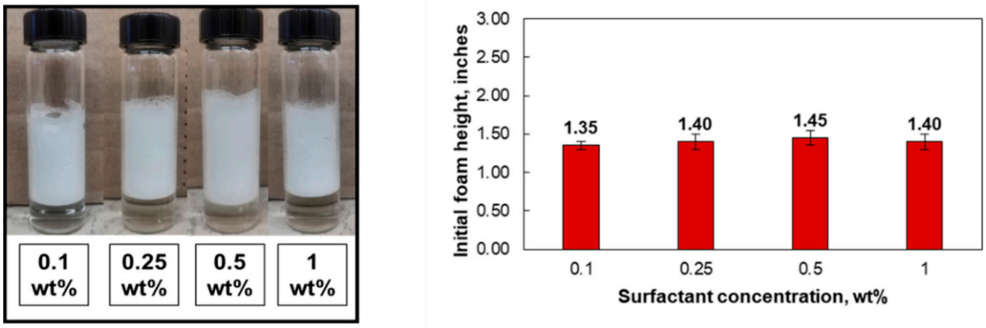

Figure 6. Effect of surfactant concentration on the initial foamability at 20 wt% NaCl, pH 6.5, and 77 °F (25 °C).

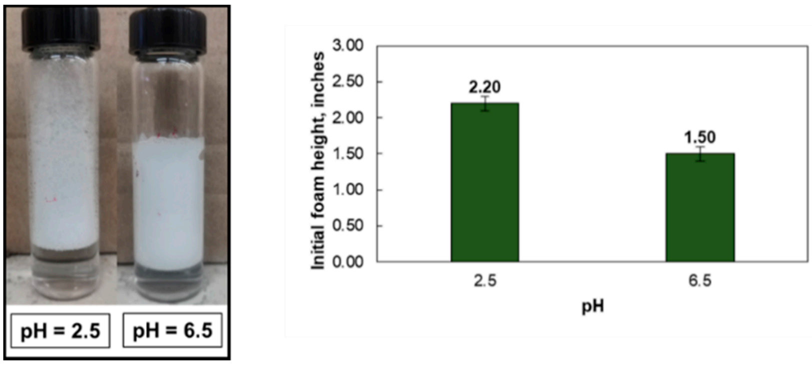

Figure 7. Effect of initial pH on the initial foamability at 10 wt% NaCl, 0.25 wt% surfactant, and 77 °F (25 °C).

Studies on the application of CO_2 foam at high-salinity conditions remain limited. Mixing of formation brine and injected brine can lead to high salinity conditions for the foam propagation in the reservoir. The effect of salinity is crucial in understanding the foamability. This paper addresses the gap in the literature and evaluates the effect of salinity on the initial foamability. Salinities of 5, 15, 20, and 25 wt% NaCl were investigated for the initial foamability. Figure 8 presents the initial foamability for 5, 15, 20, and 25 wt% NaCl solutions having the same pH of 6.5 and surfactant concentration of 0.5 wt%. The initial foamability appears to slightly decrease as the salinity increases.

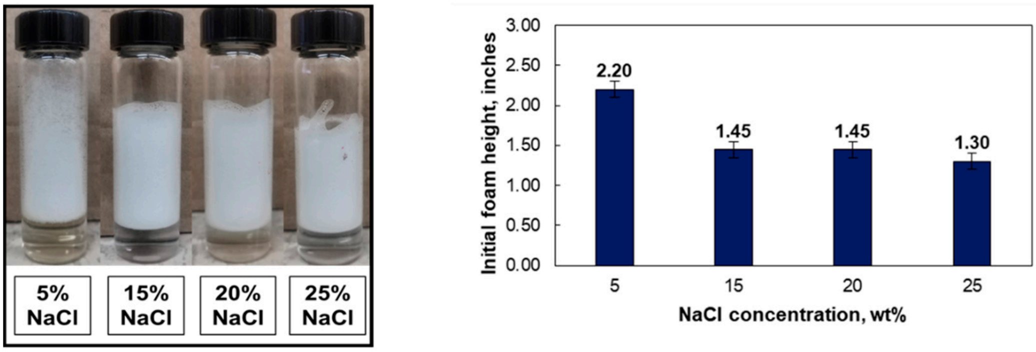

Figure 8. Effect of salinity on the initial foamability at pH 6.5, 0.5 wt% surfactant, and 77 °F (25 °C).

Foam stability is an indicator of the dynamic performance of the foam. A stable foam has good elasticity, high maximum disjoining pressure, resistance to Ostwald ripening, resistance to drainage, and resistance to defects such as oil films. Ostwald ripening is a thermodynamically driven mechanism occurring due to larger particles being more energetically favored than smaller particles in a heterogeneous system like foam. After the foam formation, the smaller foam bubbles shrink while the bigger ones grow over time [26,27]. Due to big foam bubbles being generally less stable, Ostwald ripening leads to the overall foam system instability. Foam stability testing measures the foam decay over time and is a good test to optimize the surfactant's parameters for effective treatment in the field. The foam heights were recorded at regular time intervals. Tables 1 and 2 present the foam half-life times and initial foam height for all the bottle tests conducted. The foam half-life is the time taken for the foam height to reach half of its initial value. The table indicates that the optimum surfactant concentration depends on other factors such as the solution pH and salinity. The maximum foam stability was found in a solution composition of 0.25 wt% EC12 with a brine salinity of 25 wt% NaCl and pH of 6.5. The foam half-life for this composition was recorded as 42 h at 77 °F (25 °C) and atmospheric pressure.

Table 1. Foam half-life of EC12 at room temperature and pH 6.5.

Surfactant Concentration (wt%)	Salinity (wt%)	Initial Foam Height (Inches)	Foam Half-Life (h)
0.1	5	1.80	6
0.25	5	2.10	10
0.5	5	2.20	14
1.0	5	1.50	22
0.1	10	1.35	10
0.25	10	1.50	14
0.5	10	1.60	20
1.0	10	1.30	24
0.1	15	1.35	14
0.25	15	1.35	22
0.5	15	1.45	24
1.0	15	1.30	16
0.1	20	1.35	18
0.25	20	1.40	42
0.5	20	1.45	42
1.0	20	1.40	18
0.1	25	1.30	22
0.25	25	1.30	46
0.5	25	1.30	42
1.0	25	1.30	22

Table 2. Foam half-life of EC12 at room temperature and pH 2.5.

Surfactant Concentration (wt%)	Salinity (wt%)	Initial Foam Height (Inches)	Foam Half-Life (h)
0.1	5	2.10	1
0.25	5	2.10	0.5
0.5	5	2.10	0.5
1.0	5	2.20	<0.5
0.1	10	2.00	1
0.25	10	2.20	0.5
0.5	10	2.20	0.5
1.0	10	2.20	0.5
0.1	15	1.70	10
0.25	15	1.75	6
0.5	15	1.85	6
1.0	15	2.00	3
0.1	20	1.50	15
0.25	20	1.60	22
0.5	20	1.70	26
1.0	20	1.80	10
0.1	25	1.30	22
0.25	25	1.40	42
0.5	25	1.45	38
1.0	25	1.50	18

The initial pH affected the initial foamability, as previously discussed. The change in the surfactant charge from nonionic to cationic as a result of decreasing the solution pH may also affect the foam stability. The present study evaluates the surfactant for foam stability 2.5 and 6.5. At 5 wt% NaCl and pH 6.5, the foam half-life is much longer than the same solution at pH 2.5. At a pH of 2.5, Ethomeen C12 is almost entirely protonated, while at a pH of 6.5, some of the surfactant molecules still exist in its nonionic form [28]. The foam at pH 2.5 had higher bubble density and larger bubbles, as observable in Figure 7. The bigger bubbles are highly unstable and can lead to foam collapse.

Adding salt to the acidic surfactant solution helped in improving the foam stability. There was a significant increase in the foam half-life when salt was added to the acidic surfactant solutions. As shown in Table 2, the foam half-life increased from 0.5 to about 42 h when the salinity of the acidic surfactant solutions changed from 5 to 20 wt% NaCl, respectively. This study recommends a high saline EC12 solution with a salinity greater than 15 wt% NaCl to be used for acid applications.

4.2. HPVC Foam Tests

The foam stability must be evaluated at representative field conditions to provide an optimum solution for EC12 in the field. The pressure and temperature of these tests were set at 500 psi (34.5 bar) and 150 °F (65 °C), respectively. The current work investigates the CO_2 foam stability of the surfactant at different surfactant concentrations, pH, and brine salinity and composition. Surfactant solutions were prepared with a concentration of 0.25–2 wt%. The pH was changed to 6.5 and 2.5 using HCl. Four brine compositions were tested: 5, 25 wt% NaCl, 9.5 wt% $CaCl_2$, and 6.1% Na_2SO_4. The experiments were repeated twice, and the average value was recorded.

The results of the HPVC foam test closely followed the trends observed in the bottle foam tests. Figure 9 demonstrates the effect of surfactant concentration on foam stability at 150 °F (65 °C) and 500 psi (34.5 bar). The plot shows the normalized foam height as a function of time for surfactant solution with a concentration of 0.25 to 2 wt%. The height of the foam was recorded at various intervals of time and normalized to the initial foam height. The foam half-life improved with the increase in the surfactant concentration until 1.5 wt%. Increased surfactant concentration led to the increase in the surfactant molecular density in the lamellae, strengthening the foam. There was a rapid collapse of the foam bubbles at

0.25 wt% surfactant. A 1.5 wt% surfactant solution had a foam half-life 10 times that of a 0.25 wt% surfactant solution at pH 6.5, 25% NaCl, and 150 °F (65 °C). The foam half-life for a 2 wt% surfactant solution was lower than the 1.5 wt% solutions. The foam stability is driven by the surface tension forces. There is an optimum surfactant concentration beyond which, the foam stability does not improve with the increase in the concentration because the surface tension forces do not significantly change.

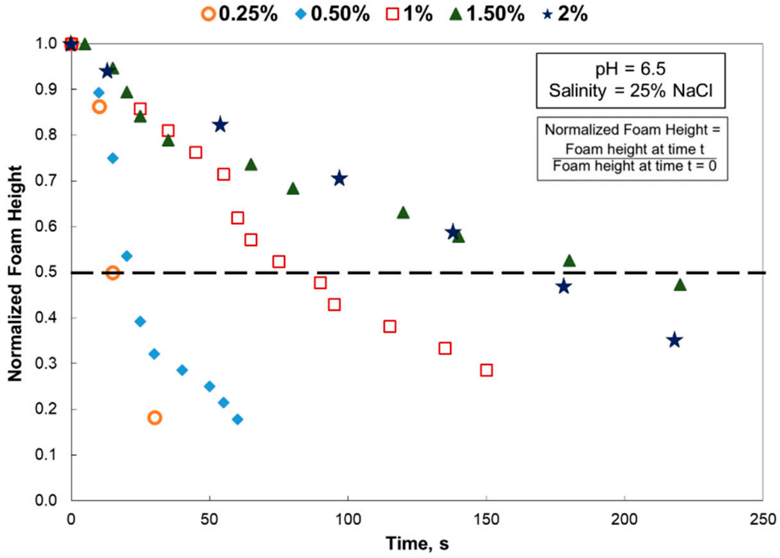

Figure 9. Effect of surfactant concentration on the foam stability at 150 °F (65 °C) and 500 psi (34.5 bar).

The role of pH on foam stability was evaluated in this study. Figure 10 presents the foam decay of EC12 at pH conditions of 6.5 and 2.5. At pH 6.5, the surfactant is partially protonated, whereas at pH 2.5, the solution is completely protonated [15]. The foam half-life was reduced by 50% when the pH was reduced to 2.5. The higher amount of positively charged amine headgroups at the acidic pH of 2.5 led to a more repulsive interaction between the surfactant molecules and lowered the surfactant molecular density in the liquid films. The lower surfactant molecular density lowered the maximum disjoining pressure and eventually led to less stable liquid films. The lower film stability resulted in the acceleration of the film thinning and film rupture. This caused the foam to collapse faster at an acidic pH environment.

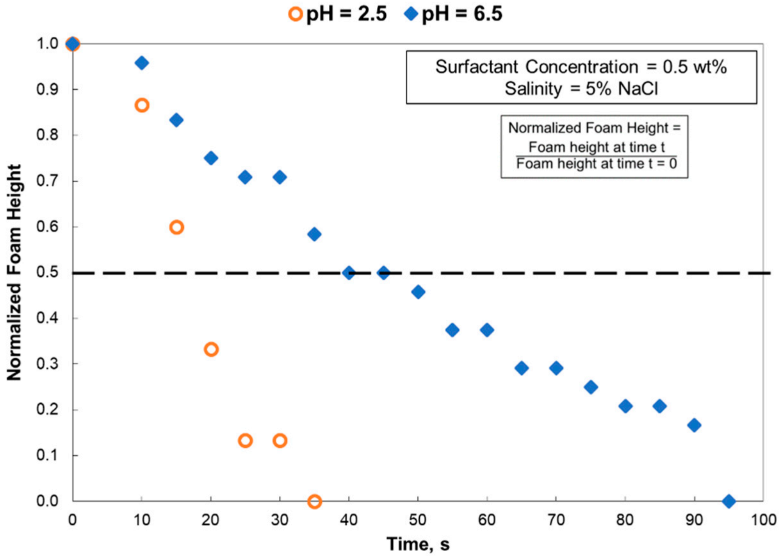

Figure 10. Effect of solution pH on the foam stability at 150 °F (65 °C) and 500 psi (34.5 bar).

The brine salinity plays an important role in stabilizing the foam bubbles. Figure 11 shows the foam half-life for 1 wt% surfactant solutions and at salinities of 5 and 25% NaCl. As shown in the figure, the increase in brine salinity improved the stability of the foam bubbles. There was also an increase in the foam half-life for the acidic surfactant solution (pH = 2.5). The improvement in the foam stability for the pH 2.5 solution at 25 wt% NaCl may be due to the increase in the Cl^- ion concentration in the solution. The increase in the anion concentration helped in counteracting the repulsive interactions between the positively charged protonated surfactant molecules, leading to tighter surfactant packing in the liquid films. This interaction between the anionic Cl^- ions and the protonated surfactant molecules leads to a more stable liquid film, resulting in longer-lasting foam even at pH 2.5.

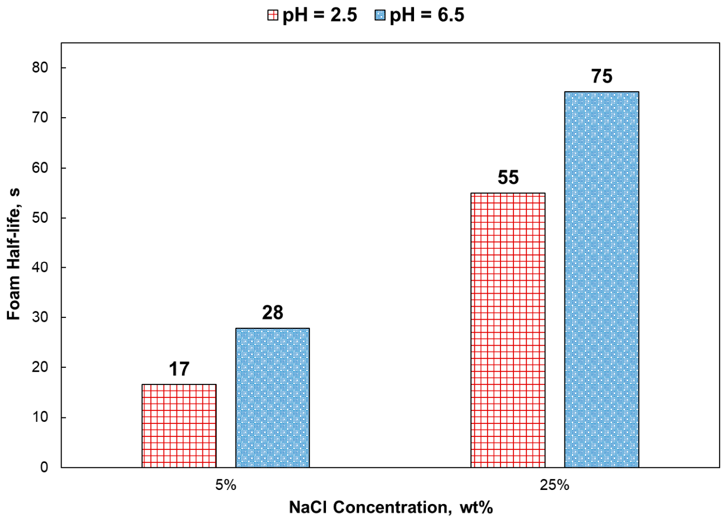

Figure 11. Effect of salinity on the foam stability at 150 °F (65 °C) and 500 psi (34.5 bar).

The brine ion composition can influence the surfactant's properties to create stable foam. The resistance to multivalent ions in creating foam is an important characteristic of a good foaming surfactant. This study compared the foam decay profile of 5 wt% NaCl, 9.5 wt% $CaCl_2$, and 6.1% Na_2SO_4 brine solutions with 0.5 wt% surfactants and pH 6.5. The brine solutions had the same cation concentration of 0.9 mol/kg. Figure 12 presents the role of brine composition on the foam stability at 150 °F (65 °C). Surfactant solution prepared with $CaCl_2$ had a similar foam decay profile as the solution prepared with NaCl. This demonstrates the resistance to foam collapse due to the presence of multivalent cations. Another test with sodium sulfate as the brine was conducted to test the effect of sulfate ions on the foam decay. Sulfate ions are commonly available in seawater brines [29]. The presence of sulfate ions was detrimental to foam stability. The foam bubbles collapsed almost instantly at 150 °F (65 °C).

4.3. Surface Tension Study

The foam stability is linked to the interfacial properties of the surfactant/CO_2 mixture. The surface tension, CMC, and surface tension gradients reveal important information to establish the effectiveness of the surfactant to create stable foam. This study evaluated the surface tension of Ethomeen C12 at 77 °F (25 °C) and 150 °F (65 °C), in the presence of CO_2. The surface tension was measured by varying the concentration from 0.0001–0.1 wt%, and the CMC and the slope of the surface tension curve were estimated.

Figures 13 and 14 show the effect of temperature on the interfacial behavior of the surfactant. An increase in the CMC was observed with an increase in temperature. At 5 wt% NaCl, the CMC increased from 1.6×10^{-3} to 4.6×10^{-3} wt% as the temperature increased from 77 °F (25 °C) to 150 °F (65 °C). However, at 25 wt% NaCl, the CMC remained constant at 1.3×10^{-3} wt%. The rate of surface tension change with surfactant concentration in the

CMC region (hereby referred to as surface tension gradient) decreased as the temperature increased from 77 °F (25 °C) to 150 °F (65 °C). At 5 and 25 wt% NaCl, the surface tension gradient decreased by 35 and 16%, respectively, as the temperature increased from 77 °F (25 °C) to 150 °F (65 °C). The decrease in the surface tension gradient translates to poorer foam stability at 150 °F (65 °C).

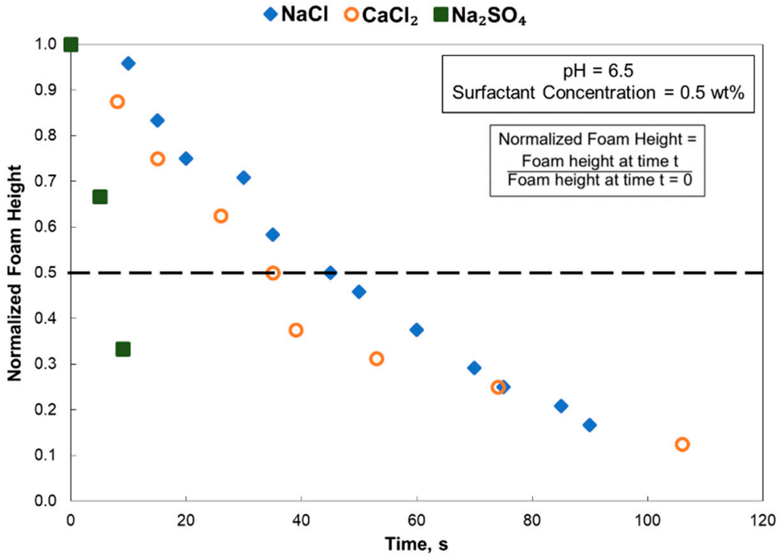

Figure 12. Role of multivalent cations and sulfate anions on the foam stability at 150 °F (65 °C) and 500 psi (34.5 bar).

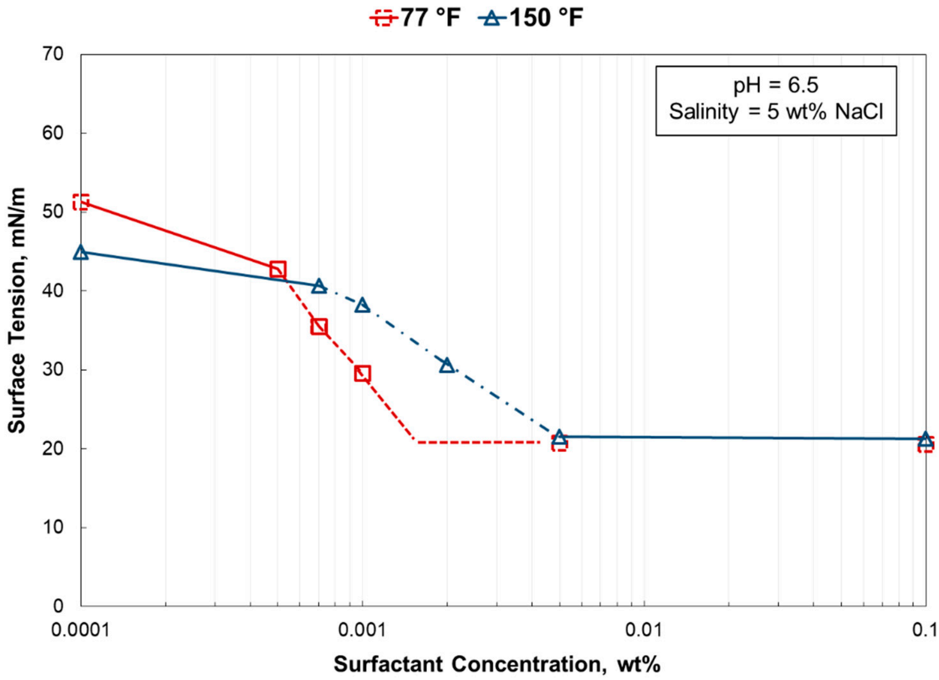

Figure 13. Effect of temperature on surfactant interfacial properties at pH 6.5 and 5 wt% NaCl.

Figures 15 and 16 show the effect of salinity on the surface tension of the CO_2/surfactant system. An increase in salinity resulted in lower CMC and surface tension values. At 150 °F (65 °C) and pH 6.5, the CMC decreased from 4.6×10^{-3} to 1.3×10^{-3} wt%, when the salt concentration increased from 5 to 25% NaCl. The surface tension gradient increased with the salinity. The increase in the surface tension gradient was a strong indicator that the foam generated in high salinity (25 wt% NaCl) environment would be more stable than that generated in a low-salinity environment (5 wt% NaCl) because of its increased elastic properties. Results from the foam stability tests were in accordance with this finding.

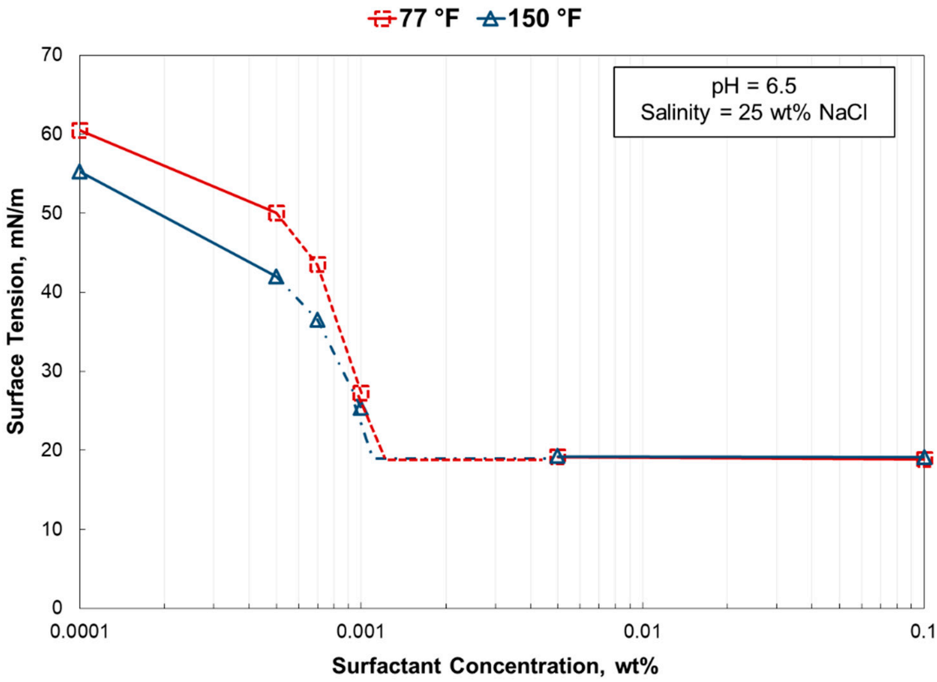

Figure 14. Effect of temperature on surfactant interfacial properties at pH 6.5 and 25 wt% NaCl.

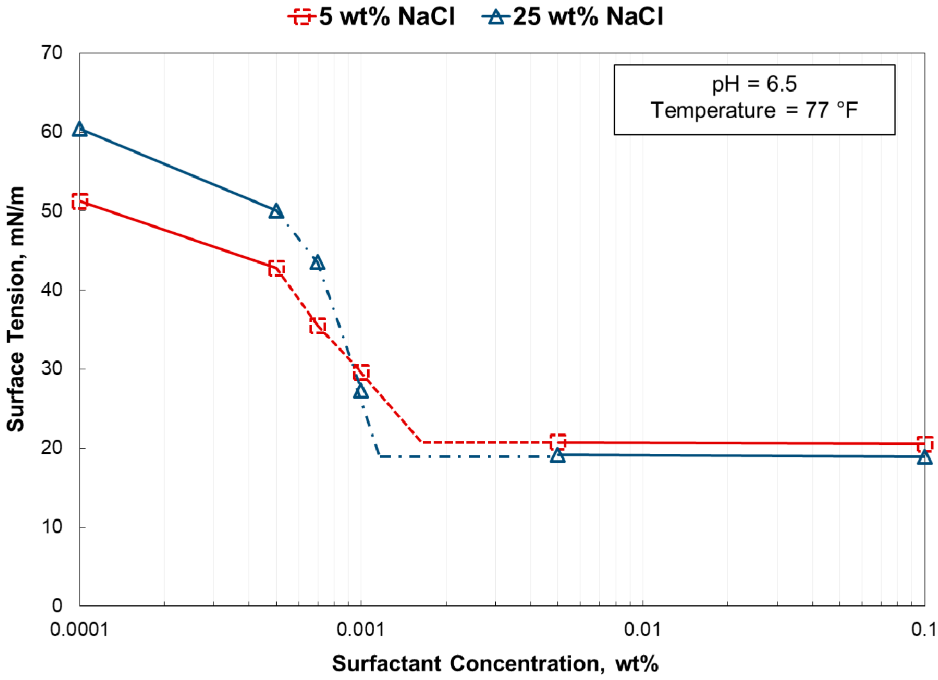

Figure 15. Role of NaCl concentration on the surface tension, CMC, and surface tension gradients at pH 6.5 and 77 °F (25 °C).

The authors also observed lower surface tension above the CMC for 25 wt% NaCl solutions compared to 5 wt% NaCl. This phenomenon was attributed to the higher abundance of counterions, Cl^-, at high NaCl concentration. The repulsive interactions of the positively charged ions in the protonated Ethomeen C12 head groups were reduced because of the high concentration of counterions, allowing for more densely packed surfactant molecules at the interface. This increase in the surfactant interface molecular density leads to a decrease in surface tension.

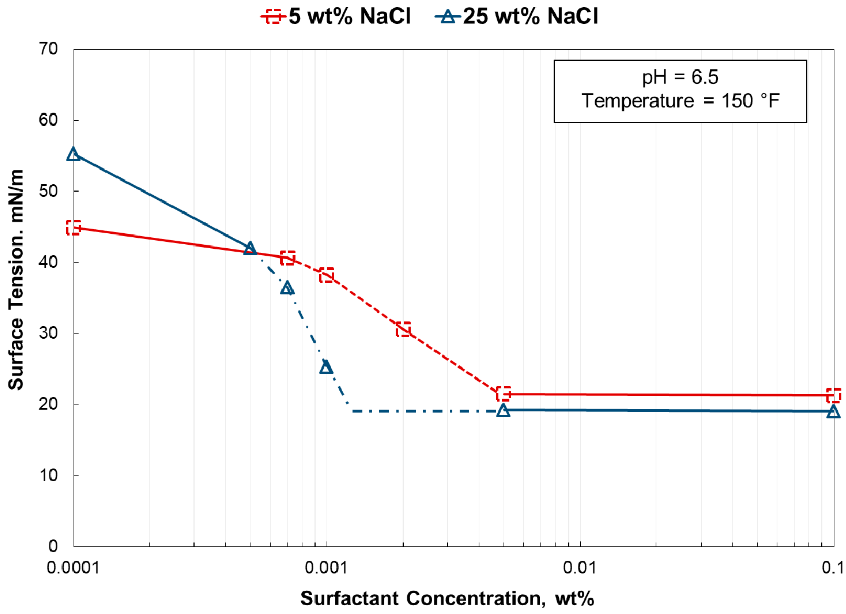

Figure 16. Role of NaCl concentration on the surfactant solution interfacial properties at pH 6.5 and 150 °F (65 °C).

Figures 17 and 18 present the effect of initial solution pH on the surface tension. The surfactant was tested for interfacial properties at pH 2.5 and 6.5. The CMC value was higher for the acidic surfactant solution. At 5 wt% NaCl & 77 °F (25 °C), the CMC increased from 1.6×10^{-3} to 2.4×10^{-3} wt% as initial pH changed from 6.5 to 2.5. There was a decrease in the surface tension gradient when the initial pH was changed from 6.5 to 2.5. This can lead to less stable foam, as shown in the foam stability tests. However, the solution pH did not affect the surface tension gradient at 25 wt% NaCl. The surface tension did not significantly decrease with a decrease in pH.

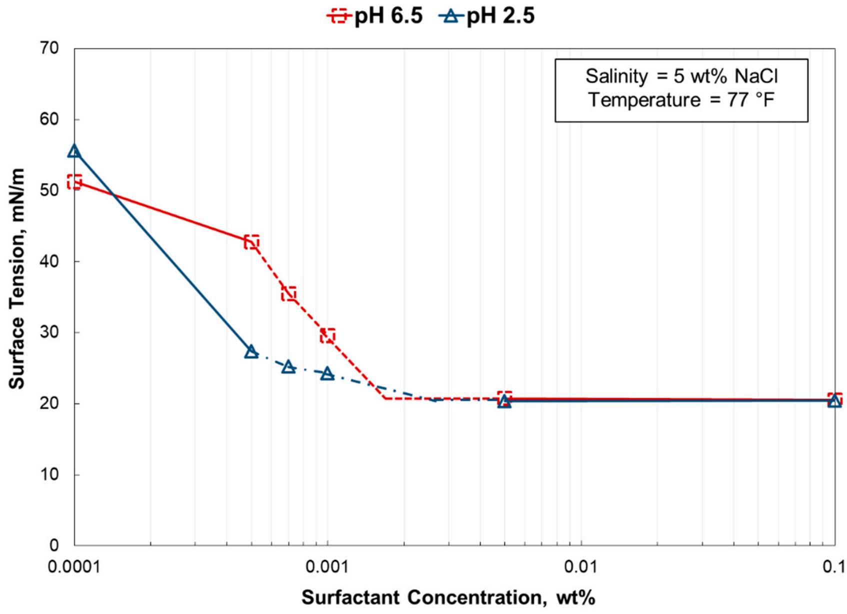

Figure 17. Effect of initial pH on surfactant solution interfacial properties at 5 wt% NaCl and 77 °F (25 °C).

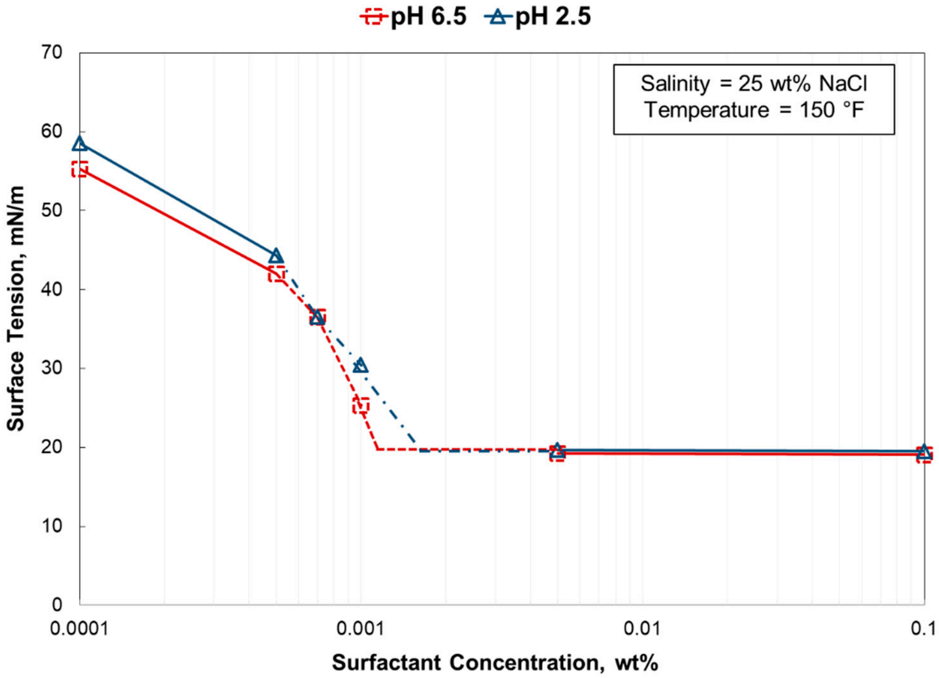

Figure 18. Effect of initial pH on surfactant solution interfacial properties at 25 wt% NaCl and 150 °F (65 °C).

The effect of multivalent cations on the interfacial properties of Ethomeen C12 were examined by comparing the interfacial properties of the surfactant solutions prepared with either NaCl or $CaCl_2$ (Figure 19). The CMC of the 5 wt% NaCl solution was 4.6×10^{-3} wt%, compared to the CMC of 2.3×10^{-3} wt% for the 9 wt% $CaCl_2$ solutions. Both of these solutions had the same salt molality, 0.9 mol/kg. Thus, the CMC difference between these solutions, on a log scale, was not significant. There was no change in the surface tension gradient between the two brine solutions. This indicates resistance to foam degradation due to the presence of multivalent ions.

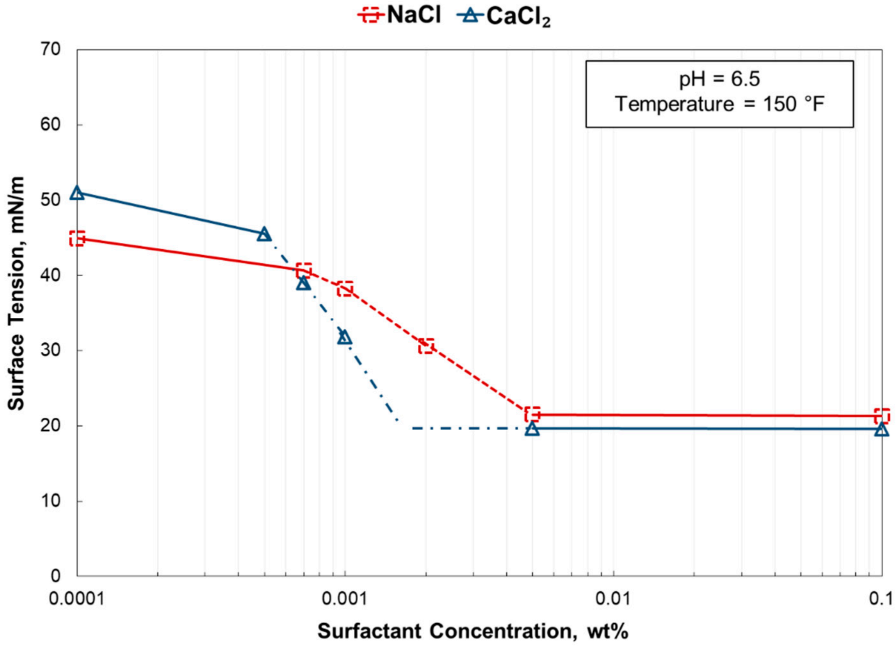

Figure 19. Surface tension as a function of surfactant concentration for 0.9 mol/kg solutions of NaCl and $CaCl_2$ at pH 6.5 and 150 °F (65 °C).

5. Conclusions

Foam CO_2 is a promising technology for EOR applications. The present work investigated and optimized a switchable ethoxylated amine surfactant, Ethomeen C12, for its foam properties under different conditions. Surfactant concentration, initial pH, and brine salinity and composition were evaluated for initial foamability and foam stability. This study presented a new analysis of foam stability through interfacial tension measurement of the surfactant solutions at various salinity, temperature, and pH conditions. The surfactant was also evaluated for resistance to multivalent ions. The results lead to the following conclusions:

1. The initial foamability increased with surfactant concentration from 0.1–0.5 wt%. Solutions with pH 2.5 yielded better initial foam than those at pH 6.5.
2. Generally, the foam stability of the pH 6.5 solutions was better than that of the pH 2.5 solutions, especially at a low-salinity environment. The foam stability reached a maximum for 1.5% surfactant solutions.
3. The addition of chloride ions had both stabilization and destabilization effects on foam stability. Destabilization occurred by depressing the electrical double layer and stabilization by tighter packing of surfactant at the liquid films. For Ethomeen C12, the stabilization effect overcame the destabilization effect at 20–25 wt% NaCl.
4. The surface tension gradients calculated from a plot of surface tension vs. surfactant concentration yielded an excellent positive correlation to the foam stability.
5. The increase in temperature resulted in a lower surface tension gradient and thus poorer foam stability at higher temperatures. An increase in salinity resulted in higher surface tension gradients.
6. In 5 wt% NaCl, the surface tension gradient was greatly affected by using a pH 2.5 solution. However, at 25 wt% NaCl, there was no impact by solution pH.
7. This surfactant showed high resistance to the presence of divalent cations in terms of the interfacial properties and foam stability at 150 °F (65 °C).

6. Recommendation

The authors recommend a 1.5 wt% surfactant solution with a pH of 6.5 and a brine salinity of 25 wt% NaCl for maximum foam stability at 150 °F (65 °C). For acidizing related activities, maintaining a high concentration of NaCl produces more stable foam. Ethomeen C12 is resistant to foam degradation when multivalent ions are present. However, EC12 is not recommended to be used with brines that are high in sulfate ions such as seawater. EC12 can be combined with foam enhancers like cocoamidopropyl betaine and tested for foam stability.

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Abbreviations

EC12	ethomeen C12
EOR	enhanced oil recovery
IFT	interfacial tension
PB	plateau borders
AOS	alpha-olefin sulfonate
EO	ethoxylated oxide
HLB	hydrophile-lipophile balance
CMC	critical micelle concentration
HPVC	high-pressure view chamber
DST	dynamic surface tension

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