Role of Counterions and Nature of Spacer on Foaming Properties of Novel Polyoxyethylene Cationic Gemini Surfactants

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Keywords: enhanced oil recovery, phenyl spacer, gemini surfactant, foam stability

Abstract:

Application of foam in various upstream operations, such as in enhanced oil recovery, has gained significant attention in recent years. A good foaming agent should generate a stable foam, must be thermally stable (>90 °C, typical reservoir temperature), must have a high tolerance to salinity, and should have low adsorption on the reservoir rock. In view of this, four thermally stable and salt-tolerant polyoxyethylene cationic gemini surfactants were synthesized with different spacers (mono phenyl and biphenyl) and different counterions (Br? and Cl?). Foaming properties were evaluated using initial foam generation, foam volume stability at a given time, bubble count, and average foam bubble radius. The effect of counterions and nature of spacers, with and without the presence of salts, on foaming properties was evaluated. It was found that number of phenyl rings (mono phenyl and biphenyl) had no significant effect on foamability and foam stability in the presence or absence of salts. However, the effect of counterions was prominent in deionized water. In deionized water, foam generated by gemini surfactants with bromide as a counterion was more stable compared to the foam generated using the surfactant containing chloride as the counterion. In saline solution, the type of counterion had no effect on the foamability or foam stability of the foam generated using synthesized cationic gemini surfactants. The foam volume stability decreased by the addition of salts; however, a further increase in salt concentration enhanced the foam volume stability. The synthesized surfactants showed good thermal stability, salt tolerance, and foaming properties and can be an attractive choice for upstream applications.

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Article

Role of Counterions and Nature of Spacer on Foaming Properties of Novel Polyoxyethylene Cationic Gemini Surfactants

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Abstract: Application of foam in various upstream operations, such as in enhanced oil recovery, has gained significant attention in recent years. A good foaming agent should generate a stable foam, must be thermally stable (>90 °C, typical reservoir temperature), must have a high tolerance to salinity, and should have low adsorption on the reservoir rock. In view of this, four thermally stable and salt-tolerant polyoxyethylene cationic gemini surfactants were synthesized with different spacers (mono phenyl and biphenyl) and different counterions (Br^- and Cl^-). Foaming properties were evaluated using initial foam generation, foam volume stability at a given time, bubble count, and average foam bubble radius. The effect of counterions and nature of spacers, with and without the presence of salts, on foaming properties was evaluated. It was found that number of phenyl rings (mono phenyl and biphenyl) had no significant effect on foamability and foam stability in the presence or absence of salts. However, the effect of counterions was prominent in deionized water. In deionized water, foam generated by gemini surfactants with bromide as a counterion was more stable compared to the foam generated using the surfactant containing chloride as the counterion. In saline solution, the type of counterion had no effect on the foamability or foam stability of the foam generated using synthesized cationic gemini surfactants. The foam volume stability decreased by the addition of salts; however, a further increase in salt concentration enhanced the foam volume stability. The synthesized surfactants showed good thermal stability, salt tolerance, and foaming properties and can be an attractive choice for upstream applications.

Keywords: foam stability; gemini surfactant; phenyl spacer; enhanced oil recovery

1. Introduction

A surfactant is a surface-active agent that lowers the surface tension or interfacial tension (IFT) between two immiscible phases. Surfactants consist of a hydrophilic part (water-soluble) and a hydrophobic part (oil-soluble), known as the head and tail of the structure, respectively. Based on the type of ions, surfactants can be classified into four major groups: anionic, cationic, zwitterionic, and nonionic surfactants. Gemini surfactants are a special type of surfactant containing more than one hydrophilic head groups and hydrophobic tail groups linked by a spacer at or close to the head groups [1–3]. Gemini surfactants can be anionic, cationic, or zwitterionic. Interesting properties of gemini surfactants have attracted the attention of many researchers and industrialists. These include foaming properties, rheological properties, lower critical micelle concentration (CMC), good water solubility, and high efficiency in reducing oil/water interfacial tension [4–7].

Surfactants are used in different oilfield applications including but not limited to enhanced oil recovery, fracturing, shale inhibition, drilling, and well stimulation [8–15]. The oilfield applications of surfactants are challenging due to harsh reservoir conditions. The reservoirs usually have a very high temperature (>90 °C) and high salinity (>200,000 ppm). At such harsh conditions, surfactants can thermally degrade. In the presence of high level of salts, surfactants can precipitate by interacting with different ions. Surfactant retention on reservoir rock is another major issue for oilfield application. Surfactant loss can be due to adsorption on reservoir rock and/or trapping in porous media. The surfactant retention increases the cost of the process, which is one of the primary criteria in the selection of surfactants for such application. In summary, a surfactant for oilfield application should have: high thermal stability at reservoir conditions, compatibility with injection fluids, high salt tolerance, and low retention on reservoir rock in addition to improvement in the primary properties (IFT, wettability, foaming, etc.) for which surfactant is being used.

The main reasons for surfactant injection in oilfield application can be IFT reduction, emulsification, demulsification, wettability alteration, and foam generation. In enhanced oil recovery (EOR), surfactants are injected to reduce the IFT between water and oil to mobilize the residual oil. An ultra-low IFT ($<10^{-3}$ mN/m) is required to achieve the capillary number to overcome the capillary forces. This level of low interfacial tension can only be achieved by injection of a suitable surfactant. Wettability alteration of rock towards a more water-wet state can also be achieved by injecting a suitable surfactant. Most of the carbonate rocks are oil-wet and the recovery factor is low as most of the oil prefers to stick to the rock surface. A suitable surfactant can change the wettability and make it water-wet to mixed-wet, which helps in recovering additional oil. Injection of surfactant with a gas can generate foam inside the reservoir, which improves the oil recovery in two different ways: a foam can improve the mobility ratio between oil and water and the sweep efficiency, which can result in a better recovery factor in addition to IFT reduction.

A foam consists of gas bubbles dispersed in liquid, where the gas is discontinuous owing to a thin liquid film [16,17]. This mixture of gas and liquid is thermodynamically unstable, and the liquid film can be stabilized using some materials like surfactants, nanoparticles, etc. Foamability and foam stability are the two important properties of foam that depend on the characteristics of the available surface-active components [18–20]. The stability of wet foam is linked to the film elasticity, while that of dry foam cannot be correlated with the film elasticity [21]. Average bubble radius (R_{avg}) and bubble count (BC) signify the homogeneity and stability of the foam [22]. The more homogenous and stable foam contains smaller bubbles and obviously larger bubble count.

In this work, four polyoxyethylene cationic gemini surfactants were synthesized having one and two phenyl rings in a spacer with different counterions. These surfactants showed excellent thermal stability, surface, and interfacial properties [23]. Most of the available cationic surfactants showed precipitation in harsh reservoir conditions. We improved salt tolerance by adding a suitable number of ethoxy group in the surfactants. The main objective of this work was to investigate how the number of phenyl rings and counterion impacts the foaming properties of polyoxyethylene cationic gemini surfactant in presence and absence of salts. This type of work has never been reported in the literature. This fundamental investigation could help in designing suitable foaming materials for foam flooding application.

2. Materials and Methods

2.1. Synthesis of Surfactants

3-(Dimethylamino)-1-propylamine (99%), glycolic acid ethoxylate lauryl ether (average M_n ~690), NaF (≥99%), *α*,*α*′-Dibromo-*p*-xylene, (97%), *α*,*α*′-Dichloro-*p*-xylene (98%), 4,4′-Bis(bromomethyl)biphenyl (98%), 4,4′-Bis(chloromethyl)-1,1′-biphenyl (98%), and aluminum oxide (99.99%), used in the synthesis of surfactants, were purchased from Aldrich Company (St. Louis, Missouri, United States) Distilled solvents were used for the preparation of gemini surfactants.

Four ammonium-based gemini cationic surfactants (12-PhBr-12, 12-PhCl-12, 12-BiPhBr-12, and 12-BiPhCl-12) containing an aromatic ring spacer were synthesized by reacting glycolic acid ethoxylate lauryl ether with 3-(dimethylamino)-1-propylamine in the presence of sodium fluoride as a catalyst to acquire intermediate amide, which was then further treated individually with α,α′-Dibromo-*p*-xylene, α,α′-Dichloro-*p*-xylene, 4,4′-Bis(bromomethyl)biphenyl, and 4,4′-Bis(chloromethyl)-1,1′-biphenyl to form 12-PhBr-12, 12-PhCl-12, 12-BiPhBr-12, and 12-BiPhCl-12, respectively (Figure 1). 12-PhCl-12 and 12-PhBr-12 contain a single phenyl ring with chloride and bromide as counterions, respectively, while 12-BiPhCl-12 and 12-BiPhBr-12 have two phenyl rings with chloride and bromide as counterions, respectively. The detailed synthesis procedure and characterization of these surfactants have been described elsewhere [23]. These surfactants were designed to systematically investigate the effect of changing the counterions (Br^-, Cl^-) and the number of phenyl rings in the spacer.

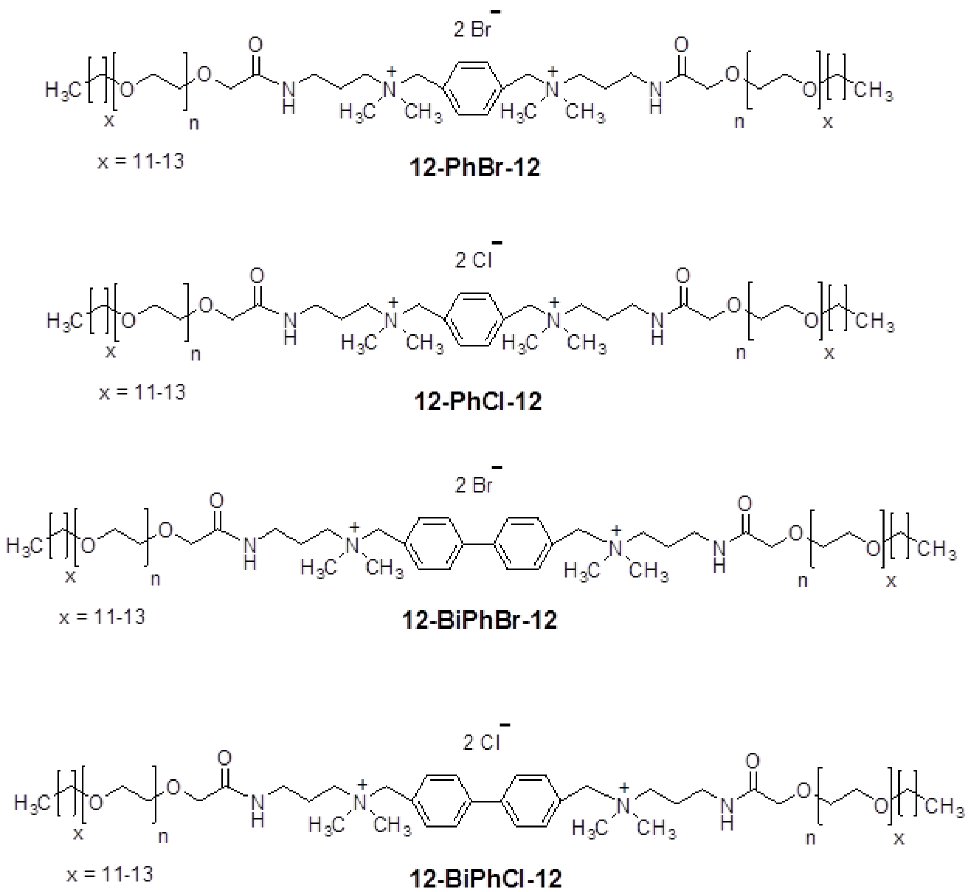


Figure 1. Chemical structure of synthesized surfactants.

2.2. Solution Preparation

Synthetic seawater was prepared in the laboratory containing both monovalent and divalent cations, having a total salinity of 57,643 ppm. The composition of seawater is given in Table 1. Surfactant solutions were prepared by weighing the desired amount and dissolving it in the required amount of water (deionized, NaCl, or seawater).

Table 1. The composition of the synthetic seawater (SW).

Ions	SW (ppm)
Na^{+}	18,300
Ca^{++}	650
Mg^{++}	2110
Cl^{-}	32,200
HCO_3^{-}	120
SO_4^{-2}	4290
TDS	57,670

2.3. Foaming Properties

The foaming properties of novel cationic gemini surfactants were measured using a Dynamic Foam Analyzer (KRÜSS, Hamburg, Germany) which is based on optical measurements. This device allowed us to find the foam formation, foam stability, bubble count, and average bubble radius along with foam images at several intervals. The foam was generated by blowing gas (air) at a flow rate of 0.2 L/min through a porous media. This was located at the bottom of a glass tube where 50 mL of the aqueous surfactant solution was placed. The foam was allowed to build up for 20 s. The bubbling was stopped, and the evolution of the foam was monitored for 1 h. The initial foam height shows foamability, while foam stability is measured by foam volume stability (FVS), calculated by Equation (1), and foam height.

$$FVS(t) = \frac{V_t}{V_f} \times 100 \quad (1)$$

where FVS(t) is the foam volume stability as a function of time. V_t is the foam volume at a given time, and V_f is the maximum foam volume usually measured when the bubbling process has stopped. Foaming properties were measured at 22 °C from using a constant surfactant concentration of 0.5 mM (>CMC). The equipment was ensured to be well-cleaned before conducting any experiment. All experiments were repeated and different parameters such as FVS, BC, and R_{avg} are average experimental values.

3. Results and Discussion

The discussion section is divided into two categories. The first section discusses the effects of the spacer nature and counterions on foaming properties, while the second part focuses on the effect of salinity.

3.1. Effects of Spacer Nature and Counterions

The foaming behavior of gemini surfactants was investigated. The foam height (h_{foam}) and FVS at a given time are considered as a measure of foam stability. The former depicts foam decay as a function of time, while the latter shows the stability of the foam quantified using Equation (1). Figure 2 presents the foam height of aqueous surfactant solutions (12-PhBr-12, 12-PhCl-12, 12-BiPhBr-12, 12-BiPhCl-12) in deionized water in terms of time. The maximum foam height of each surfactant is almost the same; namely, they have similar foamability. There is an insignificant difference in foamability among all surfactants as shown in Figure 2. However, the foam decay of these surfactants is slightly different from one to another. The foam generated using surfactants containing Br^{-} counterions decay more slowly compared to surfactants containing Cl^{-} counterions. However, surfactants containing a different number of phenyl rings have a similar type of foam decay provided that the counterions remain the same. This suggests that Br^{-} ions create slightly more stable foam as compared to Cl^{-} ions for surfactants containing either single or double rings in the spacer. This effect is also evident from the

FVS data, as shown in Figure 3. An interesting conclusion drawn from these experiments is that the addition of one more ring in the spacer has a negligible impact on both the foam height and FVS.

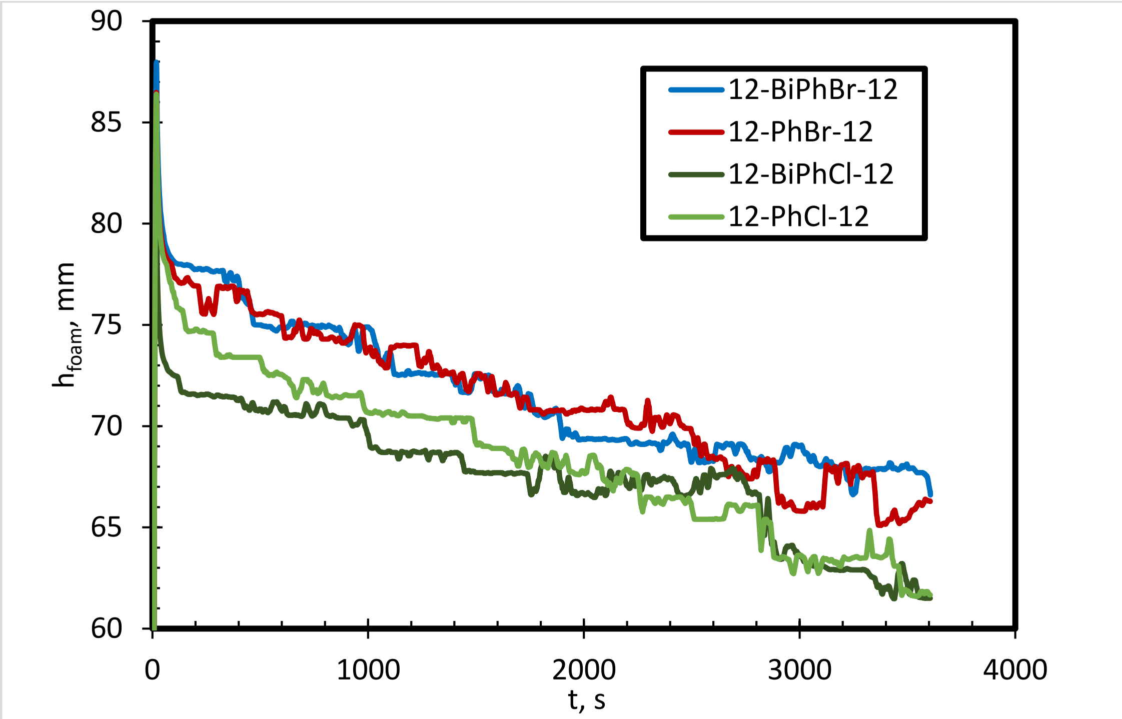


Figure 2. Comparison of foam height of different surfactants.

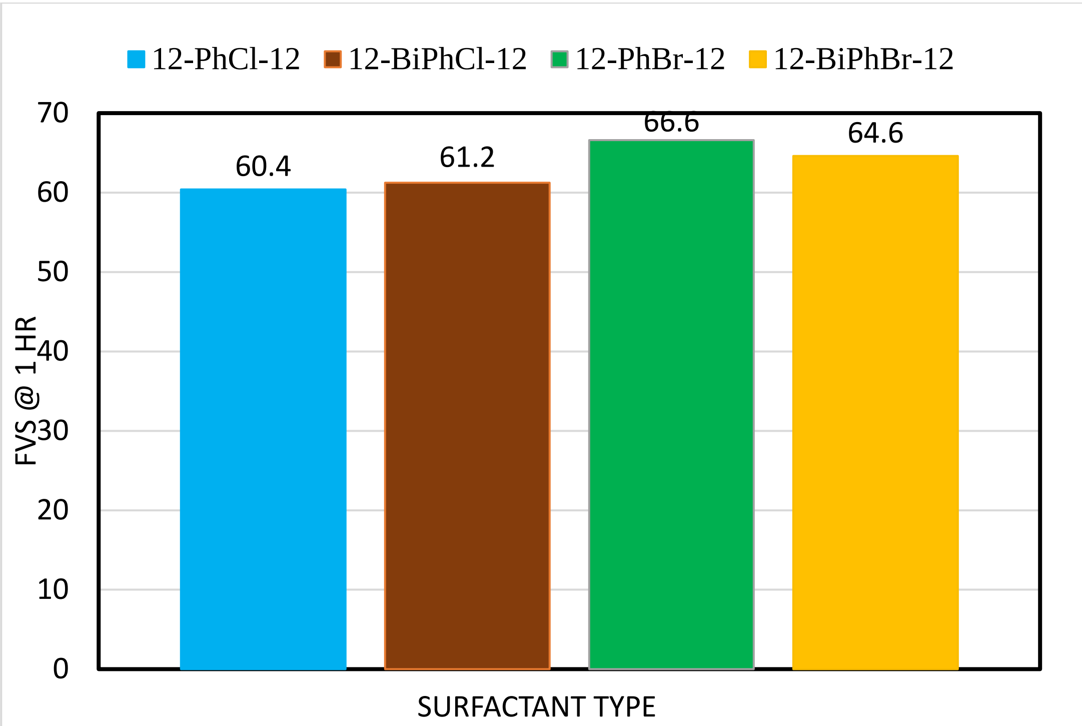


Figure 3. Comparison of foam volume stability (FVS) of different surfactants at the same concentration (0.5 mM).

Bubble count and average bubble radius characterize the foam stability [22]. The average bubble radius of the foam generated using synthesized surfactants is shown in Figure 4. The average bubble radius was calculated using Equation (2):

$$R_{avg} = \frac{1}{n}\sum_{i=1}^{n} R_i \quad (2)$$

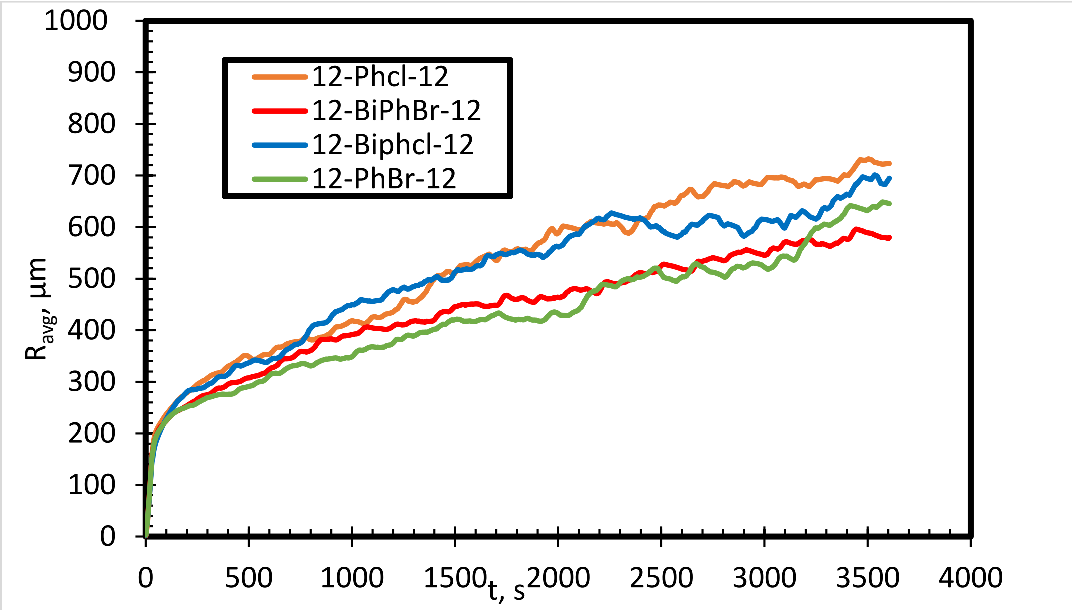


Figure 4. Effect of counterions with mono and biphenyl rings in deionized water on average bubble radius.

Here, R_i is the radius of a circle of the same area as the area of the recorded bubble and n is the total number of bubbles. Comparing the average bubble radius of all surfactants, the initial average bubble radii of all surfactants were all similar, which supports the foamability data obtained by foam height. This indicates that the foamability of the polyoxyethylene cationic gemini surfactant is independent of the type of counterion and the number of phenyl rings. In regard to time, bubble size growth was different for different surfactants. The bubble size growth of 12-PhBr-12 and 12-BiPhBr-12 with time was almost same and the R_{avg} curves overlapped. Similarly, the bubble size growth of 12-PhCl-12 and 12-BiPhCl-12 with time was identical (Figure 4), demonstrating that the bubble size growth is independent of the number of aromatic phenyl rings in the spacer for such class of surfactants. However, the bubble size growth was faster for surfactants containing Cl^- as a counterion compared to the surfactants containing Br^- as a counterion. Though the bubble size growth in the foam generated using surfactants containing Cl^- ions was fast, the difference was not significant. This data also supports the FVS and foam height data for all surfactants. A faster bubble size growth means that the surfactant is less stable. The FVS data indicate that the surfactants containing Cl^- ions have a lower FVS and foam height at a given time compared to surfactants containing Br^- ions regardless of the number of phenyl rings.

Bubble count is another important foam property that shows the quality of the foam under given conditions. The bubble count of foam generated using synthesized surfactants is given in Figure 5. The bubble count results are fairly like the results obtained for the average bubble size. The initial bubble counts for all surfactants were similar, indicating that all surfactants generate foam with almost similar homogeneity regardless of counterions and number of rings in the spacer. With time, the bubble counts of surfactants containing Br^- as a counterion (12-PhBr-12 and 12-BiPhBr-12) were alike.

On the other side, the bubble counts of surfactants containing Cl^- as a counterion (12-PhCl-12 and 12-BiPhCl-12) were also similar. This shows that bubble count is also independent of the number of aromatic phenyl rings in the spacer and is impacted by the type of counterion. Images of bubble count and size at different times for all surfactants are presented in Table 2. At any time, it is clear from Table 2 that the bubble count for 12-PhBr-12 was higher than that of 12-PhCl-12. Also, the bubble count of 12-BiPhBr-12 was higher compared to that of 12-BiPhCl-12 at any time. On the other hand, the bubble size was small for the surfactants containing Br^- counterions at any time

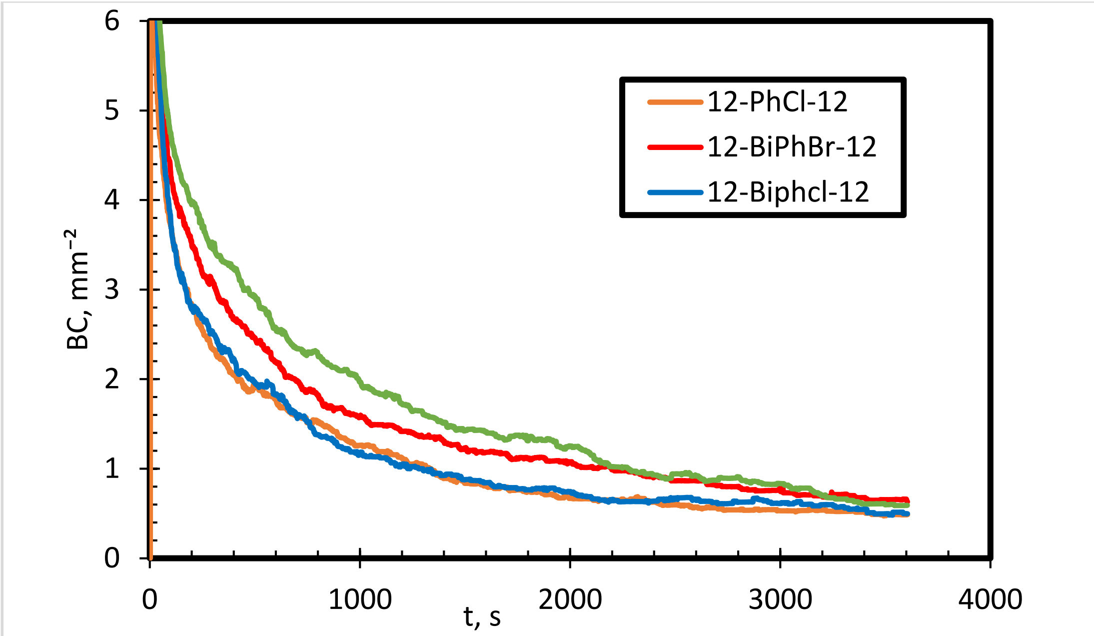
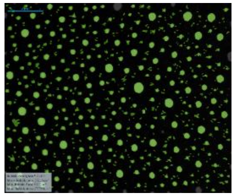
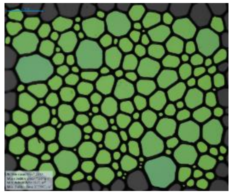
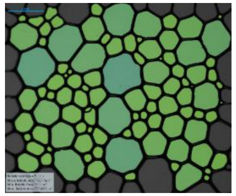
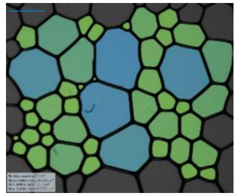
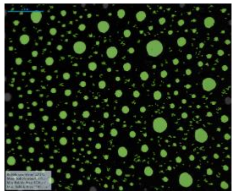
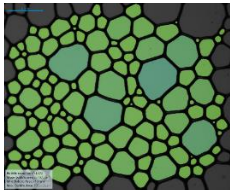
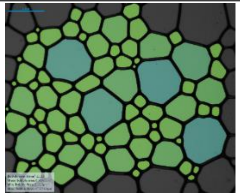
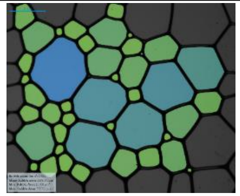
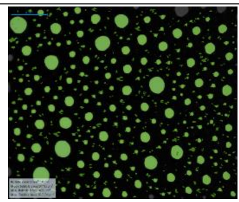
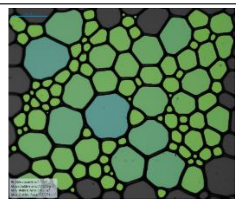
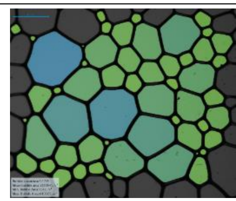
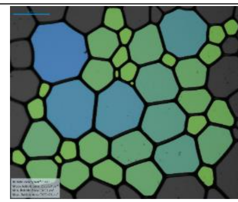
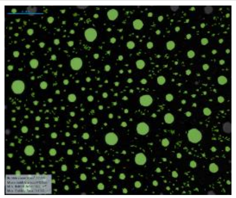
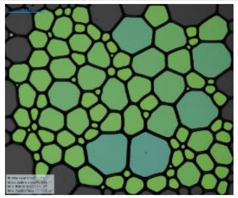
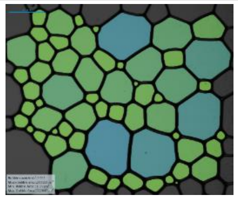
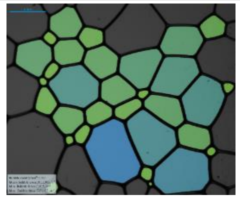


Figure 5. Bubble count of different surfactants in deionized water.

By comparing the results of foam height, bubble count, and average bubble radius, it was concluded that initial foamability and foam structure of the foam generated by all types of surfactant were similar and no difference was observed. The foam stability of the surfactants containing Br^- was slighter higher compared to the surfactant containing Cl^- ions due to the high FVS, high bubble count, and low average bubble radius of Br^--containing surfactants. The foam stability was independent of the number of aromatic phenyl rings in the spacers.

Table 2. Image view of bubble count and size at different times for all surfactants.

		Evolution of Foam			
		Start of Foaming	**15 min**	**30 min**	**60 min**
Surfactant in Deionized Water	**12-PhBr-12**				
	12-BiPhBr-12				
	12-PhCl-12				
	12-BiPhCl-12				

3.2. Effect of Salinity

Stable foam is desirable in the flooding process as it increases the displacement sweep efficiency. Pressure drop in the core and the oil recovery was found to be improved using stable foam [24]. This section deals with the impact of salt concentration on the stability of foam to evaluate the performance of these surfactants in harsh conditions. Two types of salts (NaCl, synthetic SW) were used to assess the performance. In real field applications, SW is more important as it is used as an injection fluid. Synthetic SW contains several ions (divalent and monovalent) and NaCl was used to isolate the effect of divalent ions.

The effect of salt concentration on foaming properties was evaluated using NaCl of different molar concentrations. Figure 6 shows the FVS of aqueous cationic gemini surfactants (12-PhBr-12, 12-PhCl-12, 12-BiPhBr-12, 12-BiPhCl-12) at 0.125 M, 0.25 M, and 1 M NaCl brine concentrations. Upon comparing the results with deionized water (Figures 3 and 6), it was observed that the addition of a low concentration of salts reduced the FVS—this is true for all surfactants. However, an increase in NaCl concentration leads to the improvement of foam volume stability. According to Figure 6, all four surfactants showed an increase in FVS with the increase in NaCl concentration. A possible explanation for this effect is that salt acts as an electrolyte in the liquid layer formed between bubbles, decreasing the bubble-to-bubble gas diffusion and resulting in high foam stability. However, this behavior depends upon the salt concentration. The data given in Figure 6 also suggests that the type of counterions and the number of aromatic phenyl rings have no impact on FVS in the presence of salts. The FVS of all surfactants was similar at any given salinity. This is due to the addition of salts that brings several ions, rendering the effect of counterions present in the surfactant insignificant. For practical field applications, it can be concluded that the foaming properties are not affected by the type of counterion or the number of aromatic phenyl rings.

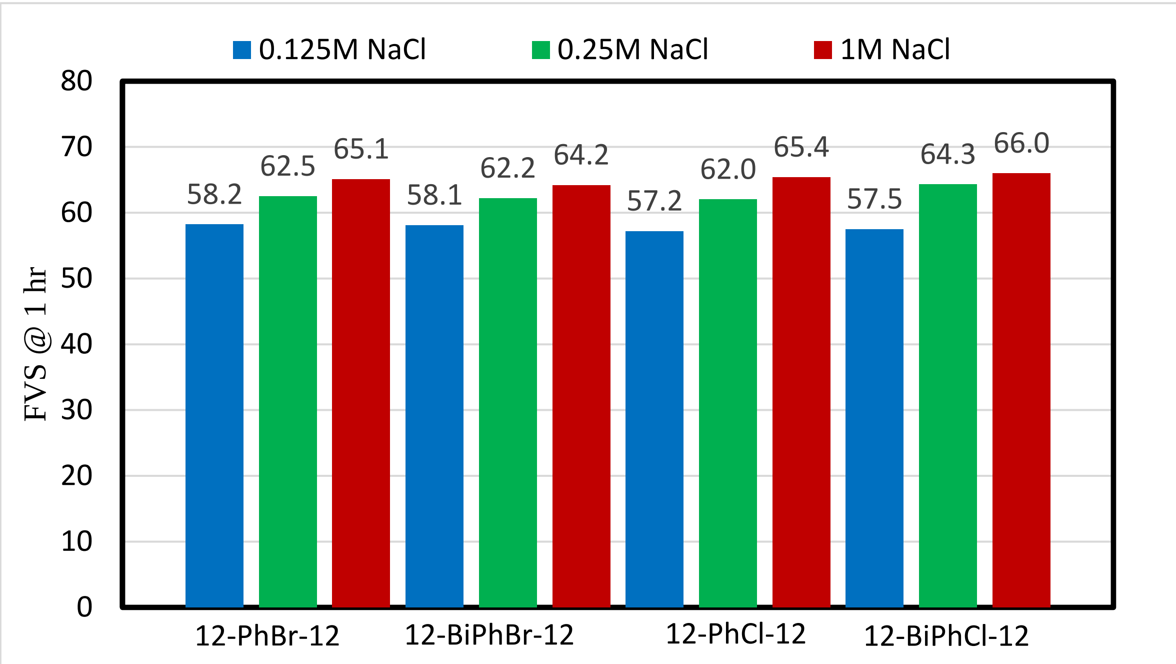


Figure 6. Effect of salinity on foam volume stability of different surfactants.

The foam stability of the surfactants was also tested for seawater. Figure 7 shows the comparison of foam volume stability of 12-PhCl-12 and 12-BiPhCl-12 in deionized water and SW. It seems that the foam volume stability was found to be insensitive to salinity when seawater was used. However, based on the previous discussion, this is due to the comparatively high salinity, as low NaCl salinity also gave low FVS, and the FVS increased with the increase in NaCl concentration. This reveals that for the wide range of field properties undergoing EOR foaming process, newly synthesized surfactants can be used as a stable foaming agent.

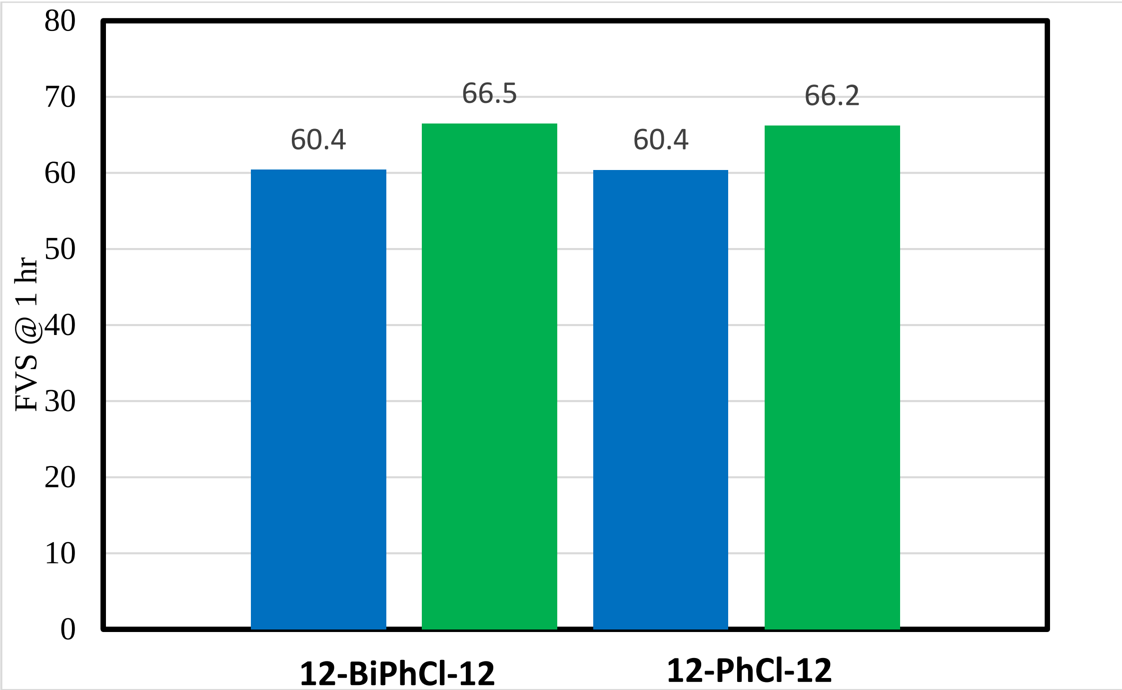


Figure 7. Foam volume stability of surfactants 12-PhCl-12 and 12-BiPhCl-12 in deionized water and SW.

The influence of salinity was investigated on bubble count and bubble size as well. Figure 8 shows the average bubble radius as a function of time for 12-PhCl-12 in 0.125 M NaCl, 0.25 M NaCl, and 1 M NaCl aqueous solutions. The average bubble radius was calculated from Equation (2). At the start of foaming, the average bubble radius was the same for the three samples. This implies that salinity has no impact on foamability. After that, the average bubble radius for all samples increased obviously. However, the average bubble size for the 12-PhCl-12 surfactant solution in 1 M NaCl increased slowly compared to the other two samples with 0.125 M and 0.25 M NaCl concentrations. The average bubble radius increased with time because of the phenomenon known as coarsening, which is related to the breakdown of the thin liquid film between two bubbles. With the increase in salinity, bubble size decreases, showing that foam stability is enhanced with the increase of salinity. The presence of NaCl strengthens the thin liquid film between bubbles and delays its rupture, which in turn enhances the foam stability. Figure 9 shows the effect of NaCl concentration on bubble count. The bubble count data also supports the observations obtained using FVS and bubble average radius. The bubble count in the start for all samples was almost the same, as shown in Figure 9. However, 12-PhCl-12 in 1 M NaCl aqueous solution showed a slightly higher bubble count. By the evolution of foam, the bubble count decreased exponentially for all samples, but the decrease in bubble count for 12-PhCl-12 in 1 M NaCl aqueous solution was lower than the other two samples. This shows that 12-PhCl-12 in 1 M NaCl aqueous solution generated more homogenous and stable foam compared to 12-PhCl-12 in low NaCl concentration. Table 3 illustrates the images of bubble count and size at different times with different salinit in 12-PhCl-12. At 15 min, it was obvious that number of bubbles for 12-PhCl-12 in 1 M NaCl aqueous solution was greater and more uniform than that of 12-PhCl-12 in 0.125 M and 0.25 M NaCl aqueous solutions. A similar trend was observed at 30 and 60 min. These results confirm that increasing the NaCl concentration increases the bubble count and decreases the average bubble radius, enhancing the stability of the foam.

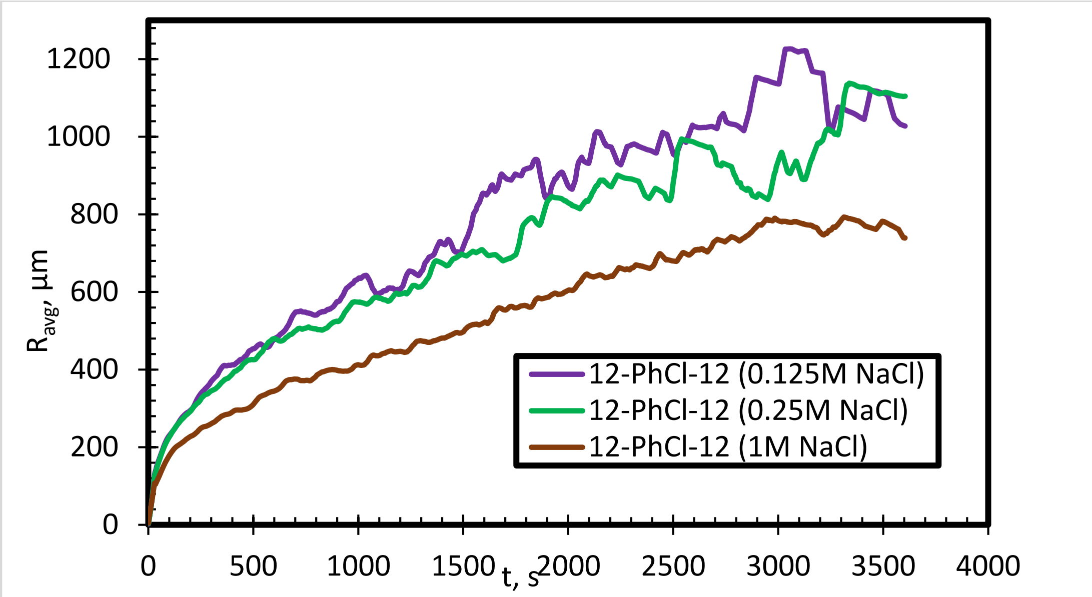


Figure 8. Effect of salinity on the bubble size of the foam generated using 12-PhCl-12.

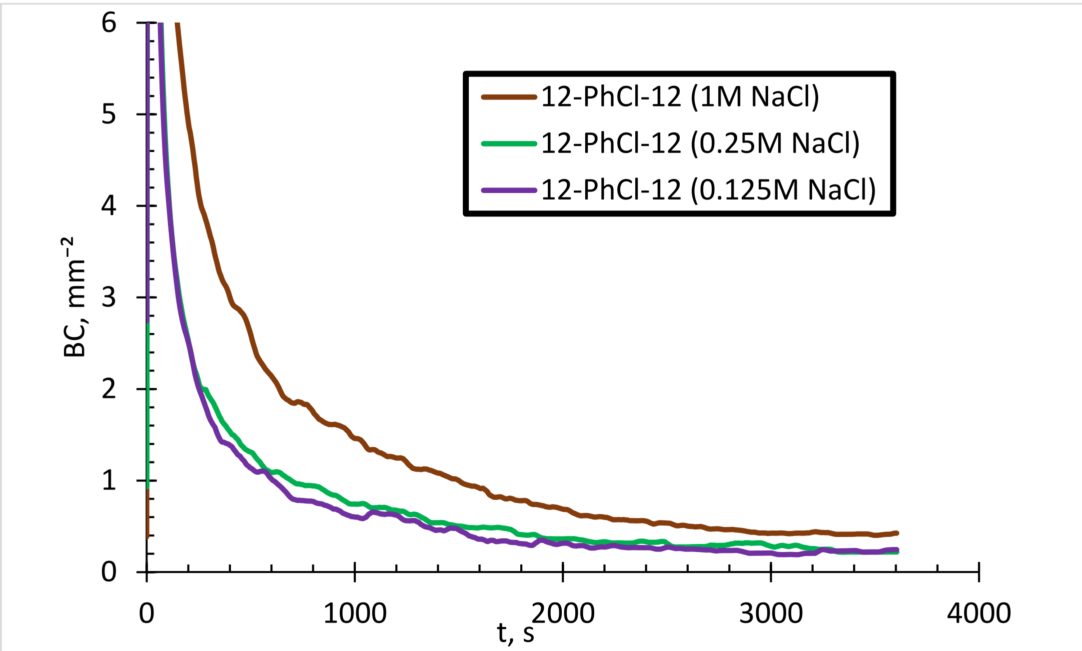
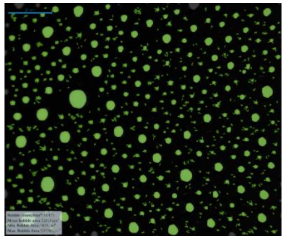
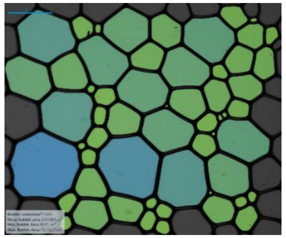
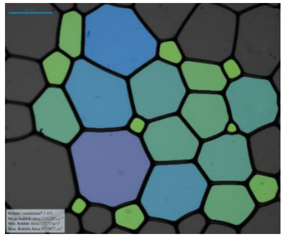
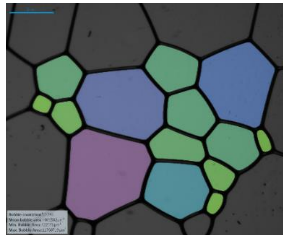
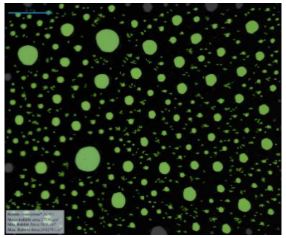
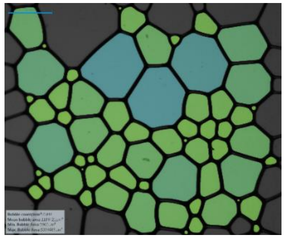
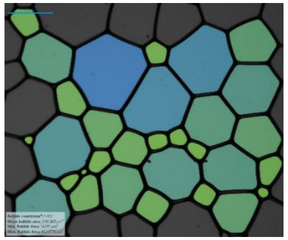
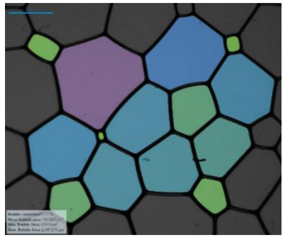
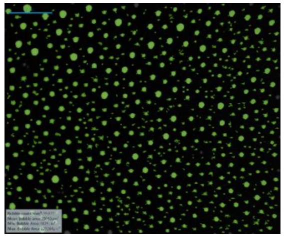
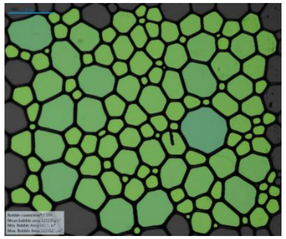
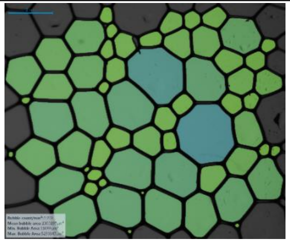
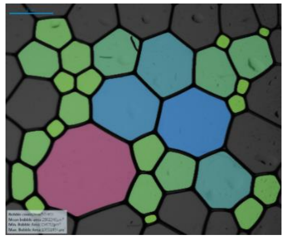


Figure 9. Effect of salinity on bubble count of the foam generated using 12-PhCl-12.

Table 3. Image view of bubble count and size at different times with salinity effect in 12-PhCl-12.

		Evolution of Foam			
		Start of Foaming	**15 min**	**30 min**	**60 min**
Salinity Effect of 12-PhCl-12	**0.125 M NaCl**				
	0.25 M NaCl				
	1 M NaCl				

4. Conclusions

Four polyoxyethylene cationic gemini surfactants containing two different counterions (Cl^- and Br^-) and two different spacers (mono phenyl and biphenyl rings) were synthesized. The surfactants were designed carefully to determine the impact of counterions and type of spacer on foaming properties in the presence and absence of salts. From the experimental results, it was concluded that:

1- All newly synthesized surfactants in this study were stable in deionized water, NaCl brine, and seawater.
2- The type of spacer and counterion have no impact on the foamability (initial foam volume produced) of these surfactants in deionized water and saline water.
3- The presence of bromide counterions generates more stable foam as compared to chloride counterions in deionized water.
4- The effect of counterions on foam stability becomes insignificant in the presence of salts.
5- The number of aromatic phenyl rings in the spacer has no significant effect on foam stability in deionized and saline water.
6- The addition of salts reduces the FVS, but with further increase in the salt concentration, the FVS increases.

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