

**UNDERSTANDING CO<sub>2</sub> FOAMING BEHAVIOR OF SWITCHABLE  
ETHOXYLATED AMINE**

A Thesis

By

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## ABSTRACT

Switchable ethoxylated amine surfactants are readily soluble in CO<sub>2</sub> and high-saline brines, as well as chemically stable at high temperatures. Additionally, in their cationic form, these surfactants exhibit low adsorption on carbonates, making them excellent candidates for EOR and other applications in high-salinity, high-temperature carbonate formations. This work focuses on investigating the foaming and interfacial properties of Ethomeen C12 (EC12) in presence of CO<sub>2</sub>. The objective is to optimize the surfactant concentration, pH, and brine salinity, and composition for maximizing the foamability and stability of CO<sub>2</sub> foam at 150°F. From the results, potential applications of EC12 for CO<sub>2</sub> foam in the oil/gas industry is recommended.

The various conducted foam tests helped determine the optimum parameters for CO<sub>2</sub> foam stability at room temperature and at 150°F. The surface tension of EC12 as a function of concentration was evaluated using a drop-shape analyzer. From the surface tension versus surfactant concentration plot, the critical micelle concentration (CMC) and the slope were calculated. EC12 was prepared at a salinity range of 0-25 wt%, surfactant concentrations of 0.0001-1 wt%, and pH 2.5 and 6.5. The influence of cation charge on the foam stability was also examined using NaCl and CaCl<sub>2</sub> brine solutions. The foam tests assisted in determining the optimal initial foamability and the foam half-life in different salinity, temperature, and pH conditions. The surface tension study illustrated the use of interfacial properties to evaluate the potential of the surfactant to create stable foam.

Maximum foam stability was observed for a solution comprising of 1.5 wt% EC12, 25 wt% NaCl, and pH 6.5. The foam stability was enhanced at high salinity conditions because of the increased interactions between the anions and the surfactant heads. The interactions 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, in presence of NaCl, the foam was stable for longer periods of time because of the decreased repulsion between the surfactant heads. The surface tension study helped in validating the foam stability tests. The surface tension gradients were a direct indicator to the foam stability. There was a strong resistance to foam degradation when multivalent cations were present, up to 25 wt% multivalent salt concentration. However, in the presence of sulfate ions, the foam degraded very quickly. This was further evidence indicating strong performance of switchable ethoxylated amine surfactant in high-salinity conditions of 25 wt% NaCl. Extensive investigation of the foaming performance and interfacial properties of this surfactant type over a wide range of salinity and pH in representative field conditions was conducted. These are the gaps in the literature that this work addresses. Additionally, recommendations on optimizing the use of EC12 depending on the reservoir conditions are provided as a result of this study.

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### **Contributors**

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## NOMENCLATURE

|      |                                |
|------|--------------------------------|
| 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     |

## INTRODUCTION AND LITERATURE REVIEW

CO<sub>2</sub> injection is a proven effective enhanced oil recovery (EOR) method and is applied extensively in various oil fields around the world. Today, CO<sub>2</sub> injection is responsible for the production of almost 500,000 barrels per day worldwide, representing 20% of total oil production through all EOR applications (IEA 2018) around the globe. As summarized by Ghedan (Ghedan 2009), there are many mechanisms driving CO<sub>2</sub> injection's commercial success; some of the most influential ones include interfacial tension (IFT) reduction, oil viscosity reduction, oil swelling, gas drive, and favorable alteration to the formation permeability, oil and water densities. Furthermore, as an injection gas, CO<sub>2</sub> also has some major advantages over others, such low miscibility pressure and minimum gas overriding problems due to its liquid-like density under reservoir conditions. However, the major limitations of CO<sub>2</sub> 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. The high-permeability layers create mobile pathways for CO<sub>2</sub> to channel through, leaving much of the recoverable oil in other low-permeability regions uncontacted.

To combat mobility and conformance issues, foam was introduced to assist CO<sub>2</sub> EOR applications (Enick et al. 2012). Talebian et al. (2013) explored the use of foam in CO<sub>2</sub> EOR. In foam-assisted CO<sub>2</sub> EOR, the mobility of CO<sub>2</sub> 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, foam also helps provide conformance control for CO<sub>2</sub> EOR. Gravity segregation, another problem of CO<sub>2</sub> EOR, is also alleviated when foam is applied by shifting the viscous/gravitational force competition. The presence of foam may also help reduce the capillary forces and residual oil saturation. As a result,

many common issues limiting the efficiency of CO<sub>2</sub> flooding projects such as gravity segregation, viscous fingering, gas override, and channeling are lessened when foam is introduced to assist CO<sub>2</sub> EOR applications. Patil et al. (2018), after performing a complete examination of the response from a CO<sub>2</sub>-foam injection in Wyoming, confirmed that foam-assisted CO<sub>2</sub> EOR demonstrated improved conformance control and sweep efficiency. This project resulted in a significant increase in oil recovery factor and a decrease in amount of CO<sub>2</sub> usage due to better CO<sub>2</sub> utilization.

In a CO<sub>2</sub> foam system, CO<sub>2</sub> exists in the gaseous phase within the bubbles dispersed in the liquid/brine phase. The dispersed foam bubbles are separated by thin liquid films, or lamellae films, which are stabilized by the absorbed surfactant molecules (**Fig. 1**). 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 (Schramm and Wassmuth 1994). 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 high-quality foam is also called dry foam (Rehm et al. 2013). Foam quality promotes the stability of the liquid films, which translates to the stability of the entire foam system. A remaining concern is that high volumetric gas fraction causes the lamellae films to be thinly spread, generating high capillary pressure. This makes dry foam more prone to faster destabilization because of lamellae drainage (Rio and Bianche 2014).

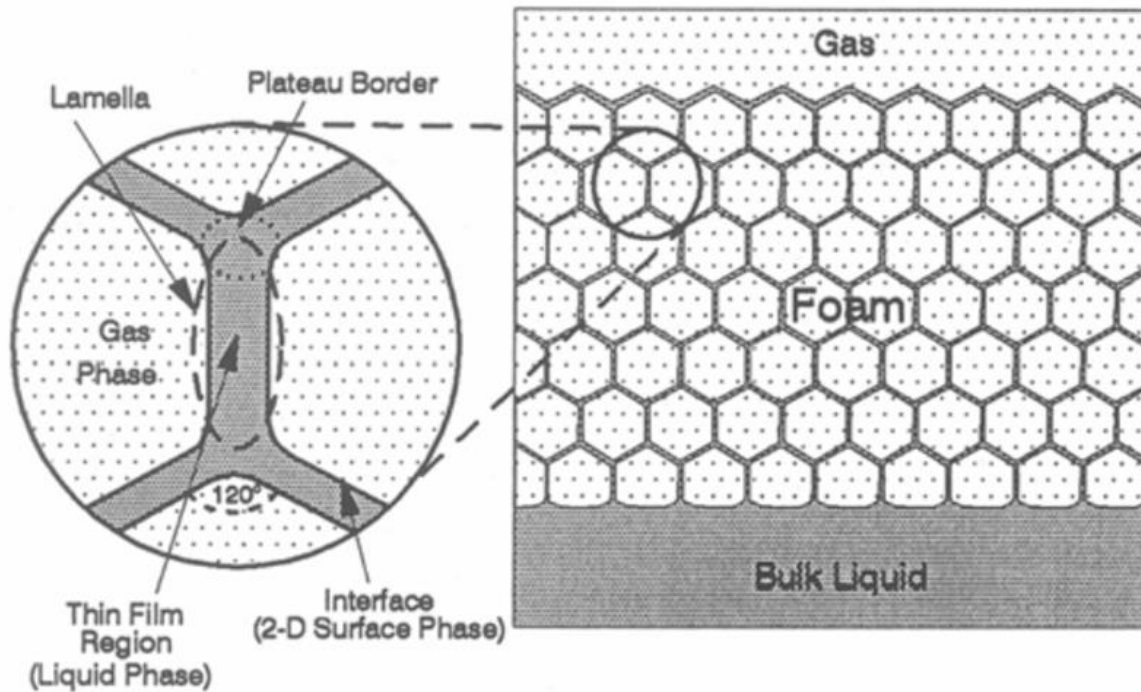


Fig. 1—Structure of the lamellae film (Bhakta and Ruckenstein 1997)

Foam is an inherently thermodynamically unstable system, due to the interactions and forces at the interfaces. Foam systems degrade over time into separate gas and liquid phases, mainly because of the drainage of liquid at the lamellae, plateau border suction, and capillary suction. For CO<sub>2</sub> EOR applications, in order for the CO<sub>2</sub> foam to be an effective displacement fluid, the lamellae in the foam system must remain stable, especially under the harsh reservoir conditions. Aronson et al. (1993) studied how the stability of foam films, which was gauged by the measured films' disjoining pressures, can be linked to the flow resistance of foam fluids in porous media. They found that strong and stable films did lead to strong foam in porous media with large resistance to flow. Furthermore, it was observed that the limiting capillary pressure for rapid coalescence of foam fluids in porous media was similar to the rupture pressure of foam lamellae obtained from lab measurements. Similar conclusions were also reached by Khatib et al. (1988). Adsorption of the surfactant at the CO<sub>2</sub>/liquid interfaces stabilizes the lamellae by slowing down liquid drainage at

the plateau borders. Surfactant can achieve this effect by changing the elasticity of the gas/liquid interfaces, decreasing the gas/liquid interfacial tension and creating a favorable repulsive/attractive interaction at the molecular level (Apaydin and Kavscek 2001). For these reasons, the selection of the right surfactant or combination of surfactants for CO<sub>2</sub> foam EOR applications is imperative and remains a topic of significant interest.

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 (Bergeron and Radke 1992; Bhakta and Ruckenstein 1996). In high-salinity environments, the process of foam coalescence starts earlier, and foam collapses at a faster rate. Generally, the addition of salts also reduces the surface tension, interfacial tension, and critical micelle concentration (CMC), all of which significantly affect the foam stability. The choice of surfactant determines the extend of these reduction interactions (Wan and Poon 1969). For these reasons, many surfactants can only be used as CO<sub>2</sub> foaming agents in low-salinity environments. Emrani and Nasr-El-Din (2017) and Ibrahim et al. (2017) investigated the use of alpha-olefin sulfonate (AOS) with additives such as SiO<sub>2</sub> nanoparticles and cocamidopropyl betaine (cocobetaine) viscoelastic surfactant for CO<sub>2</sub> EOR application, but only for solutions with salinity up to 8 wt% NaCl. These researchers further identified an insolubility threshold at salinity greater than 8 wt%. Therefore, high-salinity brines for anionic and non-ionic surfactants are undesirable due to detrimental interactions between the salt ions and the surfactant (Belhaj et al. 2019). Mixing of formation water and injected water during EOR operations can lead to reduced foam performance due to formation of high salinity conditions.

Owing to the aforementioned problems, switchable ethoxylated amine surfactants have been receiving some attention recently (Cui et al. 2018; Hirasaki et al. 2011; Ramadhan et al. 2018).

These amine-based surfactants consist of an alkyl chain, typically 12-14 C or 16-18 C, and several ethoxylated oxide (EO) groups (Chen et al. 2014; Chen et al. 2018; Zhang et al. 2019). The surfactant of interest in this work has an alkyl chain of 12-14 C and 2 EO groups.

Switchable ethoxylated amines have been found to be effective CO<sub>2</sub> foaming agents that are also soluble in CO<sub>2</sub> (Chen et al. 2014). Switchable ethoxylated amine is capable of converting reversibly between its nonionic and cationic form. A solution/environment pH threshold triggers this conversion, which, for Ethomeen C12 is around pH of 4.5 (Cui et al. 2016). At pH greater than 9, which is the pH of commercially produced Ethomeen C12, the surfactant is in its nonionic form. In the presence of H<sup>+</sup>, 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 (Cui et al. 2016). Chen et al. (2012) showed that Ethomen C12 has a cloud-point of approximately 176°F and 248°F at pH 6.5 and pH < 5.5, respectively. Previous work has shown that Ethomeen C12 is capable of forming moderately stable CO<sub>2</sub> foam at 248°F and 22% TDS brine (Cui et al. 2016). 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 (Cui et al. 2014). Ethomeen C12, therefore, has many advantages over traditional nonionic or anionic surfactants as CO<sub>2</sub> foaming agent in high temperature and high salinity carbonate reservoirs (Cui and Bourrel 2018; Gland et al. 2018). The low adsorption of the surfactant of interest on carbonate surface implies economical potential for field application.

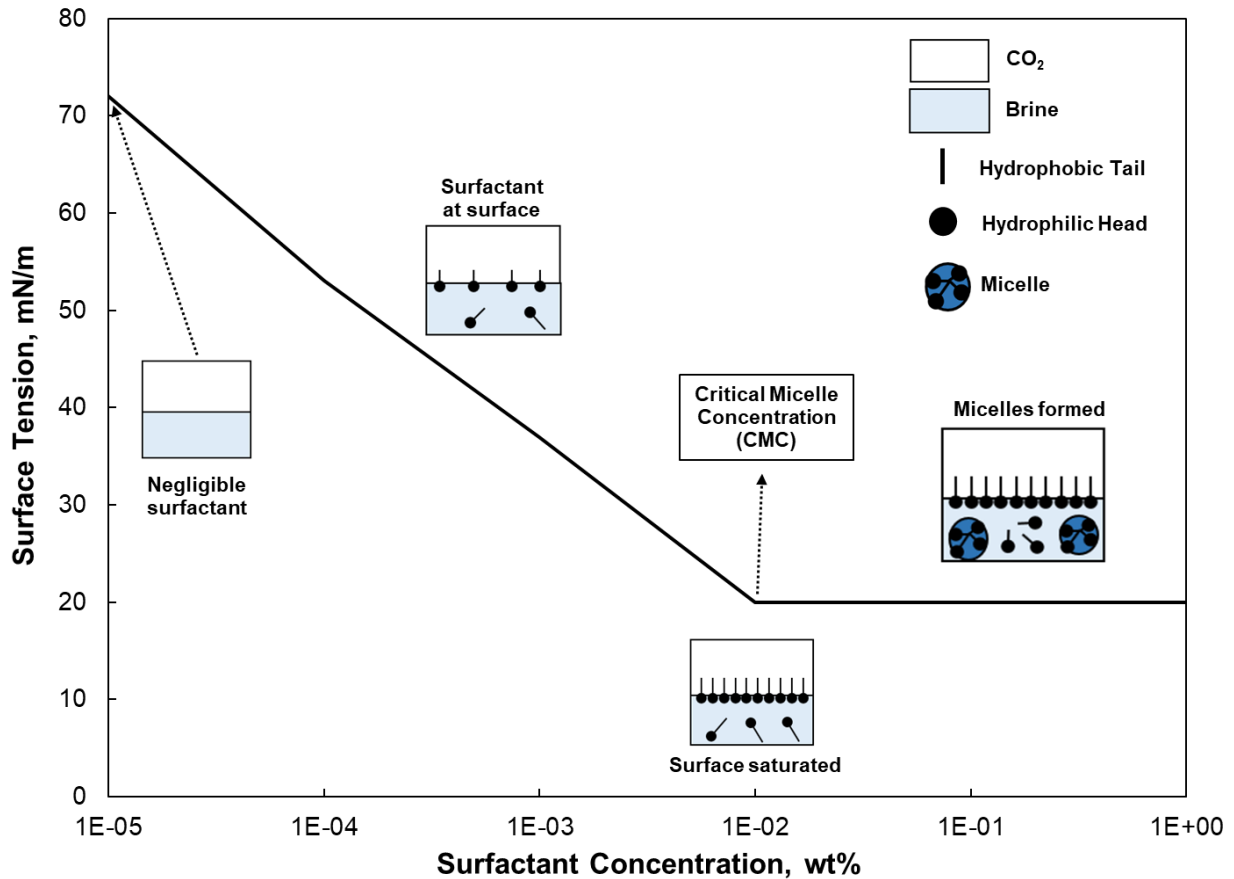


Fig. 2—Role of surfactants in reducing the surface tension and micelle formation

Fig. 2 demonstrates the different states of the surfactant solution/gas system as surfactant concentration increases. When surfactant concentration is below the critical micelle concentration (CMC), surfactant molecules exist as monomers either in the bulk solution or at the solution/gas interface. As the surfactant concentration increases, more surfactant molecules are available at the interface, lowering the surface tension between the liquid and gas phases. At the CMC, the solution/gas interface is saturated with surfactant molecules, and thus a further increase in surfactant concentration would not result in further decrease in the surface tension. Instead, the surfactant molecules start to aggregate and form micelles. The tighter packing of the surfactant

molecules at the interface leads to lower surface tension. The molar surfactant density is derived from the Gibbs adsorption equation below CMC and is given by **Eq. 1** (Chen et al. 2016):

$$\Gamma = -\frac{1}{RT} \left( \frac{\delta\gamma}{\delta \ln C_{surf}} \right)_{T,P} \quad \left[ \frac{\text{moles}}{L^3} \right] \quad (1)$$

where  $\Gamma$  is the surfactant molar density,  $R$  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 the natural log of 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. Joseph (1997) found that when it came to foam stability, the rate of change of the surface tension with the surfactant concentration indicated how rapidly the surface tension gradients develop. The surface tension gradients induce flow of liquids from low to high surface tension regions, which is known as the Marangoni effect (Velarde 1998). In a foam system, the foam bubble size increases with time, which decreases the surfactant concentration, and surface tension, at the interface. As a result of the developed surface tension gradient, liquid will flow from a low surface tension area to the interface. This process effectively heals the thinning foam bubble and provides stability (Pilling 2015). In general, the solution needs a high surface tension gradient to sufficiently enable the bubble film to withstand stress (Garret 1993; Gallego-Juárez et al. 2015). The Gibbs elasticity, describing the elasticity of the foam film, is expressed as **Eq. 2**, where  $A$  is the film surface area and  $\frac{\delta\gamma}{\delta A}$  is the derivative of the surface tension with respect to surface area.



$$E = 2A \frac{\delta\gamma}{\delta A} = 2A \frac{\delta\gamma}{\delta C_{surfactant}} \frac{\delta C_{surfactant}}{\delta A} \quad \left[ \frac{mN}{m} \right] \quad (2)$$

Higher slope in a plot of surface tension versus surfactant concentration indicates higher film's elasticity, resulting in more stable foam. For foam systems, the Gibbs elasticity is more impactful than the absolute values of surface tension or the CMC. There exists limited work in literature to evaluate the surface tension gradient of the ethoxylated amine surfactant in presence of CO<sub>2</sub>. 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.

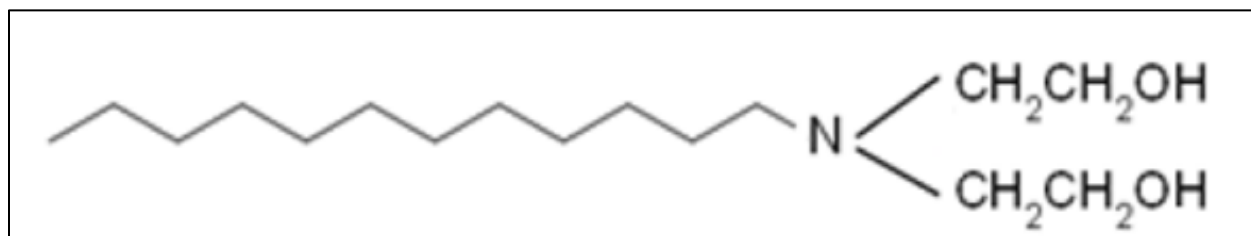
## OBJECTIVES

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. However, most of these cationic surfactants have poor solubility in CO<sub>2</sub> (Chen et al. 2012) and can oil-wet formation rocks (Hull et al. 2016). Switchable ethoxylated amine surfactants, on the other hand, have excellent solubility in CO<sub>2</sub>, when assuming their nonionic form. This high CO<sub>2</sub> solubility enables injection along with the CO<sub>2</sub> phase during EOR operations, which proved more beneficial and effective than traditional injection scheme (Le et al. 2008; Talebian et al. 2013). Another common benefit shared by both the switchable ethoxylated amine and nonionic ethoxylated surfactants is high salinity tolerance (Belhaj et al. 2019). Cui et al. (2016) investigated Ethomeen C12 foam for its apparent viscosity and conducted coreflood studies at different foam qualities, salinity, and temperature. However, the switchable surfactant needs to be evaluated and optimized for its foam stability. Ethomeen C12 is an interesting and promising surfactant with wide range of applicability that deserves closer attention. There is limited work on stability behavior of generated foam over different surfactant concentration, pH, and brine salinity, and composition. The effects of these factors on the surfactant solution/CO<sub>2</sub> interfacial properties at elevated temperature have not been discussed.

In this work, the main objective is to investigate the CO<sub>2</sub> foaming properties of EC12 such as initial foamability and foam stability at different surfactant concentrations, pH, and brine salinity and composition. This was accomplished through a series of foamability tests at both ambient temperature and pressure, using the foam bottle test, and at high-temperature and high-pressure, using the high-pressure view chamber. The surface tension of EC12 as a function of surfactant concentrations, temperature, pH, and brine salinity, in presence of CO<sub>2</sub> at 150°F will also be examined, using the pendant drop method. From these results, the CMC and surface tension gradients will be calculated from the surface tension versus surfactant concentration plot. The surface tension gradients are then used to validate the foaming properties of EC12.

## MATERIALS

The switchable ethoxylated amine surfactant, Ethomeen C12 or coco bis(2-hydroxyethyl) amine with purity of over 90%, was obtained from AkzoNobel and was used as received. It is a tertiary amine ethoxylate and its chemical structure is presented in **Fig. 3**. 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 surfactant solutions were prepared with a salinity of 0–25 wt% NaCl and a surfactant concentration of 0.0001-1 wt% using deionized water with a resistivity of 18.2 MΩ-cm at room temperature. 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 < 6.5, with tested concentration of up to 1.5 wt%. To achieve complete solubility, the solution pH was adjusted using 36.5 wt% HCl. The initial solution pH was either 6.5 or 2.5. Tests were run at pH 2.5 to investigate the foaming properties for acidizing related activities. CO<sub>2</sub> gas with a purity of 99.9 mol% was used.



**Fig. 3**—Chemical structure of the surfactant used in this study. The hydrophobic tail contains 12 carbon atoms

## EXPERIMENTAL SETUPS AND PROCEDURES

**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<sup>3</sup> of the surfactant solution was transferred into a 20 cm<sup>3</sup> vial filled with air. The vial was then shaken manually 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 two times to ensure repeatability.

Two parameters were calculated through the bottle tests. The height of the initial foam after shaking the bottle is denoted as foamability. The decay profile of the foam with time is measured as foam stability.

**High Pressure Foam Test.** A high-pressure view chamber (HPVC) was utilized to study the foam stability under pressure. **Fig. 4** shows the schematic diagram of the setup. The view chamber is constructed with a 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 CO<sub>2</sub> into the surfactant solution and create a foam column. In this diagram, Valves A, B, and S were ball valves. Valves C, D, and E were globe valves. 30 cm<sup>3</sup> of the surfactant solution was placed inside the chamber and then pressurized using CO<sub>2</sub> to a maximum of 500 psi and heated to 150°F. Sufficient time was given to allow the chamber to be heated to 150°F and achieve thermal equilibrium with the surfactant solution. Foam was created by sparging CO<sub>2</sub> from the fixed volume gas accumulator into the bottom of the chamber at a pressure of 550 psi. 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.

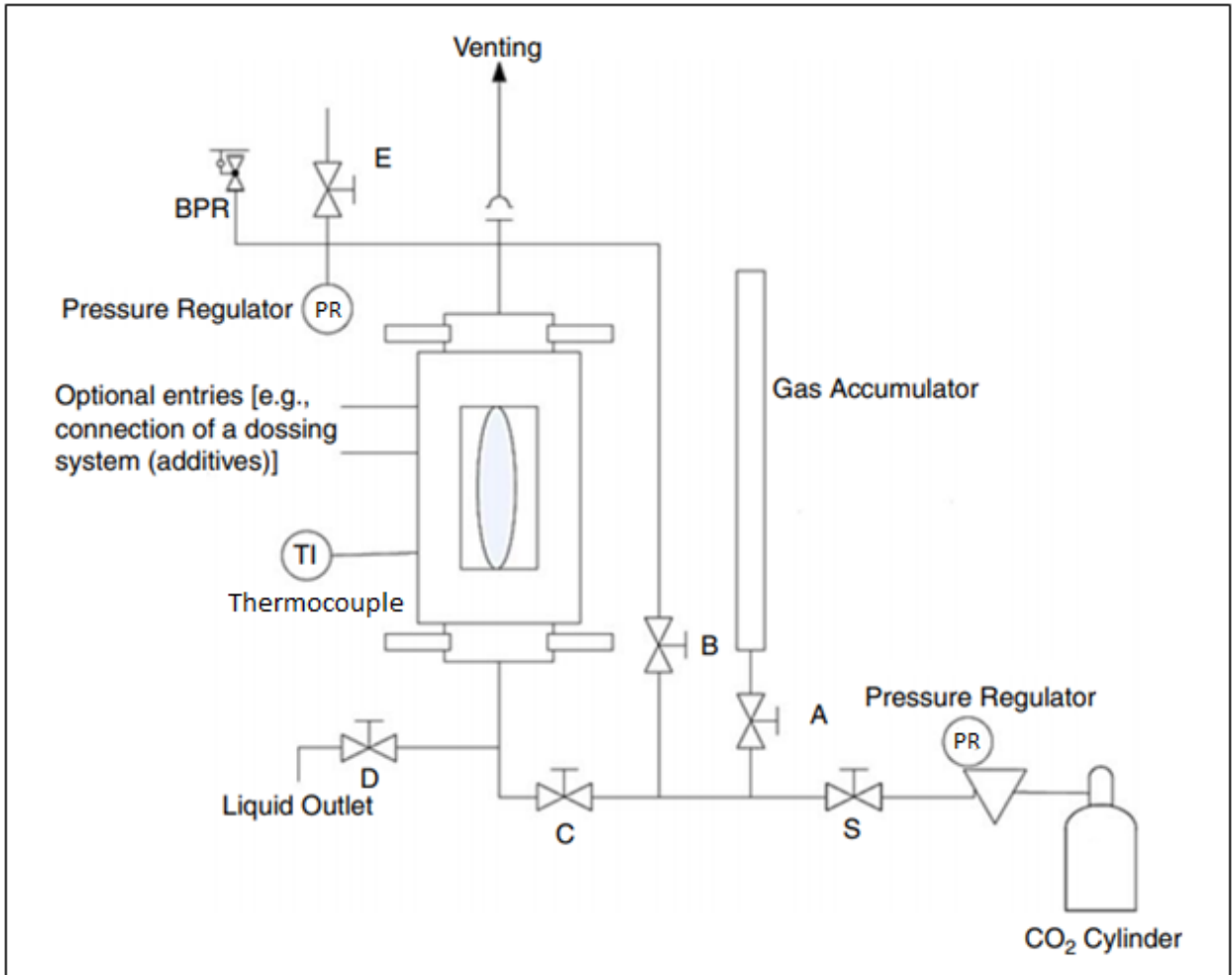


Fig. 4—Schematic diagram of the high-pressure view chamber setup for the foam stability test

**Surface Tension Study.** The interfacial properties such as surface tension, CMC, and surface tension gradients of EC12 were evaluated at different surfactant concentration, 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 **Fig. 5**.

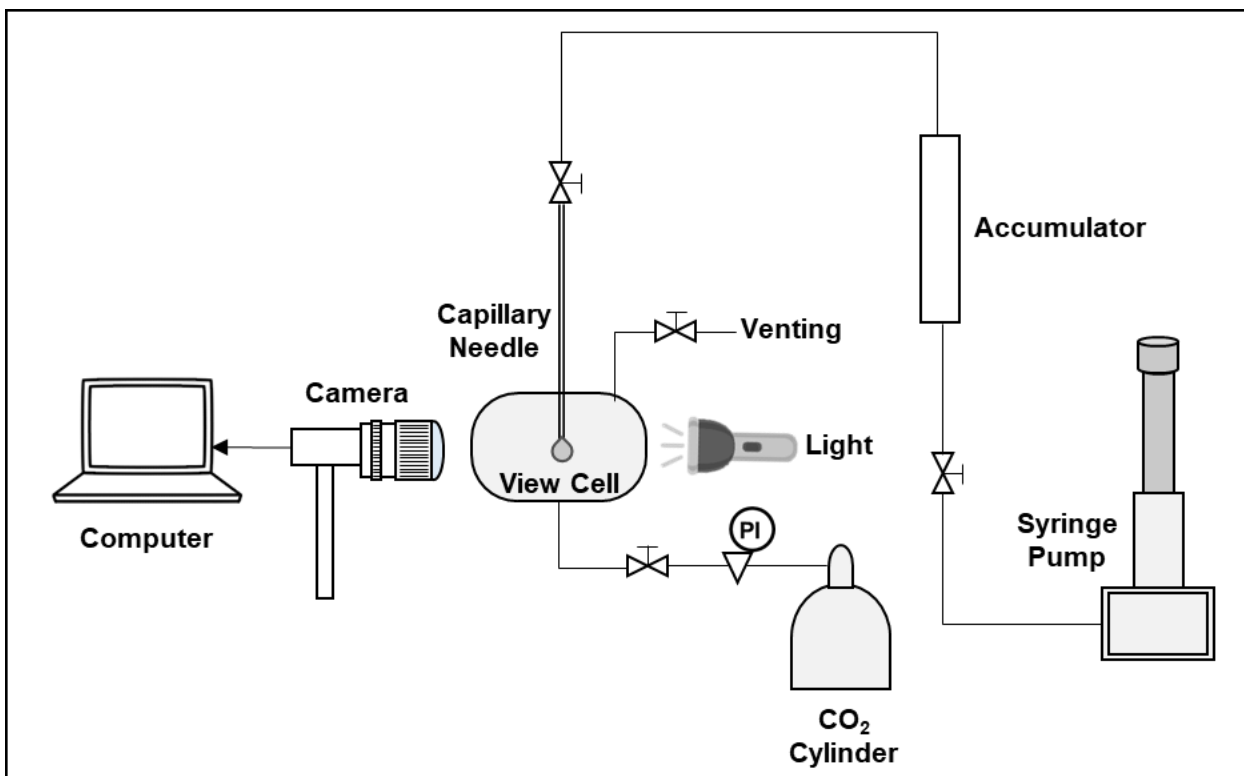


Fig. 5—Schematic diagram of the drop shape analyzer setup

Rushing et al. (2008) and Shariat et al. (2012) explained the fundamentals and nuances of setting up and using the pendant drop method with computer-aided processing to accurately measure the surface tension at elevated temperature and pressure. The prepared surfactant solution was loaded into the accumulator. The view chamber was filled with CO<sub>2</sub> and brought to the desired temperature and pressure. 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 minutes to achieve thermal and chemical equilibrium. As explained by Franses et al. (1996), dispersions containing surfactants usually exhibited a decrease in the equilibrium surface tension because of surfactant adsorption at the interface. Minimization of the surface Gibbs free energy was usually the main driving force for adsorption. The transient surface tension, defined 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 hour at 77 and 150°F, respectively (**Fig. 6**). All the recorded values for the surface tension study were at equilibrium.



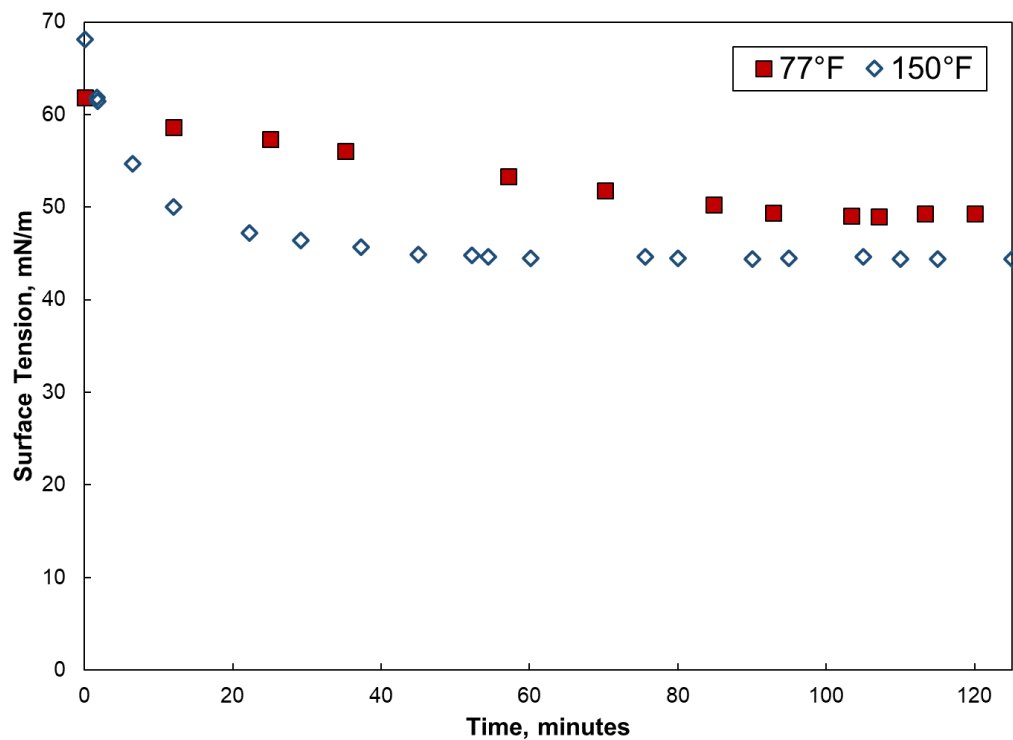


Fig. 6—Time to reach equilibrium surface tension of surfactant-CO<sub>2</sub> system

## RESULTS AND DISCUSSION

**Bottle Foam Tests at Ambient Conditions.** Optimizing the surfactant concentration, pH, and brine salinity and composition for maximum foamability and foam stability is crucial for any foam applications. 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 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<sup>3</sup> of the solution was placed in a 20 cm<sup>3</sup> 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% (**Fig. 7**). 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%. **Fig. 8** presents the initial foamability of the surfactant solutions at 20 wt% NaCl. The figure shows similar initial foamability for 0.1, 0.25, and 0.5 wt% surfactant and a negligible decrease in the initial foamability for 1 wt% surfactant.

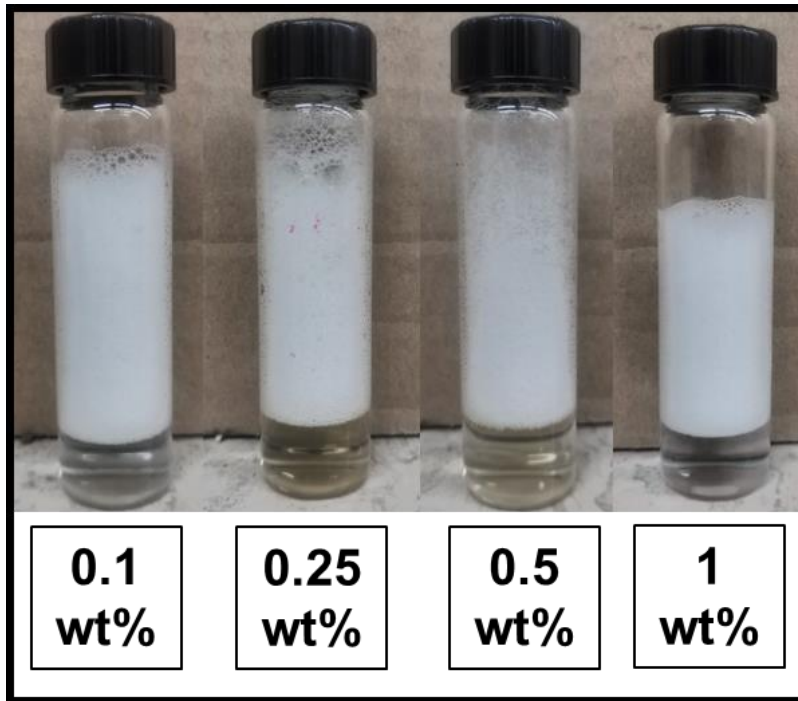


Fig. 7—Effect of surfactant concentration on the initial foamability at 5 wt% NaCl, pH 6.5, and 77°F

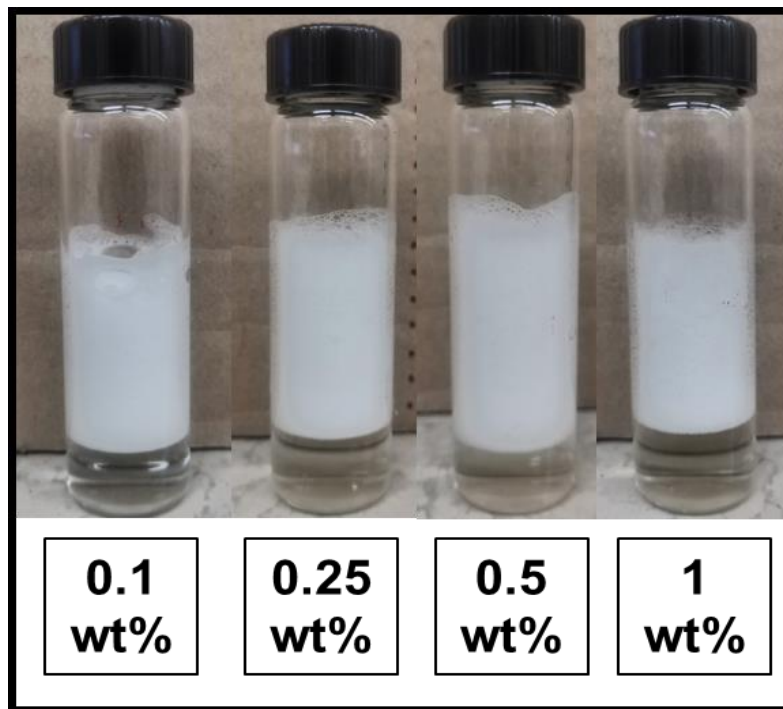
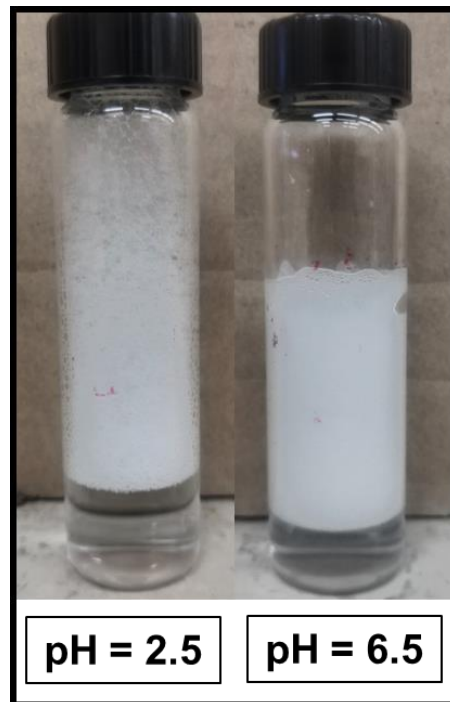


Fig. 8—Effect of surfactant concentration on the initial foamability at 20 wt% NaCl, pH 6.5, and 77°F

Ethomeen C12 is either cationic or non-ionic depending on the solution pH. It is cationic below pH 4.5 (Cui et al. 2016). The initial pH of the solution is important when evaluating such surfactants for foam CO<sub>2</sub> injection. The present paper studies the initial foamability of the surfactant solution at pH of 6.5 and 2.5. **Fig. 9** 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 an evidence of bigger bubble sizes in solutions with pH 2.5. The larger bubbles within the low-pH foam leads to poor foam stability, as will be discussed later.



**Fig. 9**—Effect of initial pH on the initial foamability at 10 wt% NaCl, 0.25 wt% surfactant, and 77°F.

Studies on the application of CO<sub>2</sub> 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. **Fig. 10** 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 slightly decreases as the salinity increases. However, this decrease in the initial foamability is more noticeable in the 25 wt% NaCl solution.

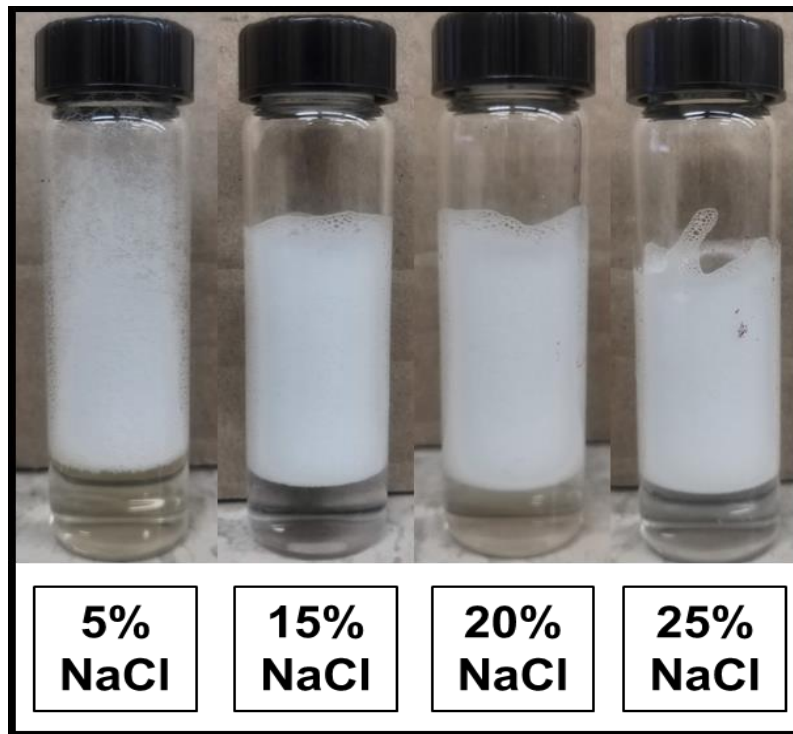


Fig. 10—Effect of salinity on the initial foamability at pH 6.5, 0.5 wt% surfactant, and 77°F.

Foam stability is an indicator for the dynamic performance of the foam. A stable foam has good elasticity, high maximum disjoining pressure, good 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 an heterogenous system like foam. After the foam formation, the smaller foam bubbles shrink while the bigger ones grow over time (Tcholakova et al. 2011). 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. **Figs. 11, 12, 13, and 14** present the foam half-life 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. At salinities lower than 15 wt% NaCl and initial pH 6.5, the foam half-life increased almost linearly with increase in surfactant concentration. At the higher salinity of 20 wt% - 25 wt% NaCl, 0.25 wt% surfactant generated the most stable foam.

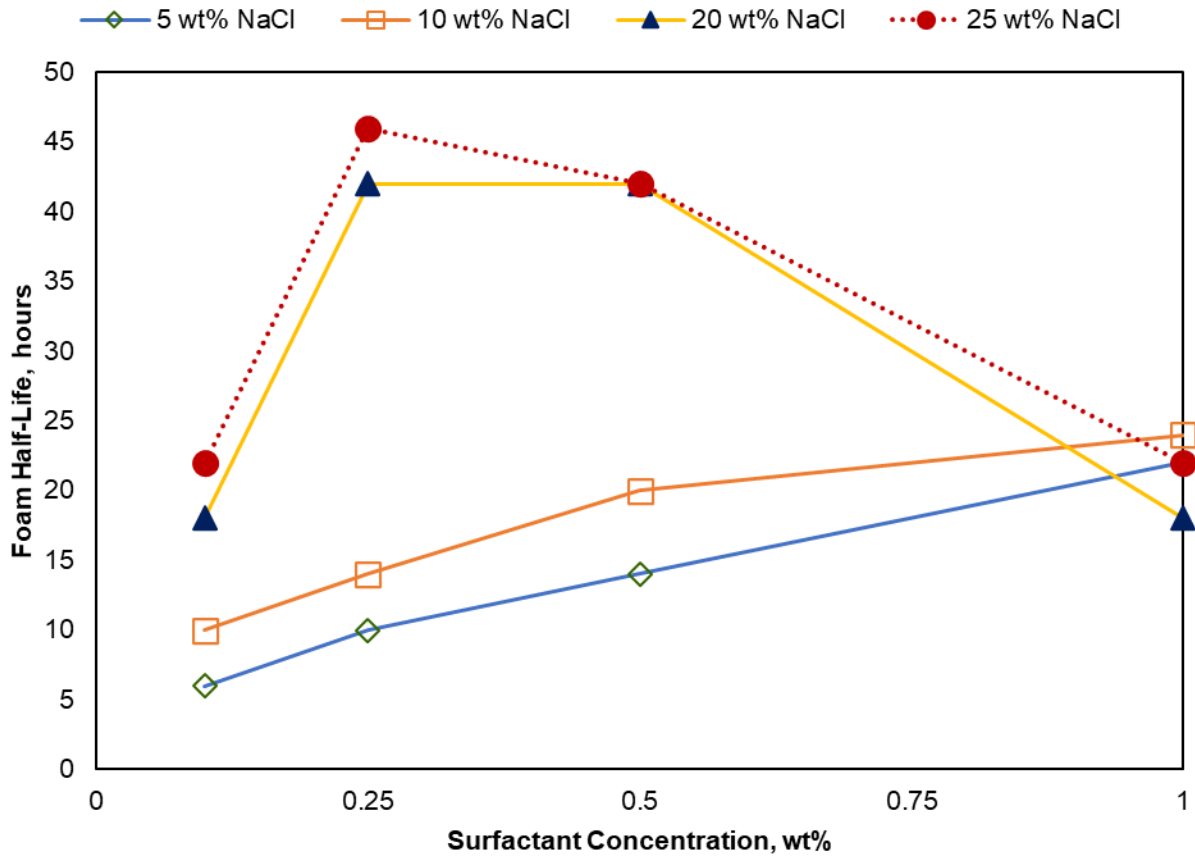


Fig. 11—Effect of surfactant concentration on the foam half-life at room temperature and pH 6.5.

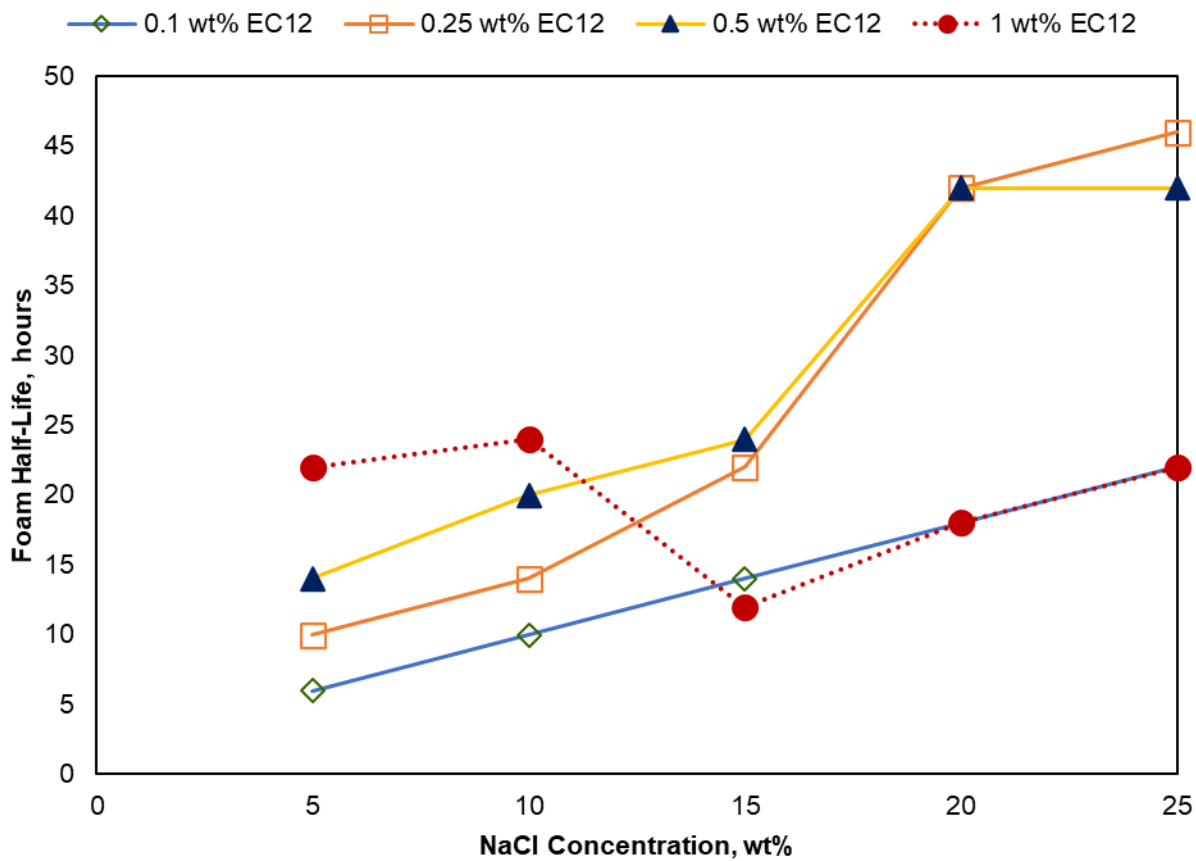


Fig. 12—Effect of salinity on the foam half-life at room temperature and pH 6.5.



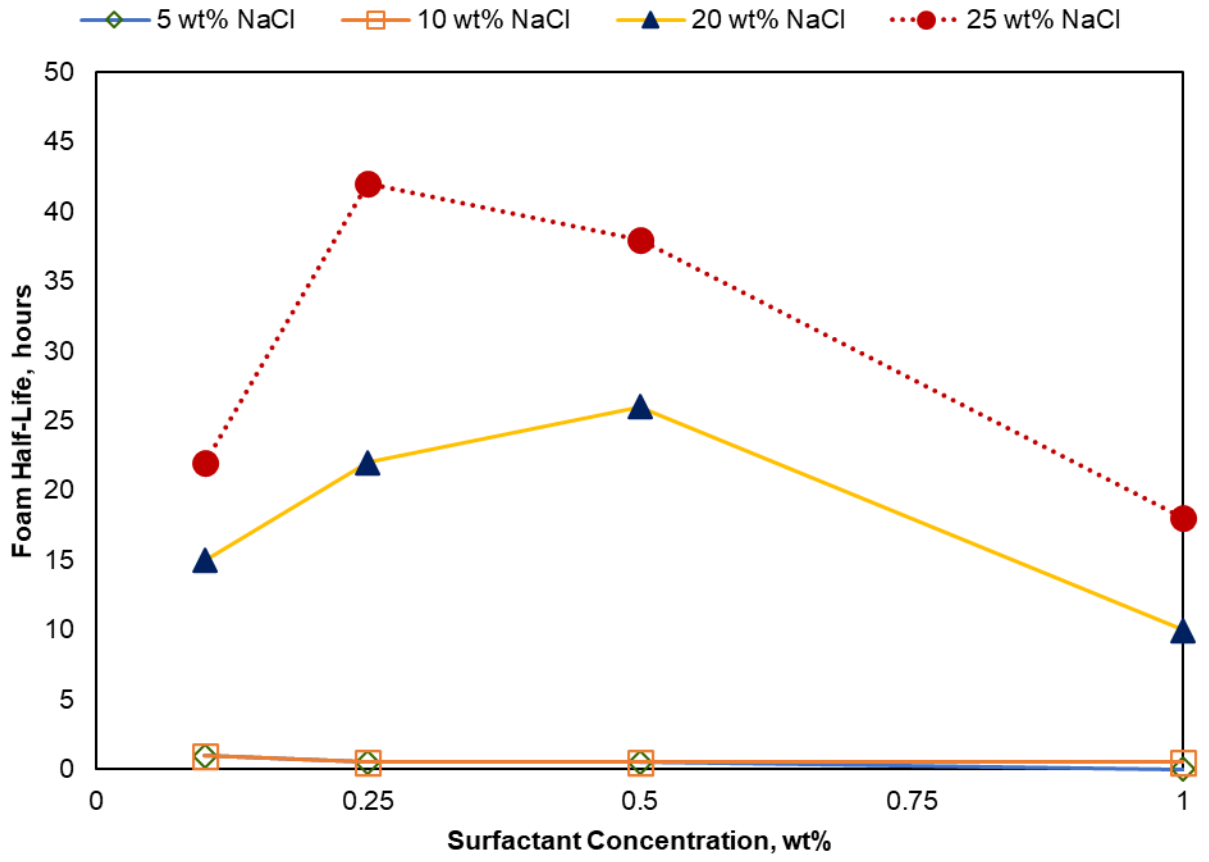


Fig. 13—Effect of surfactant concentration on the foam half-life at room temperature and pH 2.5.

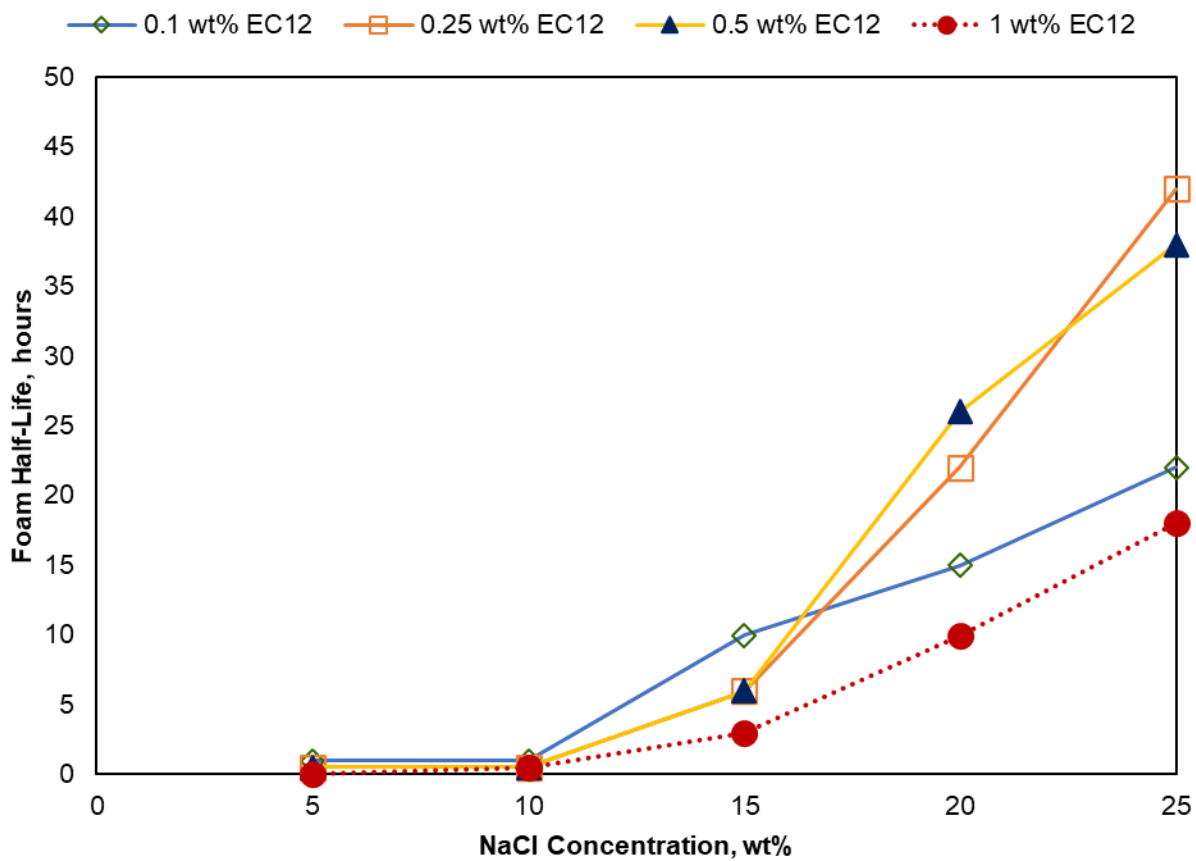


Fig. 14—Effect of salinity on the foam half-life at room temperature and pH 2.5.

The initial pH affected the initial foamability as previously discussed. The change in the surfactant charge from non-ionic 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 at pH 1.25, 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. The surfactant with pH 6.5 yielded a half-life of 8 hours, whereas a pH 2.5 surfactant solution resulted in a half-life of one hour. 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 non-ionic form (Elhag et al. 2014). The foam at pH 2.5 had higher bubble density and larger bubbles, as observable in Fig. 9, which contributed to the faster collapse of the foam through Ostwald Ripening. It was also observed that the liquid level at the bottom of the pH 2.5 foam column was marginally higher than that of the pH 6.5 foam column. Unfortunately, this difference in the free liquid level is so minimal that the authors were not able to accurately quantify them, due to the limitations in experimental setup. However, this observed negligible difference in initial free liquid level suggested that the films network of the pH 6.5 foam column started out with more surfactant solution. Thus, it was not surprising that this foam column took longer to completely collapse.

Adding salt to the acidic surfactant solution helped in improving the foam stability. At 20 wt% NaCl, the foam stability for a pH 2.5 solution had a similar decay profile to the same solution at pH 6.5. The foam was more stable at pH of 2.5 and 20 wt% NaCl compared to the foam at pH 2.5 and 5 wt% NaCl. The foam with pH 6.5 had greater foam stability than the pH 2.5 solution, for all salinity. The pH 2.5, 20 wt% NaCl solution took about 30 hours to completely decay and the pH 6.5, 20 wt% NaCl solution decayed in 42 hours. A foam stability test was run using a surfactant solution with a pH 1.2. The foam decay profile was very similar to the solution at pH 2.5. This

study recommends a high saline EC12 solution with a salinity greater than 15 wt% NaCl to be used for acid applications.

**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 and 150°F, respectively. The current work investigates the CO<sub>2</sub> foam stability of the surfactant at different surfactant concentration, pH, and brine salinity and composition. Surfactant solutions were prepared with a concentration of 0.25-1.5 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<sub>2</sub>, and 6.1% Na<sub>2</sub>SO<sub>4</sub>. Conducting the foam tests using CaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> brines at the same molality as the 5 wt% NaCl brine allows for the investigation into the effects of multivalent cations and anions on foamability and foam stability. All of these 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. **Fig. 15** demonstrates the effect of surfactant concentration on the foam stability at 150°F and 500 psi. The plot shows the normalized foam height as a function of time for surfactant solution with concentration of 0.25, 0.5, 1, and 1.5 wt%. The height of the foam was recorded at various intervals of time and normalized to the initial foam height. The normalization was done to ignore the role of initial foamability. The foam decay over time followed an exponential pattern, where the rate of foam decay is high at the start and then slows down with time. The foam half-life is an important indicator of the foam stability, which increased with the increase in the surfactant concentration. 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.

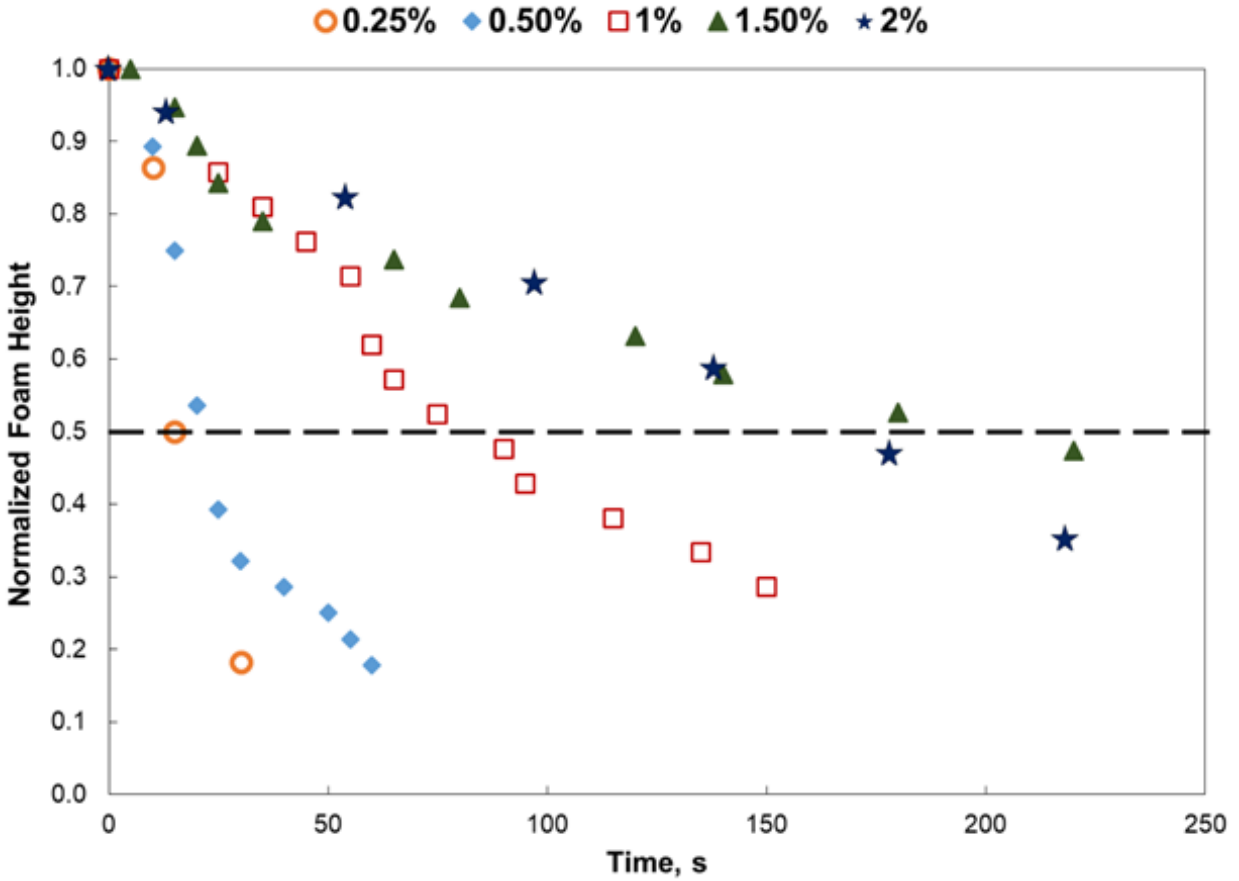


Fig. 15—Effect of surfactant concentration on the foam stability at 150°F and 500 psi, solution pH 6.5 and salinity of 25 wt% NaCl.

The normalized foam height is calculated as shown in **Eq. 3**.  $h_f$  is the foam height recorded at time  $t$  and  $h_{fmax}$  is the maximum foam height, recorded at the time zero.

$$h_f^* = \frac{h_f}{h_{fmax}} \tag{3}$$

The role of pH on the foam stability was evaluated in this study. Ethomeen C12 acts as a cationic surfactant below pH 4.5. **Fig. 16** presents the foam decay of EC12 at pH 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 (Chen et al. 2016). The foam half-life is halved when the pH is 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.

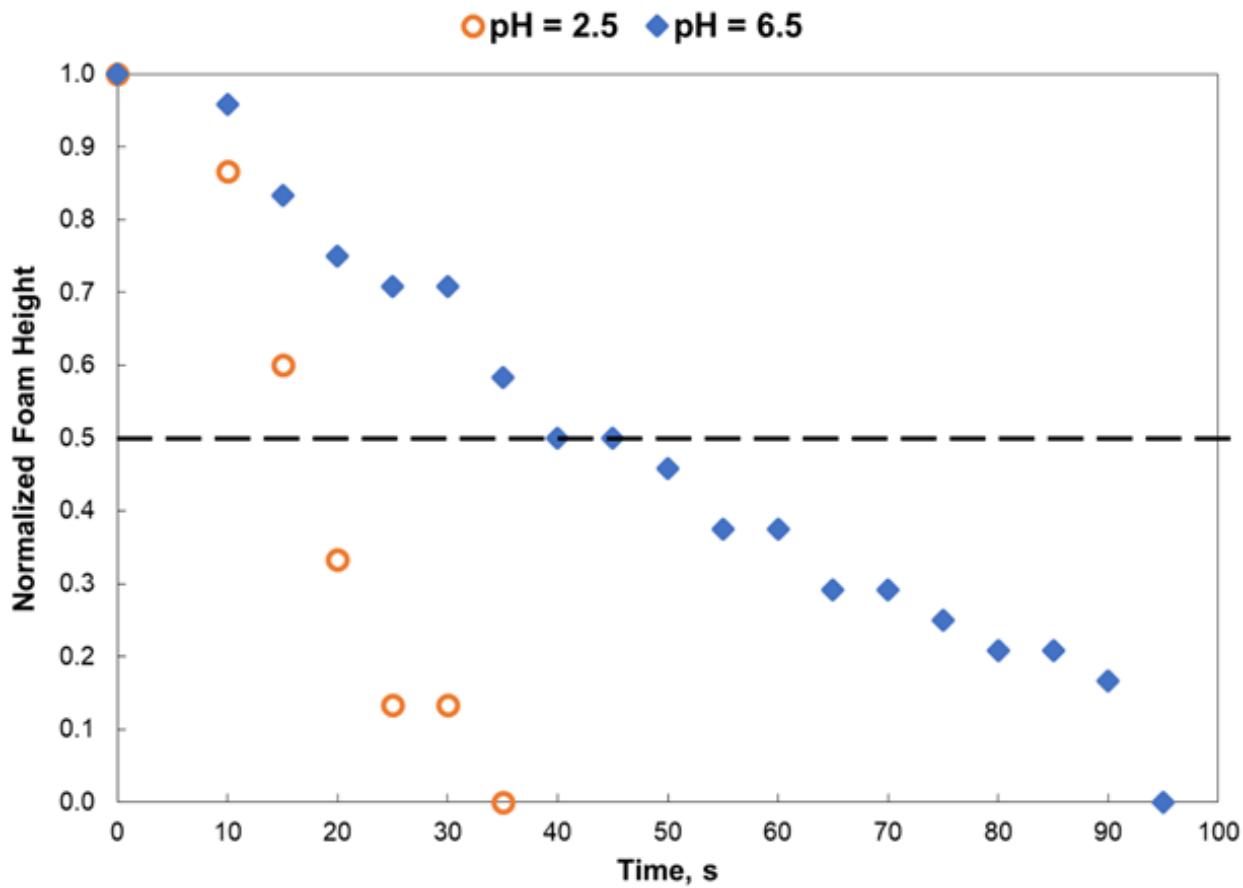


Fig. 16—Effect of solution pH on the foam stability at 150°F and 500 psi, 0.5 wt% EC12 concentration and salinity of 25 wt% NaCl.

The brine salinity plays an important role in stabilizing the foam bubbles. **Fig. 17** 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 increase in the foam stability for the pH 2.5 solution at 25 wt% NaCl may be due to the increase in the Cl<sup>-</sup> ion concentration. 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<sup>-</sup> ions and the protonated surfactant molecules leads to a more stable liquid film, resulting in longer-lasting foam even at pH 2.5.



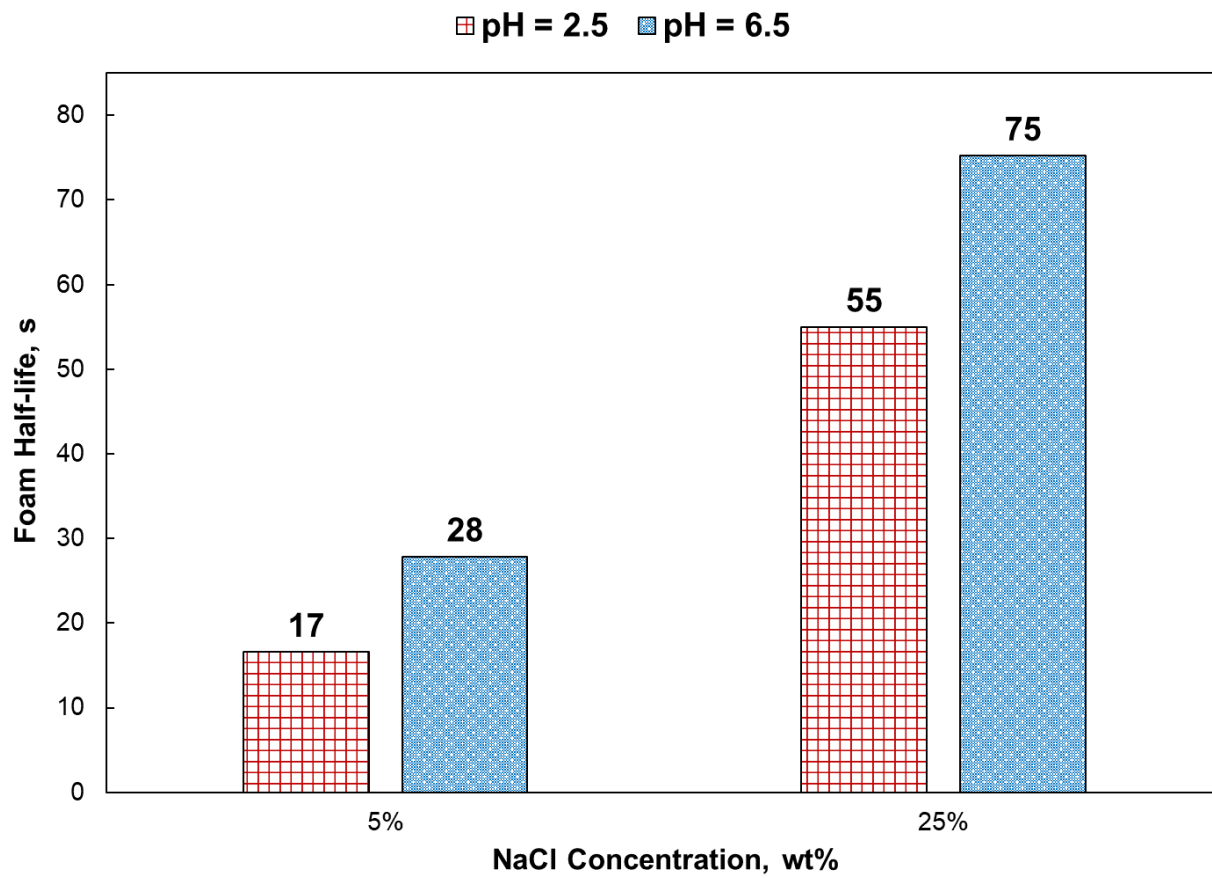


Fig. 17—Effect of salinity on the foam stability at 150°F and 500 psi, 1.0 wt% EC12 concentration.

The brine 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<sub>2</sub>, and 6.1% Na<sub>2</sub>SO<sub>4</sub> brine solutions with 0.5 wt% surfactant and pH 6.5. The brine solutions had the same cation concentration of 0.9 mol/kg. **Fig. 18** presents the role of brine composition on the foam stability at 150°F. Surfactant solution prepared with CaCl<sub>2</sub> had 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. The presence of sulfate ions was detrimental to the foam stability. The foam bubbles collapsed almost instantly at 150°F.

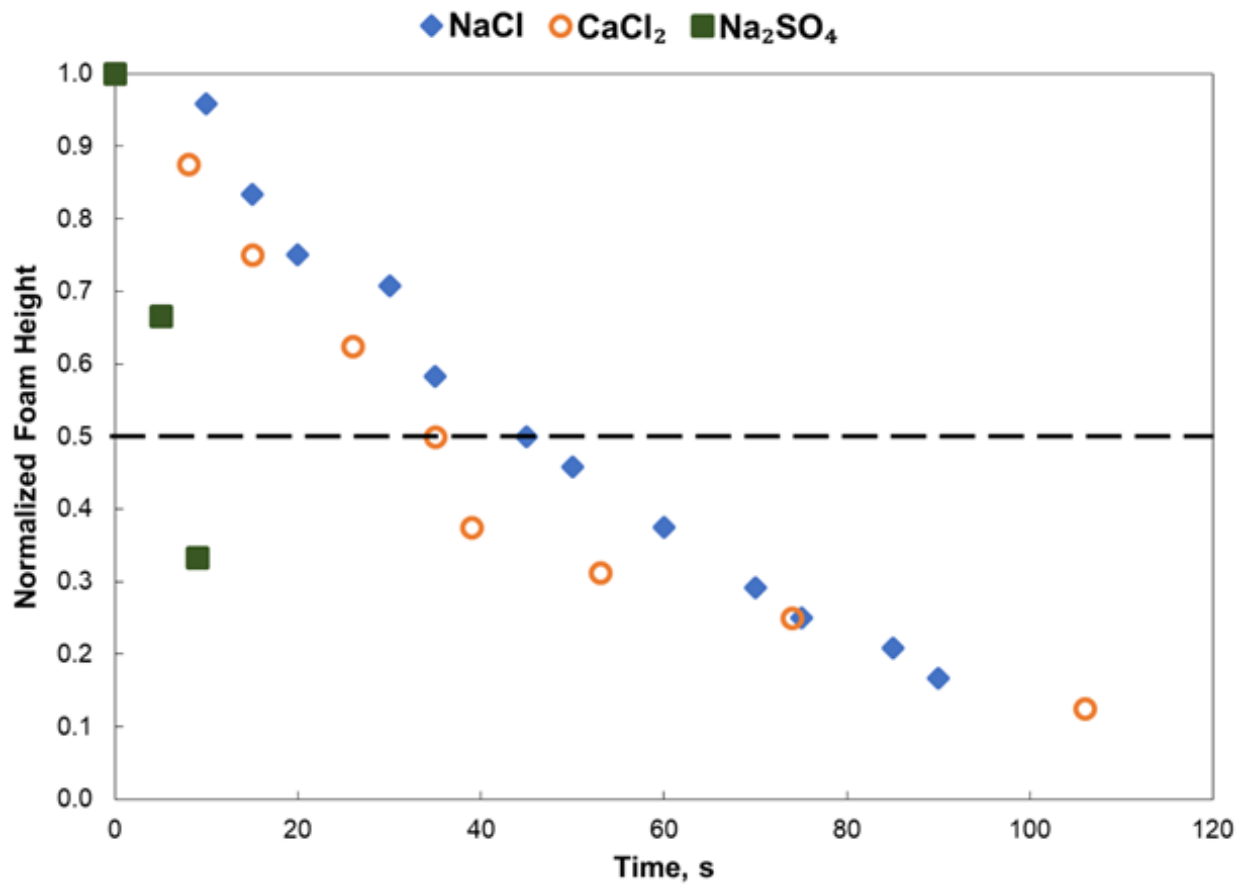


Fig. 18—Role of multivalent cations and sulfate anions on the foam stability at 150°F and 500 psi, 0.5 wt% EC12 and solution pH 6.5. All solutions have equal cation concentration of 0.9 mol/kg.

**Surface Tension Study.** The foam stability is linked to the interfacial properties of the surfactant/CO<sub>2</sub> 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 and 150°F, in presence of CO<sub>2</sub>. The surface tension was measured by varying surfactant concentration from 0.0001-0.1 wt%, and the CMC and the slope of the surface tension curve were estimated. **Figs. 19** and **20** shows 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 1.6E-3 to 4.6E-3 wt% as the temperature increased from 77 to 150°F. However, at 25 wt% NaCl, the CMC remained constant at 1.3E-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 to 150°F. In other words, the CMC region became more diffused with an increase in temperature. At 5 and 25 wt% NaCl, the surface tension gradient decreased by 35 and 16%, respectively, as the temperature increased from 77 to 150°F. The decrease in the surface tension gradient translates to poorer foam stability at 150°F. The analysis is consistent with the foam stability tests done.

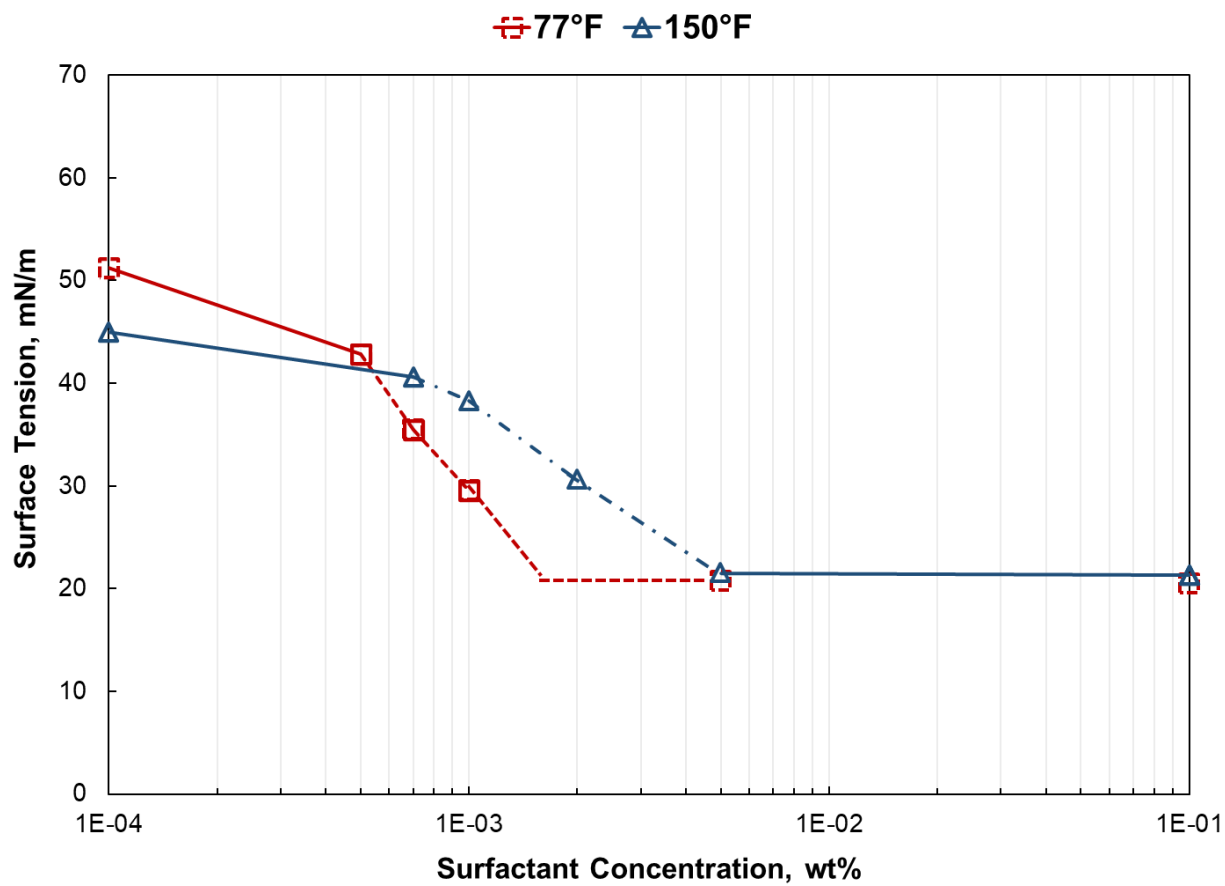


Fig. 19—Effect of temperature on surfactant interfacial properties at pH 6.5 and 5 wt% NaCl.

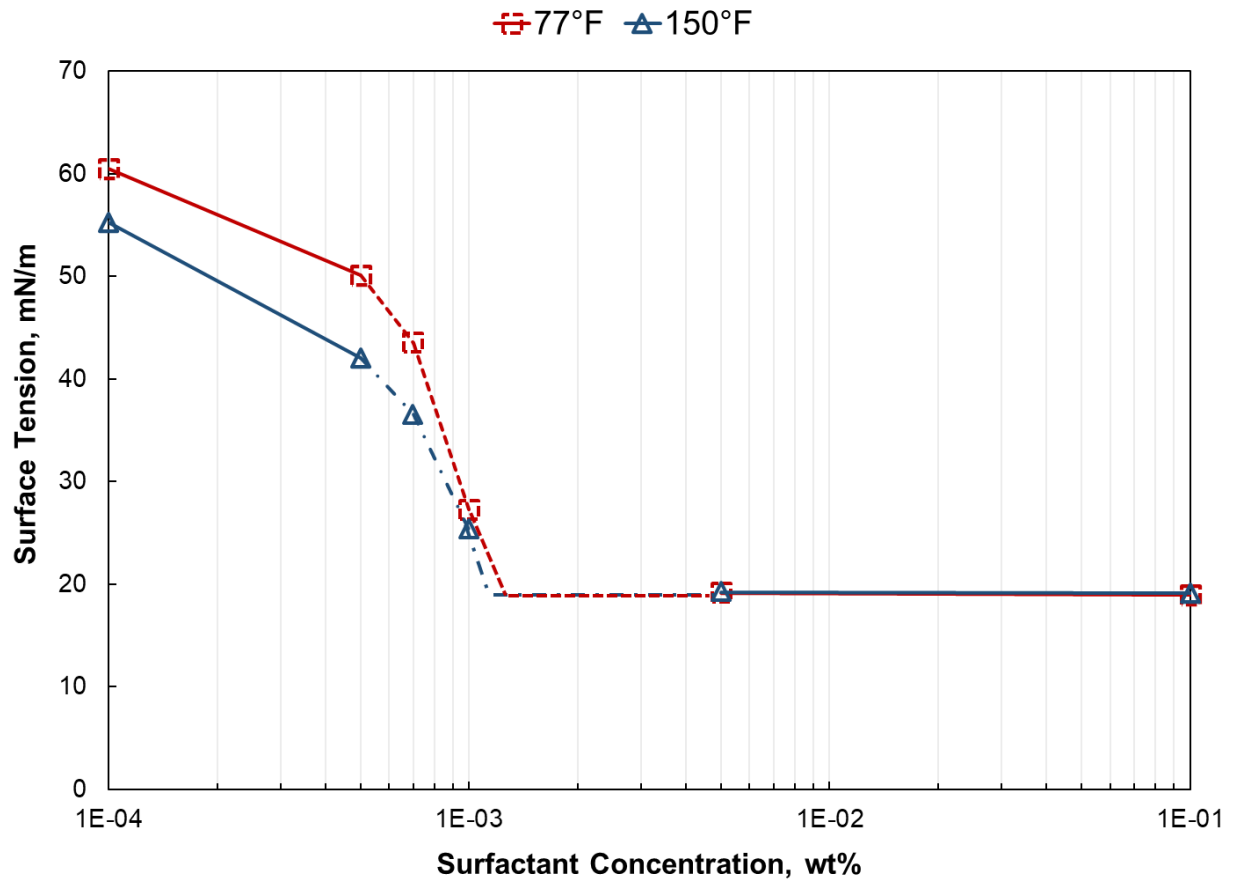


Fig. 20—Effect of temperature on surfactant interfacial properties at pH 6.5 and 25 wt% NaCl.

Figs. 19 and 20 also show that the surface tension at surfactant concentration greater than the CMC, increased negligibly with temperature. This was due to the decrease in molecular density,  $\Gamma$ , at the interface at higher temperatures. From Eq. 1, it is evident that the increase in temperature and the decrease of the surface tension gradient, contributed to the decrease in surface molecular density. Lowering the interface molecular density lowers the surface tension as well. The drop in the molecular density is more noticeable at 5% NaCl than 25% NaCl, because of a bigger change in the surface tension gradient. Therefore, it is recommended to use high salinity brines to create stable foam using EC12. This is a good candidate for foam EOR operations where the mixing of formation brine and injected brine can lead to high salinity conditions for the foam.

**Figs. 21** and **22** show the effect of salinity on the surface tension of the CO<sub>2</sub>/surfactant system. An increase in salinity resulted in a lower CMC and surface tension values. At 150°F and pH 6.5, the CMC decreased from 4.56E-3 to 1.33E-3 wt%, when the salt concentration increased from 5 to 25% NaCl. The surface tension gradient increased with the salinity. The sharper CMC region, indicated by the steep slope, was a strong indicator that the foam generated in high salinity (25 wt% NaCl) environment would be more stable than that generated in low-salinity environment (5 wt% NaCl), because of its increased elastic properties. Results from the foam stability tests were in accordance with this finding.

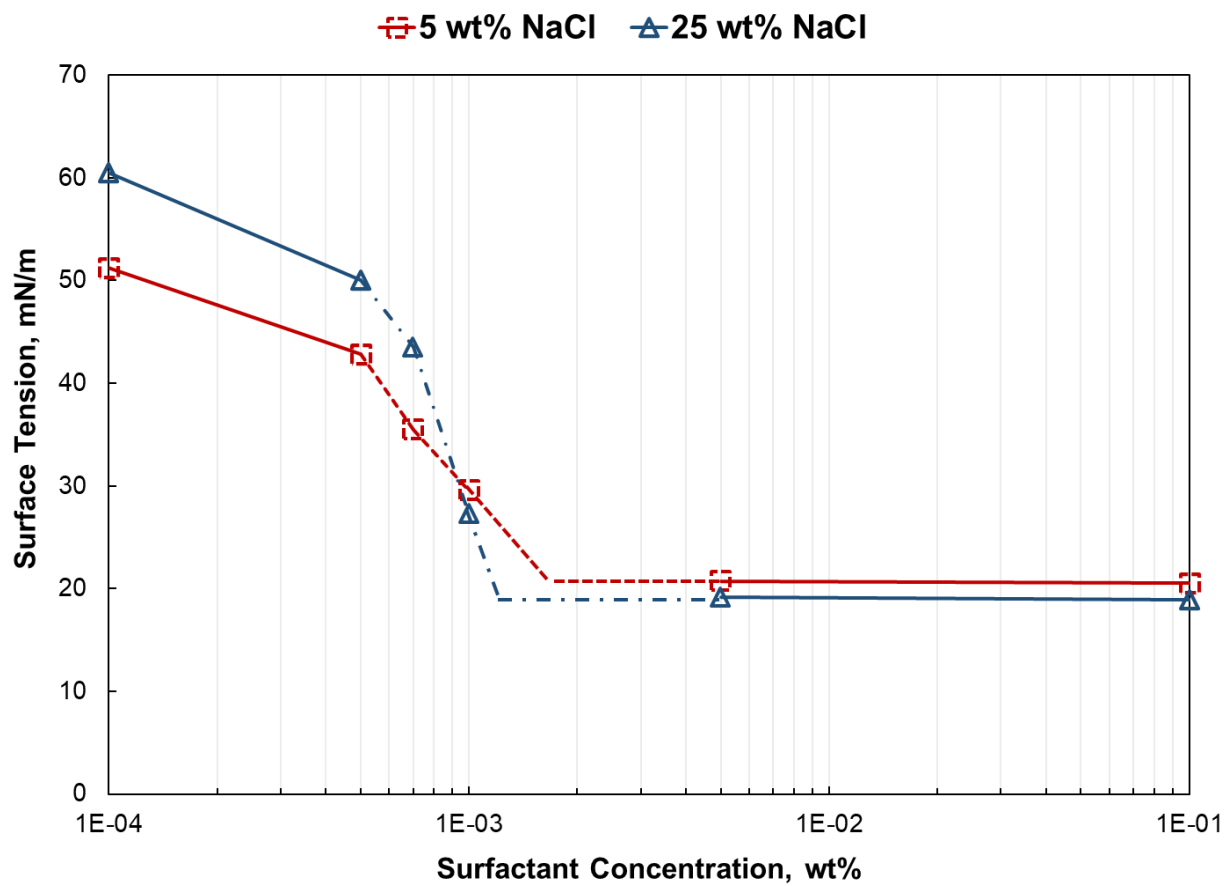


Fig. 21—Role of NaCl concentration on the surface tension, CMC, and surface tension gradients at pH 6.5 and 77°F.



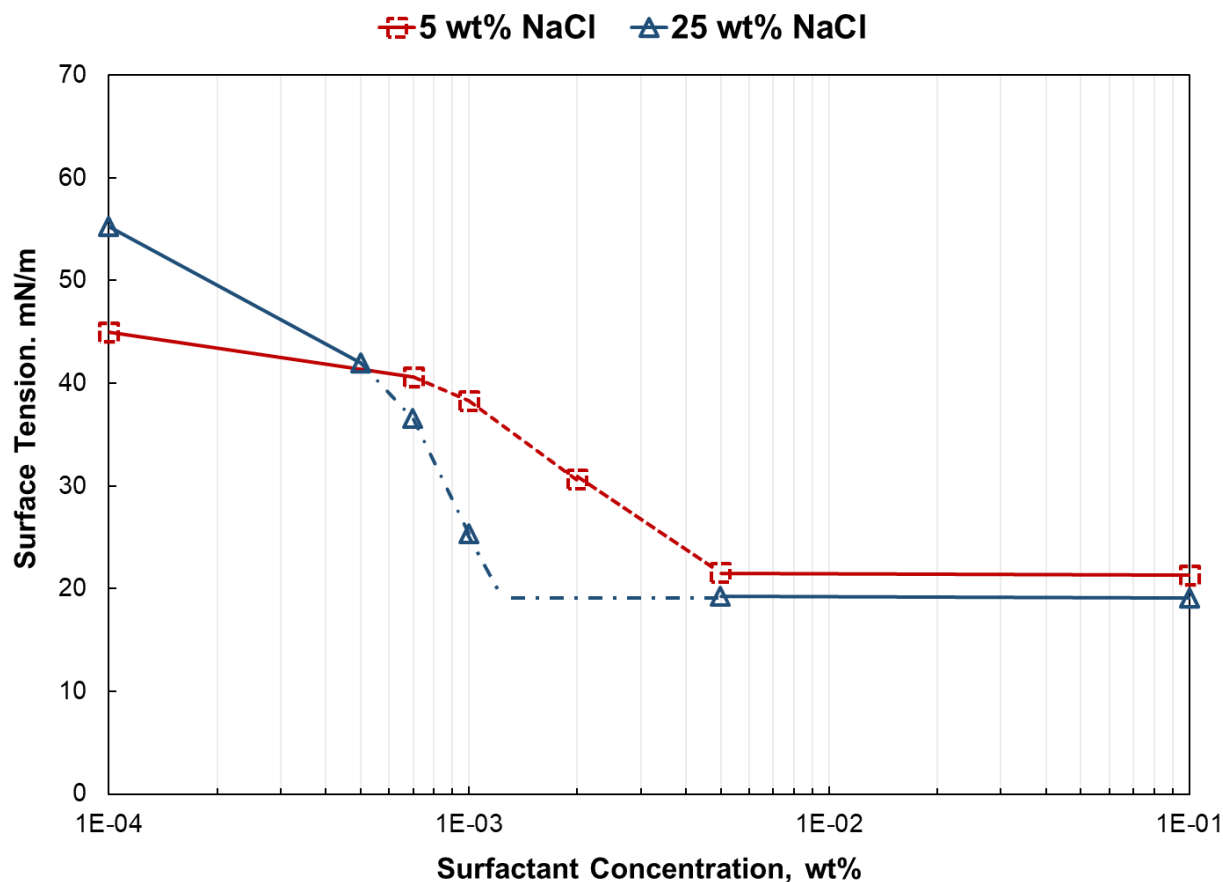


Fig. 22—Role of NaCl concentration on the surfactant solution interfacial properties at pH 6.5 and 150°F.

Lower surface tension above the CMC for 25 wt% NaCl solutions was also observed. This phenomenon was attributed to the higher abundance of counter ions,  $\text{Cl}^-$ , 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 counter-ions, allowing for more densely packed surfactant molecules at the interface. This increase in the surfactant interface molecular density lead to the decrease in surface tension.

**Figs. 23 and 24** 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, the CMC increased from 1.59E-3 to 2.43E-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.

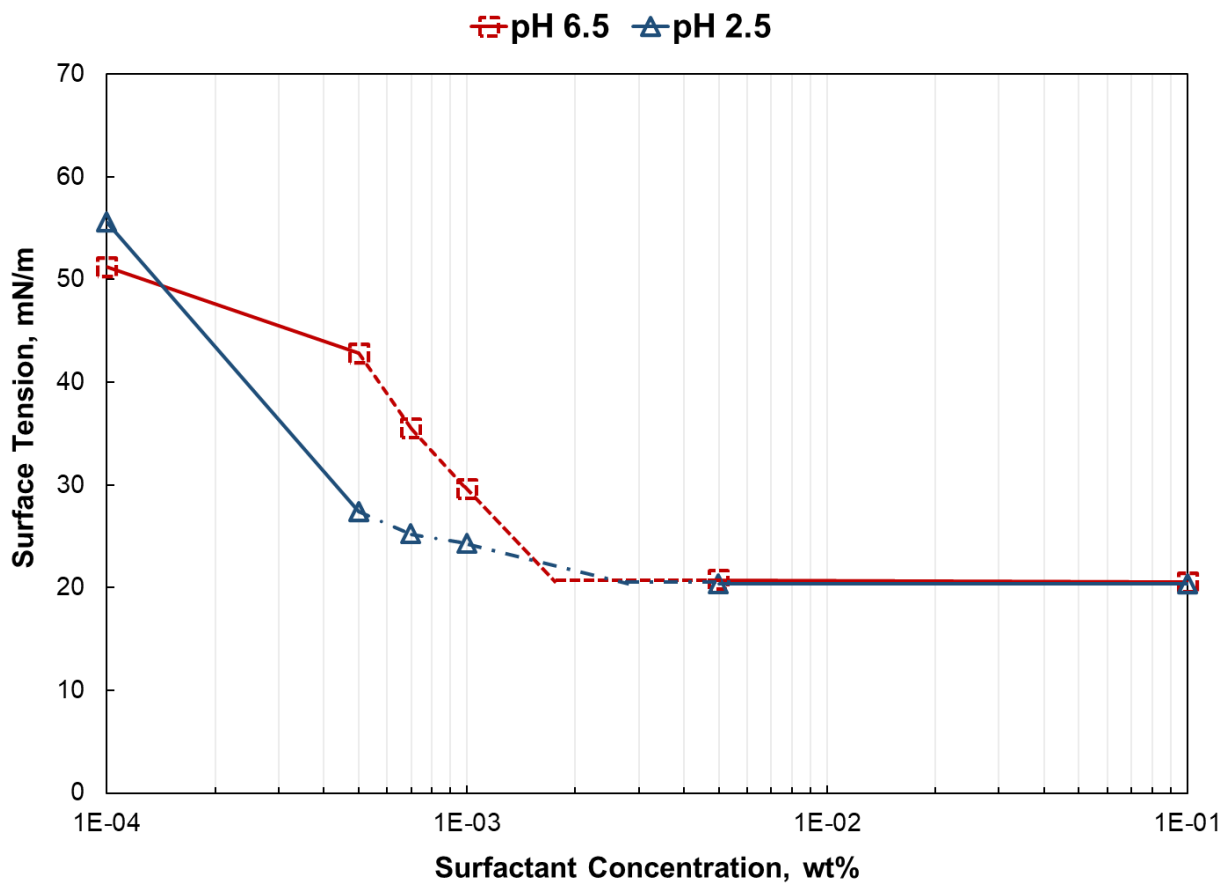


Fig. 23—Effect of initial pH on surfactant solution interfacial properties at 5 wt% NaCl and 77°F.

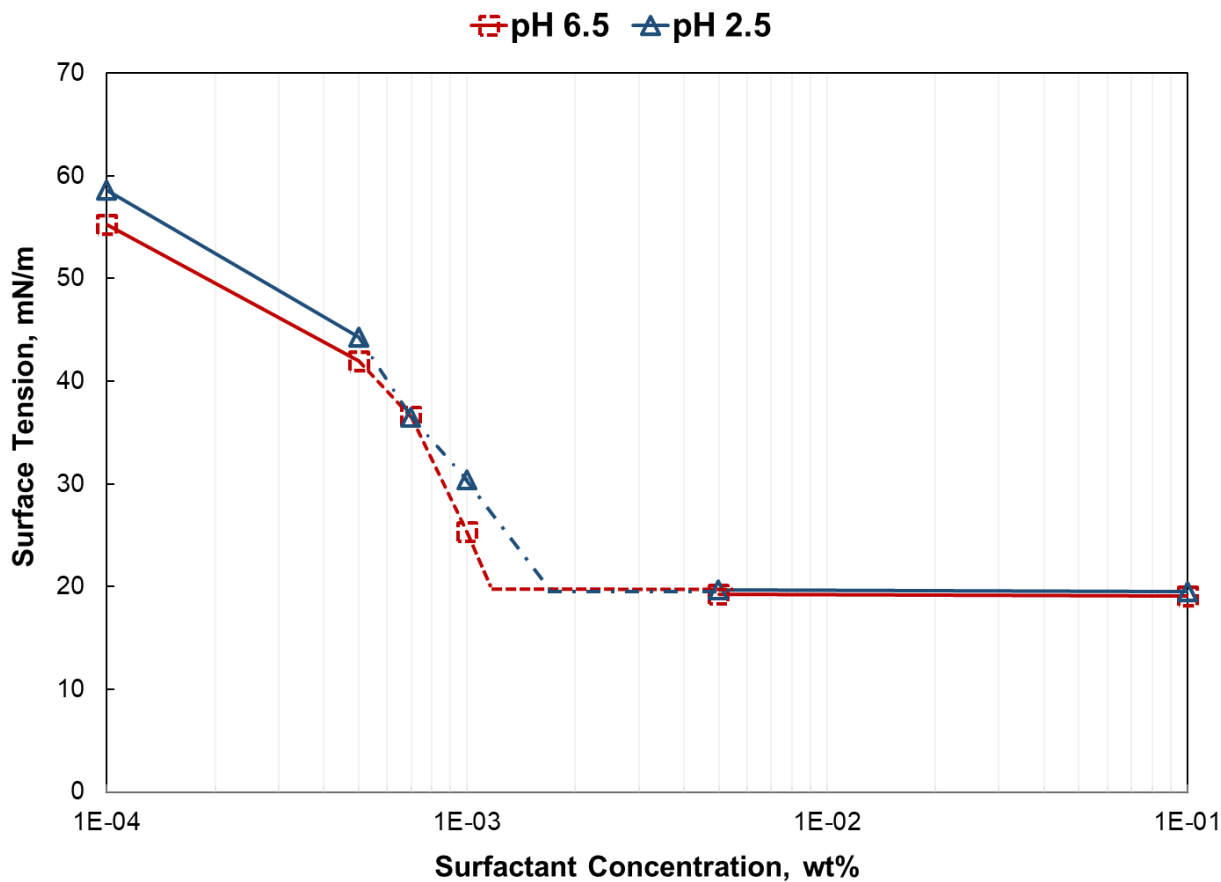


Fig. 24—Effect of initial pH on surfactant solution interfacial properties at 25 wt% NaCl and 77°F.

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<sub>2</sub> (**Fig. 25**). The CMC of the 5 wt% NaCl solution was 4.56E-3 wt%, compared to the CMC of 2.28E-3 wt% for the 9 wt% CaCl<sub>2</sub> solution. Both these solutions had the same salt molality, 0.9 mol/kg. However, the ionic strength of the 9 wt% CaCl<sub>2</sub> solution (2.7 mol/kg) was three times that of the 5 wt% NaCl solution (0.9 mol/kg). The CMC of the 5 wt% NaCl solution was found to be lower than that of the 9 wt% CaCl<sub>2</sub> solution. 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.

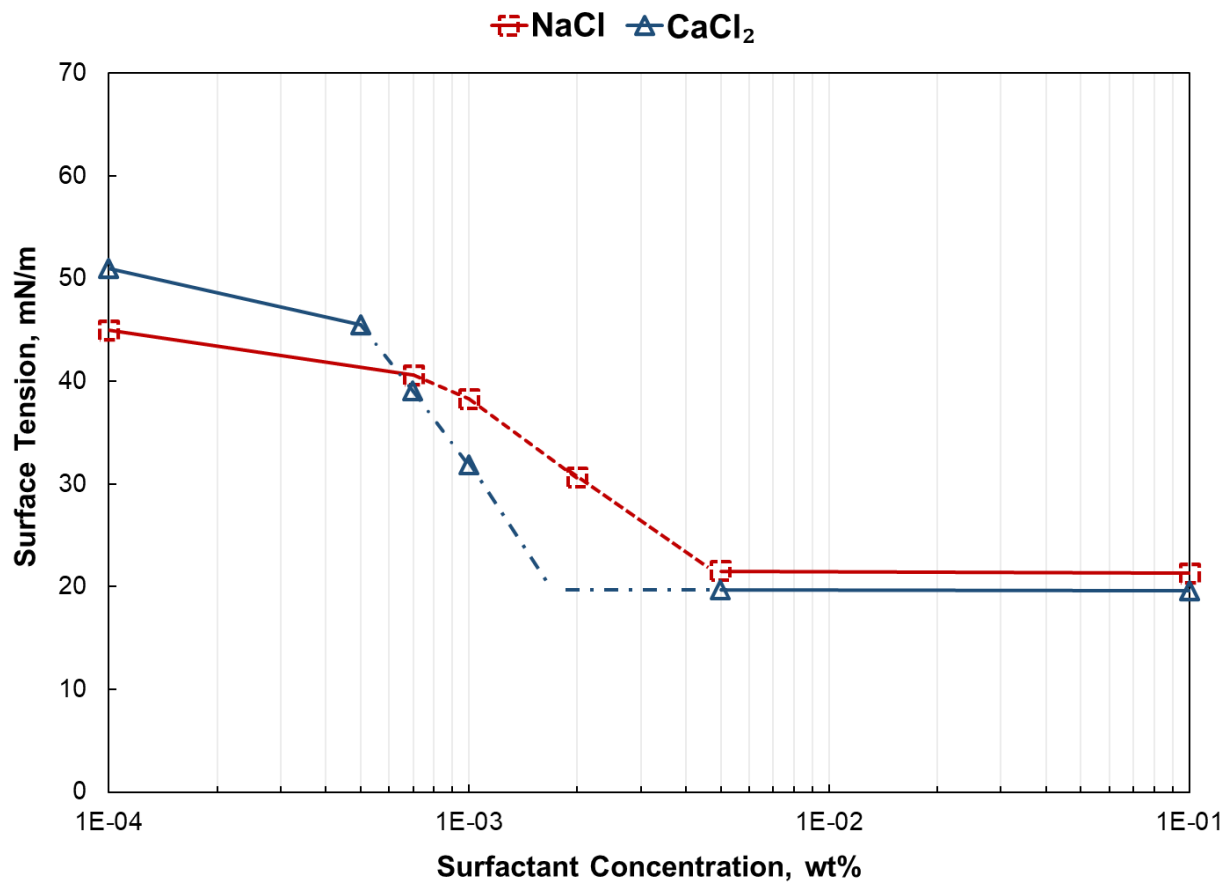


Fig. 25—Surface tension as a function of surfactant concentration for 0.9 mol/kg solutions of NaCl and CaCl<sub>2</sub> at pH 6.5 and 150°F.

## CONCLUSIONS

Foam CO<sub>2</sub> is a promising technology for EOR applications. The present work investigated and optimized a switchable ethoxylated amine surfactant, Ethomeen C12, for its foam performance 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 for the 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 from a plot of surface tension vs surfactant concentration yielded an excellent relationship to the foam stability.
5. The increase in temperature resulted in a lower surface tension gradient. This indicated that the foam stability would be poorer at higher temperatures. 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 at 150°F.

Most studies on Ethomeen C12 or switchable ethoxylated amine surfactants only focus on its foaming capability and performance in high salinity environment. This work covers the entire spectrum of salinity and demonstrate the stark difference in foaming behaviors of this surfactant in low versus high salinity environment. While under low salinity condition, Ethomeen C12 does not exhibit any outstanding foaming behavior compared to other existing popular surfactants, under high salinity condition this surfactant shows exceptional foaming capability. Ethomeen C12 demonstrates great foaming potential for EOR applications in high-salinity high-temperature reservoirs.

This study also is the first one to incorporate pH with salinity in examining the foaming capability and stability of Ethomeen C12. For certain operating salinity condition, the pH can have a significant effect on the foam performance. This is especially true under lower salinity, less than 15 wt% NaCl, condition, where low pH poses a detrimental effect on the foam stability. However, at high salinity environment, over 20 wt% NaCl, the effect of pH on both foamability and stability is lessened, although the overall trend remains consistent. In general, an environment pH of 6 – 6.5 is most ideal to produce strong and stable foam. The author(s) 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. 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 sulfate brines. Experimental results also

showed that the pH and salinity effect on foam performance does not change with temperature, eliminating one factor from consideration when it comes to designing the optimal surfactant configuration for either EOR or acidizing purposes.

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