

Supplementary File

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Experimental Investigation of Foam Stability under Various Salinity Levels, Oil Types, and Surfactant Conditions: Effect of Natural Polymer Lignin

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In deionized water, the surface tension of the pure solvent was measured at approximately 70.27 mN/m. Upon the addition of CTAB, the surface tension decreased sharply with increasing concentration and reached a near-constant value of about 34.3 mN/m around 400–500 ppm, indicating the formation of micelles and the establishment of the CMC. This behavior reflects the strong interfacial activity of CTAB due to its long hydrophobic tail and cationic headgroup, which promotes efficient adsorption at the air–water interface. In contrast, the initial surface tension of synthetic seawater was higher, approximately 75.68 mN/m, due to the ionic strength contributed by dissolved salts such as Na^+ and Cl^- . The addition of CTAB to seawater resulted in a slower decrease in surface tension compared to deionized water. The CMC in seawater was found to be approximately 550 ppm, slightly higher than in deionized water, suggesting that ionic interactions in saline media partially shield the electrostatic forces among surfactant molecules, requiring a higher concentration for interfacial saturation. Nevertheless, the final surface tension plateau in seawater (around 29–32 mN/m) was slightly lower than in deionized water, indicating enhanced micellization in ionic environments.

For SDS, a similar trend was observed but with notable differences. In deionized water, the surface tension decreased more gradually than with CTAB, starting at 70.89 mN/m and stabilizing around 31.75 mN/m at approximately 2000 ppm. This gradual decline indicates a higher CMC for SDS and reflects its lower interfacial efficiency compared to CTAB. The anionic nature of SDS leads to electrostatic repulsion between surfactant headgroups at the interface, which hinders tight molecular packing and delays micelle formation. In seawater, SDS exhibited a more pronounced reduction in surface tension, with values dropping to around 29 mN/m at 3000 ppm. Interestingly, a slight increase in surface tension was observed at higher concentrations, potentially due to complex ion–surfactant interactions that influence micelle dynamics. This behavior suggests that, despite its relatively high CMC, SDS can still perform effectively in ionic environments, albeit less efficiently than CTAB.

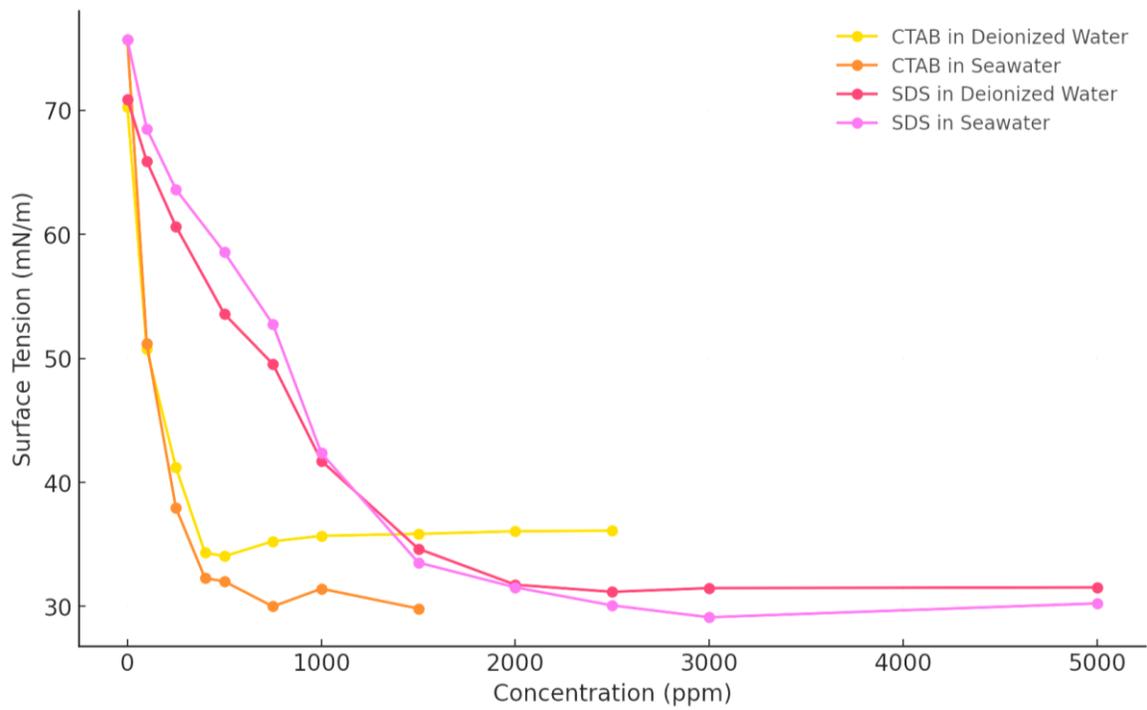


Fig. S1. Comparison of surface tension reduction in deionized water and seawater with increasing concentrations of CTAB and SDS surfactants.

As can be seen in Fig. S2, the concentration of CTAB used is fixed at 400 ppm in deionized water and 550 ppm in seawater, corresponding to the respective CMC values determined earlier.

The blue line in Fig. S2 illustrates the stability of foam as the concentrations of lignin in deionized water increase. The surface tension initially drops from 70 mN/m to 65 mN/m as lignin concentration increases from 0 to 1000 ppm. This initial reduction can be attributed to the surfactant-like behavior of lignin (amphiphilic nature of lignin), which disrupts the water's hydrogen bonds, reducing the cohesive forces and hence the surface tension. The surface tension increases to 67 mN/m at 2000 ppm. This unexpected increase could be due to lignin molecules crowding the water-air interface, leading to an increase in cohesive forces or the formation of aggregates that temporarily reduce the effectiveness of lignin in lowering surface tension. After the peak at 2000 ppm, the surface tension steadily decreases, reaching 61 mN/m at 10,000 ppm.

At higher concentrations, more lignin molecules are able to interact with the surface, forming a stable monolayer, which reduces surface tension more effectively. For seawater with lignin (orange line), the surface tension increases from 65 mN/m to 70 mN/m as the lignin concentration increases from 0 to 2000 ppm. This initial increase may be caused by the interaction between lignin and the ions (salts) present in seawater. The salts could form complexes with lignin, enhancing the cohesive forces at the surface and leading to a temporary rise in surface tension. After the peak at 2000 ppm, the surface tension decreases sharply, reaching 60 mN/m at 10,000 ppm. At higher lignin concentrations, the interaction between lignin and seawater stabilizes, and lignin molecules act more effectively as a surfactant, reducing surface tension as expected. For distilled water with lignin and CTAB (green line), the surface tension starts much lower (around 35 mN/m) compared to the systems without CTAB, which highlights the strong surfactant properties of CTAB. CTAB disrupts the cohesive forces at the water surface more effectively than lignin, leading to a much lower initial surface tension. There is a slight fluctuation in the surface tension between 33 and 35 mN/m as the lignin concentration increases. This indicates that lignin, when combined with CTAB, has a limited additional impact on surface tension, and CTAB is the dominant factor in controlling surface tension at these concentrations. After 2000 ppm, the surface tension gradually decreases to about 31 mN/m at 10,000 ppm. This final decrease shows that lignin contributes slightly to further reducing surface tension when combined with CTAB at high concentrations. For seawater with lignin and CTAB (red line), the surface tension begins around 33 mN/m and shows minor fluctuations as the concentration increases. Like the system with distilled water and CTAB, the

presence of CTAB significantly reduces the surface tension right from the start, and lignin's additional effect is minimal. Beyond 2000 ppm, the surface tension decreases steadily to about 30 mN/m at 10,000 ppm. The reduction is slightly more pronounced in seawater compared to distilled water, possibly due to the interaction of CTAB and lignin with the salts in seawater.

In comparing distilled water to seawater (without CTAB), lignin initially reduces surface tension in distilled water; however, there is a slight increase around 2000 ppm before the tension decreases again. In seawater, however, lignin first increases the surface tension before reducing it beyond 2000 ppm. This can be attributed to the ionic interactions between the salts in seawater and lignin molecules, which disrupt the typical lignin surfactant behavior. In seawater, the presence of ions such as Na^+ and Cl^- may lead to partial charge shielding of lignin, reducing its effectiveness in lowering surface tension. The rise in surface tension peaks around 2000 ppm, likely due to ion-lignin interactions where the ionic strength is highest, limiting lignin's ability to act as a surface-active agent. After 2000 ppm, the surface tension begins to decrease. This indicates that lignin, despite the ionic competition, eventually starts to dominate the interfacial behavior as the concentration increases. At higher lignin concentrations, lignin molecules either overcome the ionic effects or begin to displace ions at the interface, causing surface tension to drop. Furthermore, the addition of CTAB results in a significantly lower surface tension in both distilled water and seawater compared to the systems without CTAB. In both water types, CTAB dominates the surface tension behavior, and the additional effect of lignin is minimal. The surface tension remains relatively stable between 30-35 mN/m across different lignin concentrations when CTAB is present. Seawater with CTAB shows a slightly lower surface tension at higher lignin concentrations compared to distilled water, likely due to the interaction between CTAB, lignin, and salts in seawater. Once lignin concentration is sufficiently high, it overcomes the influence of salts in seawater and begins to reduce surface tension. In distilled water, the reduction is more straightforward and follows typical surfactant behavior. Overall, it can be concluded that lignin is more effective at reducing surface tension in distilled water than in seawater, where its interaction with salts temporarily increases surface tension. Thus, the drop in surface tension in distilled water occurs rapidly, while in seawater, it shows an initial increase. This suggests that the ions in seawater initially hinder lignin's ability to reduce surface tension.

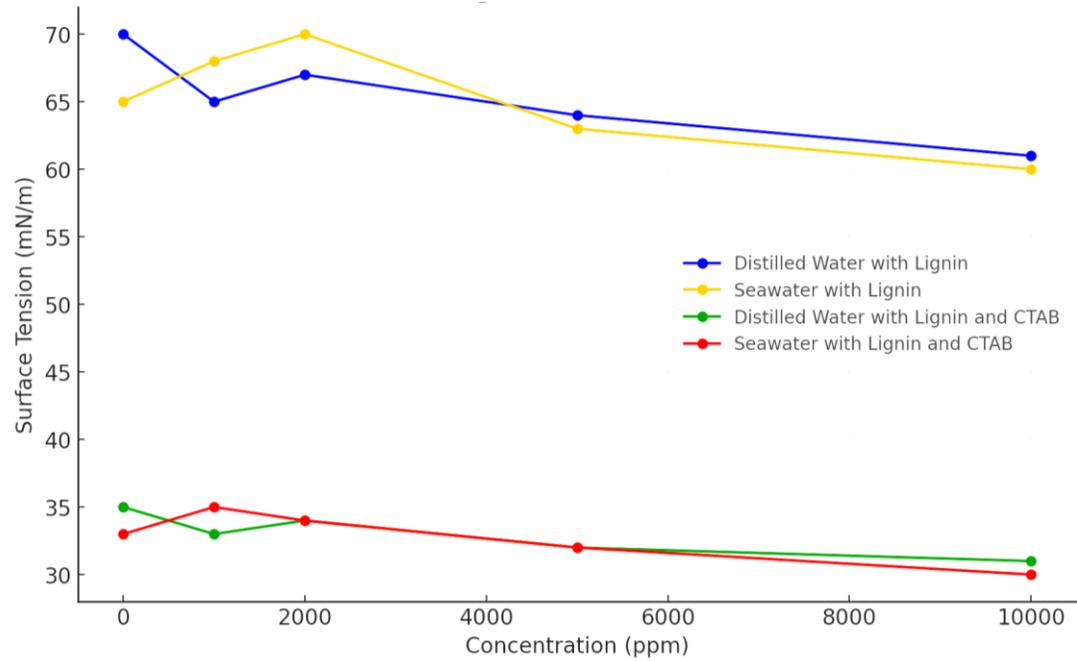


Fig. S2. Effect of lignin and CTAB on surface tension variation in distilled water and seawater across different concentrations

Fig. S3 (Supplementary data) illustrates the interfacial tension (IFT) between distilled water and heptol under two experimental conditions: (i) varying asphaltene concentrations alone, and (ii) increasing lignin content at a fixed asphaltene concentration of 500 ppm. In the asphaltene-only system (blue line), the IFT initially decreases from 31.5 to 29.48 mN/m as the asphaltene concentration increases to 500 ppm. This reduction is attributed to the adsorption of asphaltene molecules at the oil–water interface, where their amphiphilic nature allows them to accumulate and disrupt cohesive forces among water molecules. The polyaromatic core of asphaltenes contributes to interfacial anchoring, while aliphatic chains interact with the oil phase, reducing interfacial energy. However, at 1000 ppm, the IFT exhibits a sharp increase to 34.32 mN/m. This anomaly likely stems from concentration-dependent aggregation of asphaltene molecules into colloidal clusters, micelles, or floc-like structures. Such aggregates reduce the availability of free asphaltene molecules at the interface and can also form more rigid, cohesive interfacial layers that resist further tension reduction. Moreover, at high concentrations, steric hindrance and π – π stacking interactions may hinder proper orientation of molecules at the interface. As the concentration rises to 1500 and 2000 ppm, the IFT gradually decreases again to around 29.67 mN/m. This decline suggests partial disintegration or rearrangement of aggregates, possibly facilitated by increased interfacial shear or solvation effects. The newly available asphaltene monomers may then re-adsorb at the interface, restoring surface activity and reducing tension.

In the asphaltene–lignin system (orange line), lignin is incrementally added while maintaining the asphaltene concentration constant at 500 ppm. Initially, IFT increases slightly from 29.48 to 30.53 mN/m at 500 ppm lignin. This modest rise may be due to competitive adsorption between lignin and asphaltene at the interface, leading to suboptimal packing or displacement of more surface-active asphaltene molecules. Upon further addition of lignin, a significant decrease in IFT is observed, reaching a minimum of 27.04 mN/m at 1000 ppm lignin. This marked drop implies a synergistic interaction between lignin and asphaltene, likely arising from hydrogen bonding between hydroxyl and carboxylic groups on lignin and heteroatoms within asphaltenes, as well as π – π interactions between their aromatic domains. These interactions may promote more organized molecular alignment and reduce interfacial free energy more effectively than either component alone. Beyond 1000 ppm, IFT stabilizes around 27.5 mN/m, suggesting interfacial saturation or the formation of a compact, stable surface film. At this stage, lignin molecules likely form a cohesive layer alongside asphaltenes, resisting further structural rearrangement or tension

reduction. Comparatively, the lignin-containing system displays more stable behavior and consistently lower IFT values than the asphaltene-only system. This indicates that lignin not only improves interfacial performance through its own amphiphilic character but also enhances the functional efficiency of asphaltenes by reducing aggregation and facilitating better interfacial packing.

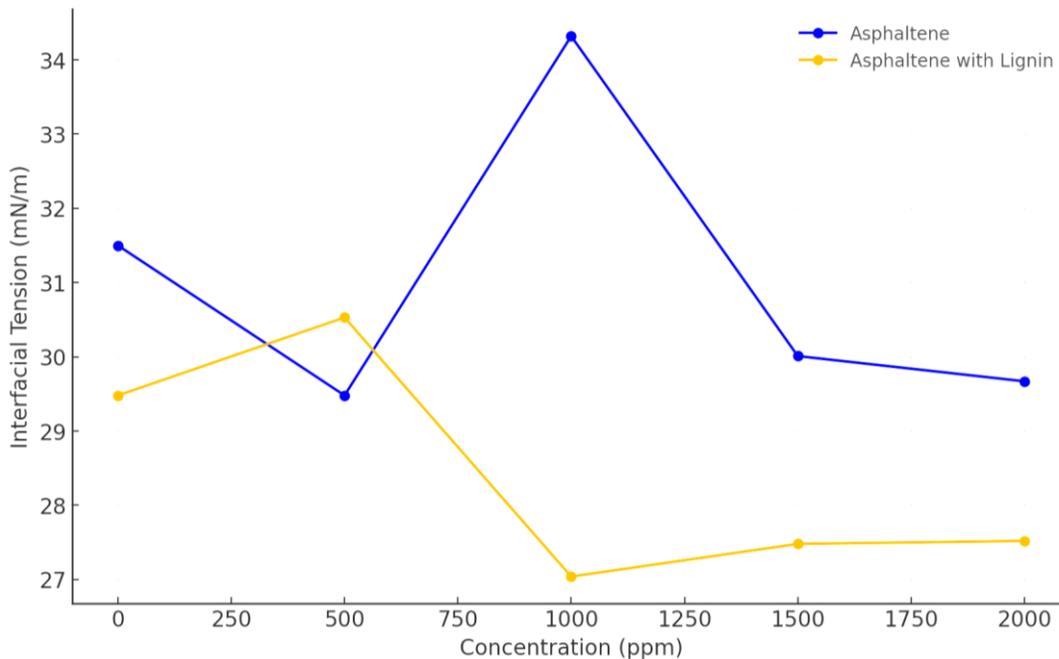


Fig. S3. Interfacial tension variation between distilled water and heptol under two conditions: increasing asphaltene concentration and fixed asphaltene concentration (500 ppm) with increasing lignin concentration

As shown in Fig. S4, the foam stability trends in both deionized water and seawater, quantified by foam half-life (solid lines with circular markers) and total foam stability (dashed lines with square markers) across a range of CTAB concentrations. For deionized water (blue lines), both foam half-life and total stability increase steadily with increasing CTAB concentration. The half-life rises from approximately 342 seconds at 100 ppm to about 1140 seconds at 1000 ppm, while the total foam stability increases sharply from 1233 seconds at 100 ppm to around 2578 seconds at 600 ppm, plateauing thereafter. This behavior indicates that in salt-free systems, CTAB molecules are free to adsorb efficiently at the air–water interface, reducing surface tension and enhancing foam lamella stability by forming a cohesive interfacial film. The plateau observed beyond 500–600 ppm is a classic sign of reaching the CMC. At this point, the interface is saturated with monomeric CTAB, and additional surfactant aggregates into micelles within the bulk solution instead of further contributing to interfacial activity. As a result, foam stabilization no longer improves with increasing concentration. This saturation behavior confirms that the CMC of CTAB in deionized water lies around 500 ppm, consistent with the surface tension data.

In contrast, for seawater (green lines), both half-life and total foam stability peak at much lower concentrations—437 seconds and 720 seconds at 200 ppm, respectively—before declining steadily at higher concentrations. This starkly different behavior is attributed to the presence of dissolved salts (e.g., Na^+ , Cl^-), which screen the electrostatic repulsion between the cationic CTAB head groups. This screening compresses the electrical double layer, reduces molecular packing efficiency at the interface, and leads to early micellization. Consequently, CTAB's CMC in seawater shifts down to around 200 ppm. Additionally, salt-induced interactions can promote premature aggregation or the formation of CTAB–ion complexes, reducing the number of free surfactant molecules available for interfacial adsorption. This explains the decline in foam stability at higher concentrations in seawater. The surfactant molecules, instead of organizing at the interface, either remain inactive in bulk micelles or interact with counter-ions, weakening their surface activity.

From a comparative perspective, foam stability in deionized water is significantly superior to that in seawater. The maximum half-life in deionized water (~1140 seconds) is more than 2.5 times greater than that in seawater (~437 seconds), and the total foam stability (~2578 seconds) is over 3.5 times higher than the seawater maximum (~720 seconds). These differences underscore the negative impact of salinity on the performance of ionic surfactants like CTAB in foam-based EOR

systems. In summary, CTAB performs optimally in deionized water where it reaches its CMC around 500 ppm, resulting in stable foam films. In seawater, however, CTAB's effectiveness is greatly reduced due to ionic interactions and lower CMC (~200 ppm), which hinder interfacial adsorption and accelerate micelle formation, ultimately leading to a decrease in foam lifetime and stability at higher concentrations.

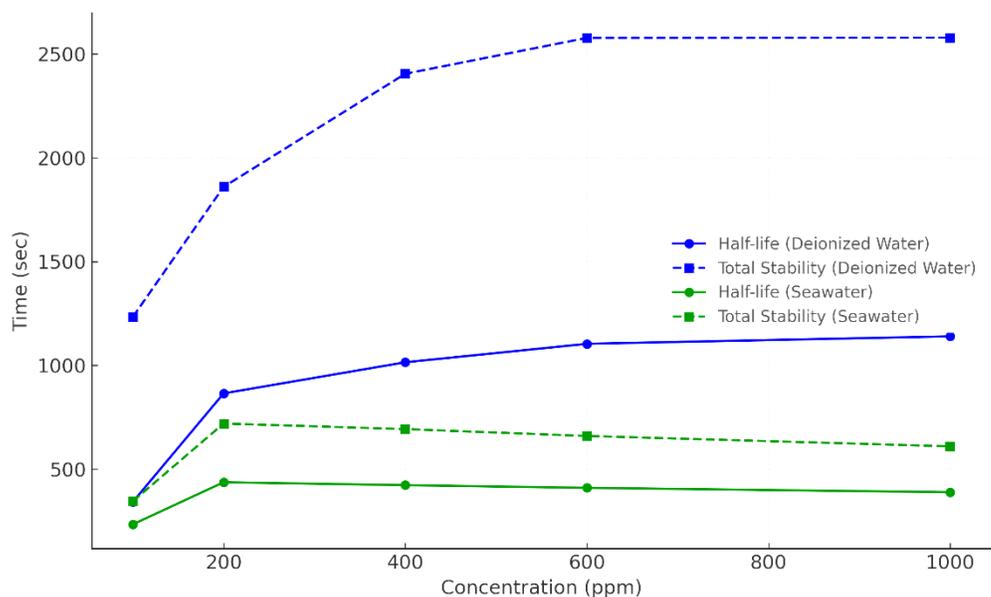


Fig. S4. Foam stability in deionized water and seawater as a function of CTAB concentration: comparison of foam half-life and total foam stability. The same color is used for each salinity condition (blue for deionized water, green for seawater), while different markers represent half-life (●, solid line) and total

As can be seen in Fig. S5, the half-life increases from approximately 9000 s at 1000 ppm to over 14,500 s at 3000 ppm, and total foam stability increases from ~20,500 s to ~23,800 s over the same range. This trend suggests that SDS is highly effective in deionized water for stabilizing foam. The foam performance improvements occur beyond the critical micelle concentration (CMC), which, based on surface tension measurements, is approximately 2000 ppm. As the SDS concentration exceeds the CMC, micelle formation begins, and the surfactant molecules saturate the air-water interface. Despite being beyond the CMC, continued increases in SDS concentration maintain or slightly enhance foam stability, likely due to improved packing at the interface and increased film thickness, resulting in better drainage resistance.

In contrast, SDS performance in seawater (gray lines) is significantly reduced. The foam half-life (solid gray line) peaks at around 1500 ppm (≈ 1550 s) and declines slightly at higher concentrations. Similarly, total foam stability (dashed gray line) shows a maximum near 2000 ppm (≈ 4600 s), followed by a minor decline. This behavior indicates that SDS reaches its optimal effectiveness around 1500–2000 ppm in seawater, likely due to salt-induced micelle formation and electrostatic screening, which reduce SDS's interfacial activity. The presence of divalent ions such as Mg^{2+} and Ca^{2+} can also lead to charge neutralization or precipitation of SDS, further decreasing foam stability.

These results demonstrate that while SDS is a strong foam stabilizer in deionized water, its performance is hindered in saline environments. The reduced effectiveness in seawater is attributed to electrostatic interactions between sulfate head groups and salt ions, which disrupt surfactant alignment and micelle integrity. SDS's anionic nature, which promotes strong electrostatic repulsion between micelles in pure water, is compromised in seawater due to ionic shielding. Overall, SDS outperforms CTAB in deionized water, exhibiting far greater half-life and total foam stability. However, in seawater, both surfactants experience diminished performance, with SDS retaining a slight advantage due to better resistance to salt interference.

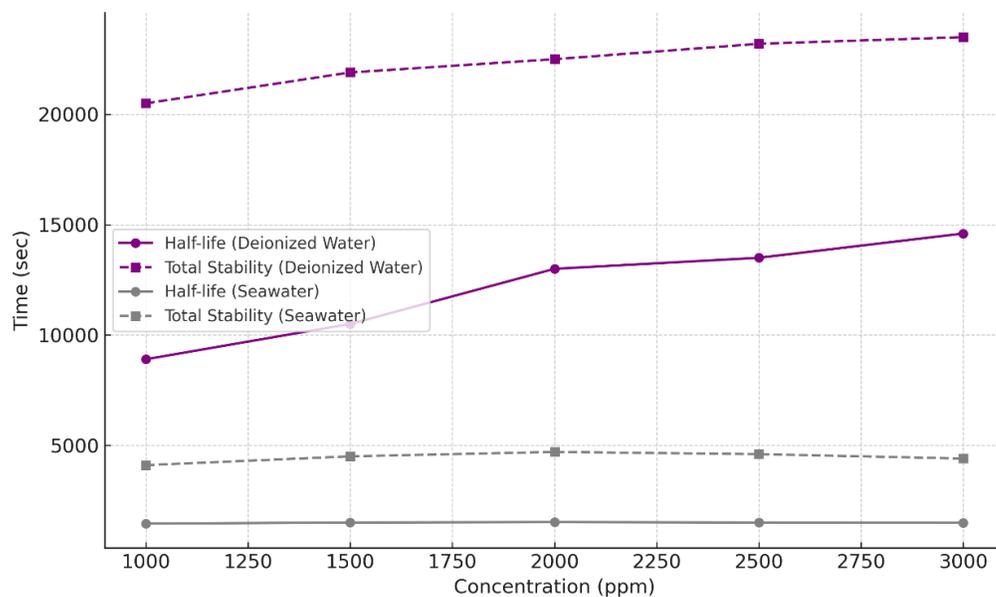


Fig. S5. Foam stability in deionized water and seawater with increasing SDS concentrations. Same color is used for the same salinity (purple for deionized water, gray for seawater), while different line styles and markers distinguish half-life (solid lines with circles) and total foam stability (dashed lines with squares).

Fig. S6 illustrates the effect of seawater dilution on foam half-life and total foam stability using optimal CTAB concentration (500 ppm).

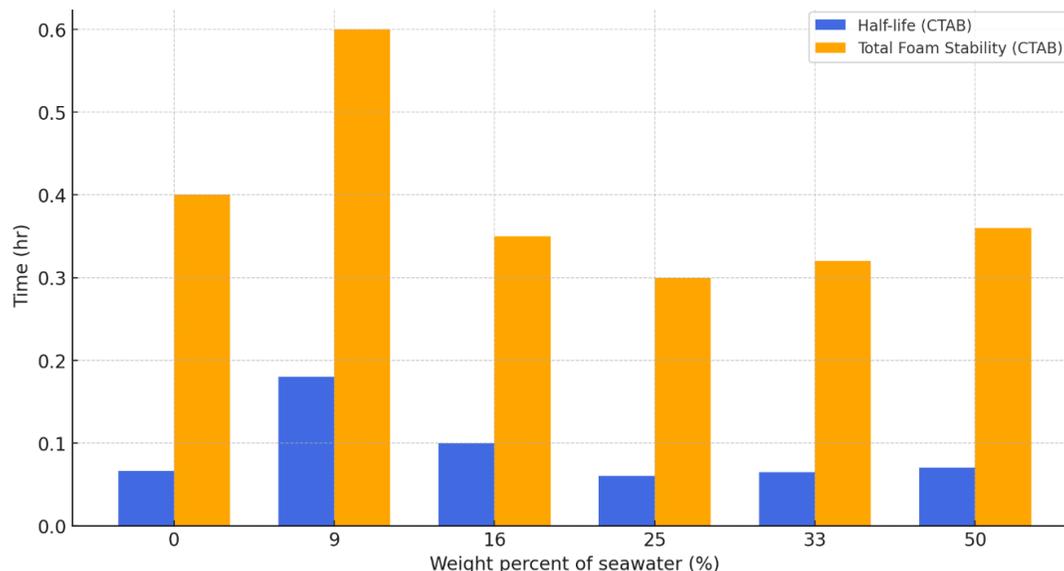


Fig. S6. Effect of seawater dilution on foam half-life and total foam stability using optimal CTAB concentration (500 ppm). Seawater was diluted with deionized water to various weight percentages (0%, 9%, 16%, 25%, 33%, and 50%).

As can be seen in Fig. S6, in the intermediate seawater concentrations (33%, 25%, 16%), foam stability remains relatively low and does not vary significantly. This plateau suggests that beyond a critical ionic strength threshold, additional ions do not further disrupt surfactant function—possibly due to saturation of surface interaction sites or limited further mobility of CTAB molecules. However, at 9% seawater, a striking recovery in foam stability is observed: the half-life increases to 0.18 hours (~11 minutes) and total foam stability reaches a maximum of 0.6 hours (36 minutes). This unexpected enhancement may arise from moderate ionic strength improving CTAB adsorption kinetics without inducing excessive charge screening. At low salt concentrations, electrostatic interactions may be tuned just enough to allow better interfacial packing, enhanced film elasticity, and reduced liquid drainage—all contributing to prolonged foam life. In summary, CTAB exhibits its highest foam-stabilizing effectiveness in deionized water due to the absence of salts. Seawater salts reduce its efficiency through electrostatic screening and micelle aggregation effects. Nevertheless, mild salinity (e.g., 9% seawater) appears to introduce a

synergistic effect where limited ionic presence facilitates better CTAB arrangement and stronger foam structure. These results underscore the delicate balance between surfactant concentration and ionic strength for optimal foam performance in saline environments.

Fig. S7 illustrates the effect of seawater dilution on foam half-life and total foam stability using the optimal SDS concentration (3000 ppm). Seawater was diluted with deionized water to prepare six brine solutions with different salinities (0%, 9%, 16%, 25%, 33%, and 50% seawater by weight).

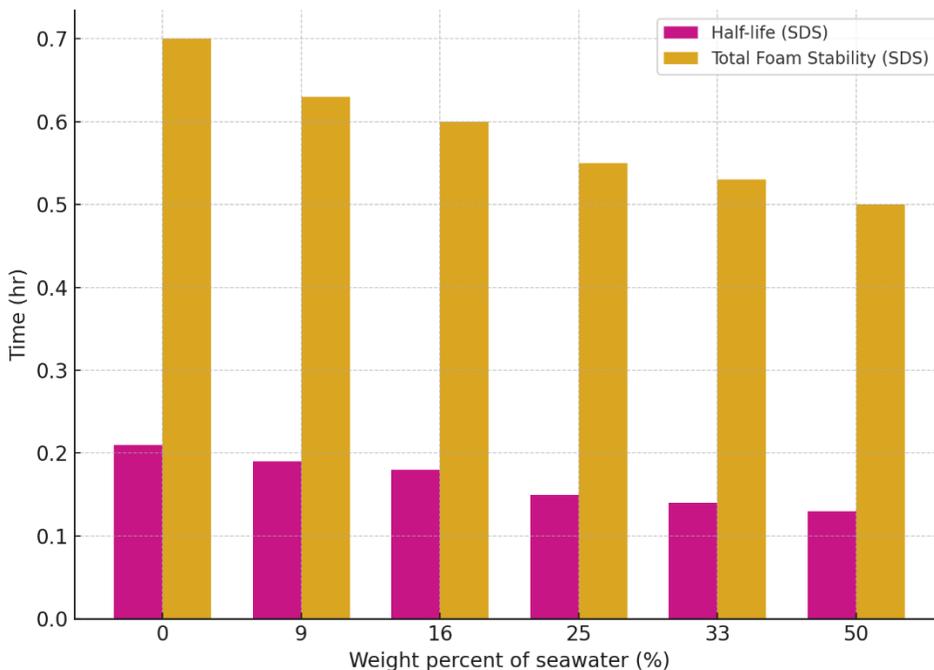


Fig. S7. Effect of seawater dilution on foam half-life and total foam stability at optimal SDS concentration (3000 ppm). Seawater was diluted with deionized water to various weight percentages (0%, 9%, 16%, 25%, 33%, and 50%).

As shown in the Fig. S7, both half-life and total foam stability decline progressively as seawater concentration increases. The foam half-life drops from approximately 0.21 hours (756 seconds) in deionized water to around 0.13 hours (468 seconds) at 50% seawater. Similarly, total foam stability decreases from 0.7 hours (2520 seconds) to 0.5 hours (1800 seconds) over the same range. This trend confirms that the presence of salts in seawater negatively affects the foam stabilization ability of SDS. The decrease in foam stability with increasing salinity can be attributed to electrostatic interactions between SDS molecules and salt ions. SDS is an anionic surfactant with negatively charged sulfate head groups, which rely on strong electrostatic repulsion to maintain micelle structure and stabilize the foam film. However, cations present in seawater (e.g., Na^+ , Ca^{2+} , Mg^{2+}) can screen these negative charges, weakening the repulsion between SDS molecules. This leads to decreased micelle stability, faster bubble coalescence, and ultimately

shorter foam life. Additionally, the competitive adsorption of salt ions at the air–water interface may hinder the ability of SDS to fully occupy the interface, thereby reducing its efficiency in reducing surface tension. Unlike CTAB, SDS does not show a temporary recovery at moderate salinity levels; instead, the destabilizing effect of salts increases steadily with increasing ionic strength. These findings highlight the significant role of water salinity in determining the effectiveness of SDS as a foam stabilizer and suggest that SDS-based systems may require salt-resistant additives or surfactant combinations for use in saline reservoir conditions.

Fig. S8 illustrates the effects of different weight concentrations (1% to 10%) of three salts— Na_2SO_4 , CaCl_2 , and MgCl_2 —on foam half-life and total foam stability in the presence of CTAB (500 ppm). For Na_2SO_4 , a clear trend is observed: total foam stability (yellow bars) increases with salt concentration, peaking at 3% with a maximum value of 0.65 hours. Foam half-life (blue bars) also shows a slight increase from 0.065 to 0.072 hours within the 1% to 3% range. This suggests that at moderate ionic strength, Na^+ ions can enhance foam stability by screening repulsive electrostatic forces just enough to promote surfactant adsorption at the interface, without inducing premature micelle formation or precipitation. Beyond 3%, a decrease in both total stability and half-life occurs, indicating that excessive ionic strength suppresses interfacial performance, likely due to compression of the electrical double layer and increased surfactant aggregation.

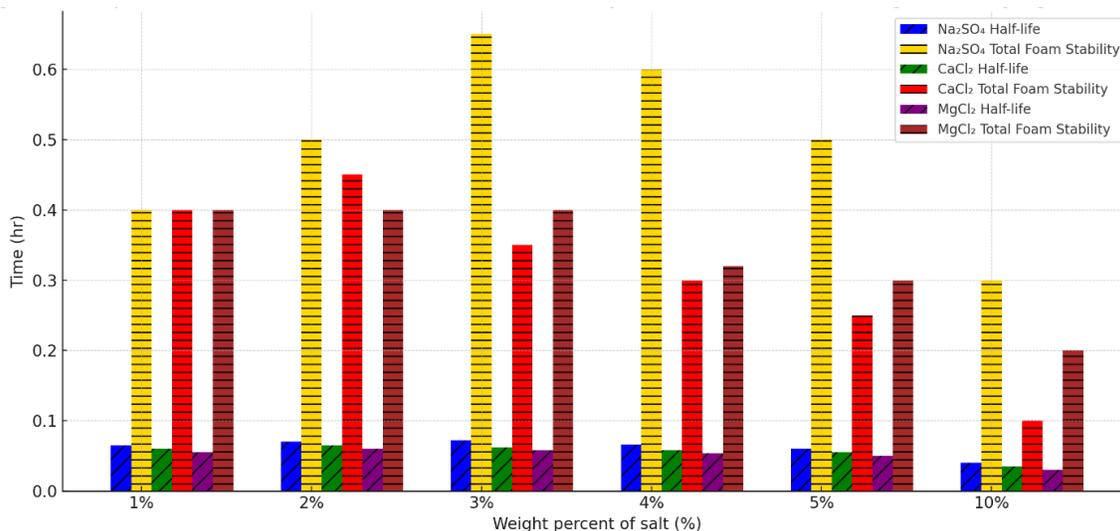


Fig. S8. Comparison of foam half-life and total foam stability for Na_2SO_4 , CaCl_2 , and MgCl_2 at varying concentrations (1%, 2%, 3%, 4%, 5%, and 10%) in the presence of optimal CTAB concentration (500 ppm). Bars with diagonal hatching represent half-life values, while horizontally hatched bars indicate total foam stability

In contrast, CaCl_2 (red and green bars) exhibits a steeper decline in foam performance after 2% concentration. Foam half-life remains low across all concentrations (~ 0.06 hours), while total foam stability peaks at 2% (0.45 hours) and then rapidly drops to just 0.1 hours at 10%. This reflects the stronger electrostatic interactions of divalent Ca^{2+} ions, which more effectively neutralize the positively charged head groups of CTAB. This leads to coalescence of surfactant

molecules, destabilization of the foam film, and shorter foam lifetimes. MgCl_2 (brown and purple bars) behaves similarly to CaCl_2 but with a slightly more gradual decrease in foam performance. Total foam stability is relatively constant (0.4 hours) up to 3% and then slowly declines to 0.2 hours at 10%. Foam half-life also shows a minor decline from 0.055 to 0.03 hours across the same range. The stronger hydration shell and smaller ionic radius of Mg^{2+} contribute to more localized but persistent interference with surfactant film structure. Compared to Ca^{2+} , Mg^{2+} causes more progressive destabilization due to stronger binding to the surfactant's polar groups.

As can be seen in Fig. S9, the x-axis represents either the weight percent (for heptol) or concentration in ppm (for n-heptane and toluene) of each compound, and the bars compare their performance on foam behavior.

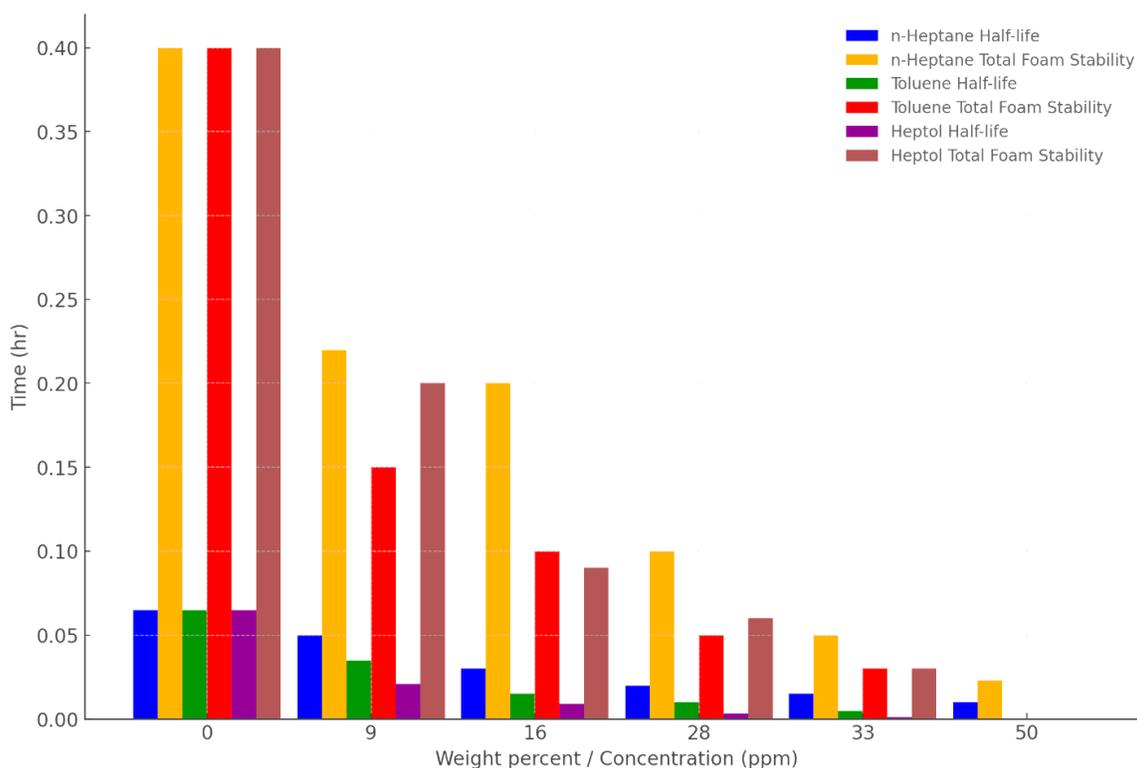


Fig. S9. Comparison of foam half-life and total foam stability in the presence of n-heptane, toluene, and heptol (1:1 volumetric mixture of n-heptane and toluene) at varying concentrations. Concentrations of n-heptane and toluene are given in ppm, while heptol is presented as weight percent in water.

In the presence of n-heptane, foam half-life (blue bars) is initially high at 0 ppm (0.065 hours or ~4 minutes), but steadily declines as concentration increases, reaching only 0.01 hours (36 seconds) at 50 ppm. Similarly, total foam stability (yellow bars) drops from 0.4 hours (~24 minutes) at 0 ppm to 0.023 hours (~1.4 minutes) at 50 ppm. This decline is attributed to the hydrophobic nature of n-heptane, a non-polar solvent that interferes with the surfactant-water interface. As its concentration rises, the disruption of hydrogen bonding and surfactant alignment at the air-water interface intensifies, leading to faster coalescence of bubbles and foam collapse.

Toluene (green and red bars), an aromatic solvent, exhibits even stronger destabilizing effects. Foam half-life falls from 0.065 hours at 0 ppm to 0.0 hours at 50 ppm, while total foam stability

declines from 0.4 hours to 0 hours. The aromaticity of toluene enables it to solubilize surfactant molecules more aggressively, disrupting micelle formation and undermining interfacial integrity. Its higher affinity for hydrophobic surfactant tails exacerbates destabilization, making the foam more prone to rapid decay.

Heptol, a 1:1 mixture of n-heptane and toluene, demonstrates the most severe reduction in foam stability. Half-life (purple bars) and total foam stability (brown bars) plummet faster and more drastically than for the individual components. At just 33% weight, foam stability becomes negligible. This compounded effect arises from the combined non-polarity of n-heptane and aromaticity of toluene. The synergy between the two enhances surfactant desorption from the interface, weakens cohesive film formation, and amplifies the collapse rate of foam.

In summary, n-heptane reduces foam stability steadily but more moderately. Toluene induces a sharper drop due to its aromaticity and interaction with surfactants. Heptol, combining both destabilizing mechanisms, causes the fastest and most complete foam collapse—even at low concentrations.

Figure S10 (See supplementary data) illustrates the impact of increasing concentrations of asphaltene in heptol on foam half-life (pink bars) and total foam stability (gray bars). As the concentration of asphaltene increases, there is a sharp decline in both foam half-life and total foam stability.

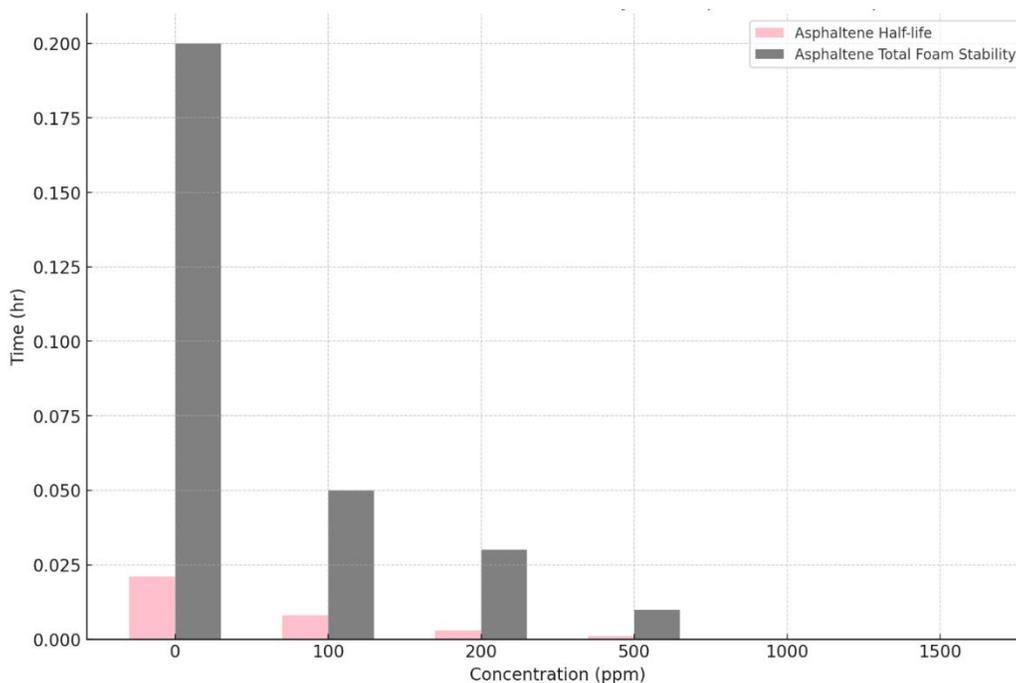


Fig. S10. Foam half-life and total foam stability for asphaltene in heptol at varying concentrations

At 0 ppm concentration the foam half-life is at its maximum, approximately 0.021 hours (~1.26 minutes) and the total foam stability is around 0.2 hours (~12 minutes), the highest among all concentrations. With no asphaltene present, the foam structure remains stable for a longer period, as there are no destabilizing particles to interact with the surfactant film. At 100 ppm concentration, there is a noticeable decline in half-life to 0.008 hours (~30 seconds). The total foam stability also decreases significantly to 0.05 hours (~3 minutes). The introduction of asphaltene particles begins to disrupt the foam stability. Asphaltene is known to aggregate and create insoluble particles that weaken the surfactant film, leading to faster foam collapse. At 200 ppm, the half-life further decreases to 0.003 hours (~10.8 seconds) and the foam stability reduces to 0.03 hours (~1.8 minutes). With higher concentrations of asphaltene, there is more surface disruption as the particles aggregate more effectively, reducing the ability of the foam to remain stable. At the concentration of 500 ppm, asphaltene is causing severe destabilization, likely due to a higher concentration of

insoluble particles that interrupt the surfactant network and accelerate foam collapse. At 1000 ppm and 1500 ppm concentrations, both the half-life and total foam stability are zero. There is no foam stability at these concentrations. At extremely high concentrations of asphaltene, the particles completely overwhelm the surfactant film. The foam cannot form or stabilize, leading to immediate collapse upon generation. Asphaltenes are large, complex molecules that tend to aggregate in non-polar solvents like heptol. These aggregates act as insoluble particles that interfere with the surfactant's ability to stabilize foam. The higher the concentration of asphaltene, the larger the number of aggregates disrupting the foam, leading to faster collapse. Asphaltene molecules are highly hydrophobic, and their presence in a foam solution leads to poor interaction with the water phase. This results in the formation of unstable films, as the hydrophobic asphaltene particles weaken the water-surfactant-air interface. The role of surfactants in foam stability is to reduce surface tension at the air-water interface. Asphaltene aggregates likely disrupt the surfactant's ability to do so, causing localized increases in surface tension, which accelerates foam collapse.

Fig. S11 (See supplementary data) presents the effect of CO₂ injection on foam stability for two surfactants, CTAB and SDS, in both distilled water (solid lines) and seawater (dashed lines). The figure compares foam half-life and total foam stability over a range of surfactant concentrations. In distilled water, the half-life of CTAB (blue solid line) shows a steady increase from 288 to 520 seconds as concentration increases from 100 to 1000 ppm, indicating enhanced foam stability. The total foam stability (red solid line) follows the same trend, rising to a maximum of 768 seconds at 1000 ppm. This behavior suggests that CTAB forms a stable interfacial film under CO₂, though its performance plateaus beyond 500 ppm.

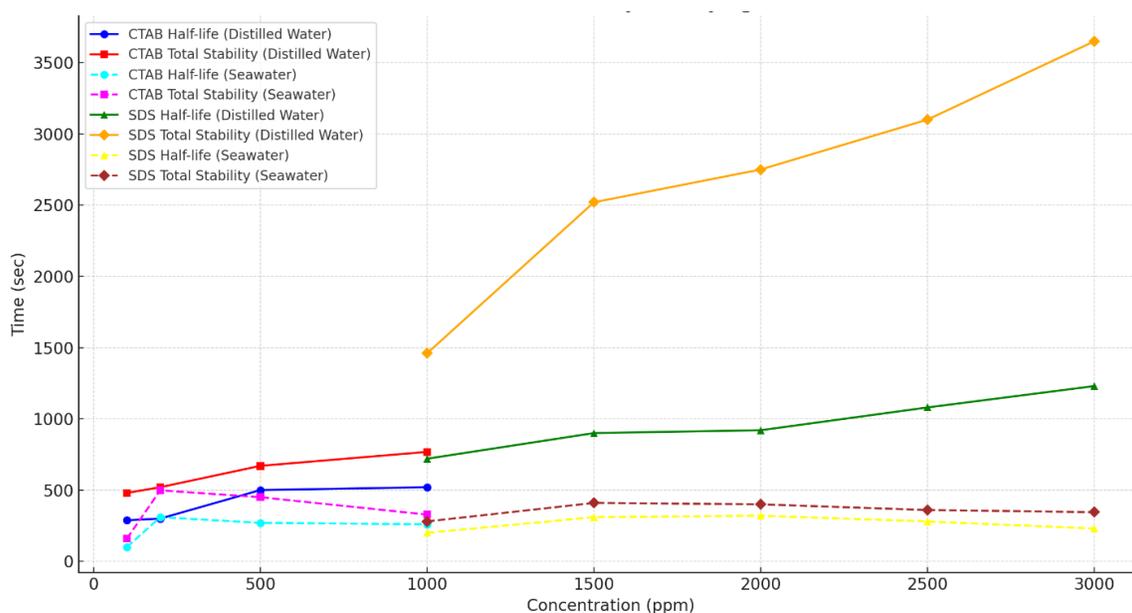


Fig. S11. Foam stability of CTAB (100–1000 ppm) and SDS (1000–3000 ppm) in distilled water (solid lines) and seawater (dashed lines) under CO₂ injection.

For SDS in distilled water (green and orange solid lines), foam half-life increases consistently from 720 to 1230 seconds, and total stability shows a sharp rise from 1460 to 3650 seconds as SDS concentration increases from 1000 to 3000 ppm. This indicates that SDS is significantly more efficient than CTAB at stabilizing foam under CO₂ injection. The anionic head of SDS provides stronger electrostatic repulsion, resulting in thicker lamellae and enhanced foam resistance.

In seawater, however, foam stability is noticeably reduced. CTAB's half-life (cyan dashed line) initially increases from 100 to 310 seconds at 200 ppm but then declines. Total stability (purple dashed line) follows a similar trend, peaking at 498 seconds and decreasing afterward. The presence of divalent ions (Mg²⁺, Ca²⁺) in seawater reduces electrostatic repulsion and interferes

with CTAB's organization at the interface, destabilizing the foam. For SDS in seawater, half-life (yellow dashed line) peaks at 320 seconds at 2000 ppm but then declines. Similarly, total stability (brown dashed line) increases until 1500 ppm (410 seconds), then decreases. Though affected by seawater, SDS still performs better than CTAB. The decline at higher concentrations is attributed to ionic screening by divalent ions, which reduces the effectiveness of SDS's electrostatic stabilization.

Overall, SDS outperforms CTAB in both media, especially under CO₂ injection. Foam structures stabilized by SDS are more resilient due to its anionic nature and stronger interfacial film formation. However, the presence of salts in seawater compromises the performance of both surfactants, more severely for CTAB, emphasizing the need to consider ionic strength and surfactant type in CO₂-based enhanced oil recovery applications.

The graph in Fig. S12 represents foam stability in the presence of different surfactants (CTAB and SDS), two types of water (distilled water and seawater), crude oil, and under CO₂ injection conditions. The data provides a comprehensive comparison of foam half-life and total foam stability across varying concentrations of the surfactants CTAB and SDS (ranging from 500 to 2000 ppm). This analysis highlights the differences in foam behavior as a function of surfactant type, salinity, and the presence of oil under CO₂ flow.

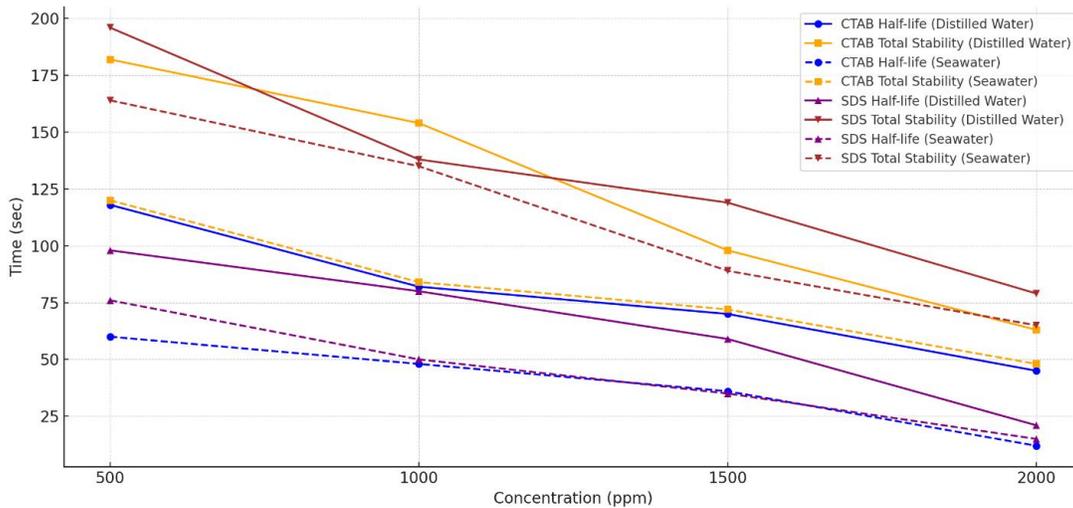


Fig. S12. Foam stability for CTAB and SDS surfactants at different concentrations (500, 1000, 1500, and 2000 ppm) in the presence of distilled water and seawater with oil under CO₂ injection: Comparison of half-life and total foam stability using solid lines for distilled water and dashed lines for seawater

Based on Fig. S12, the data reveal a consistent decline in foam stability for both surfactants as concentration increases, with the decline being more pronounced in seawater, and especially in the presence of oil. In the case of CTAB, foam stability in distilled water initially demonstrates acceptable performance, but both the half-life and total stability decline rapidly with increasing concentration. The decline at higher concentrations may stem from surfactant saturation at the oil–water–gas interface, leading to inefficient micelle formation and destabilization of foam films. Moreover, CO₂ injection accelerates foam collapse by permeating the lamellae (thin liquid films between bubbles), causing them to thin and rupture more quickly. When CTAB is used in seawater, foam stability is significantly lower across all concentrations. This cannot be fully attributed to salinity alone, as that factor has been discussed previously. Instead, the pronounced destabilization in this setup is better explained by the combined effect of oil and CO₂. The presence of crude oil

introduces a defoaming tendency, as oil tends to spread at the gas–liquid interface, displacing the surfactant film and creating rupture sites. Meanwhile, CO_2 contributes to destabilization not only by reducing interfacial tension but also by dissolving into the aqueous phase and lowering pH. This acidification alters CTAB's surface behavior, reducing its effectiveness in stabilizing the foam. In seawater, where multivalent ions such as Mg^{2+} and Ca^{2+} are present, the interaction between these ions and surfactant head groups further impairs the interfacial film. These competitive ionic interactions exacerbate the destabilizing effect of oil and CO_2 , leading to much faster foam collapse in seawater systems compared to distilled water.

SDS, on the other hand, exhibits better foam stability than CTAB in both distilled water and seawater. In distilled water, SDS maintains higher total stability and longer half-life over the entire concentration range. Its anionic sulfate head group forms stronger electrostatic repulsions in the foam film, which helps maintain the film thickness and integrity even in the presence of CO_2 and oil. However, even SDS is not immune to destabilization; its foam stability also declines with increasing concentration. The most plausible explanation is that CO_2 diffuses into the foam films, and the acidic environment alters SDS micelle behavior, especially near its critical micelle concentration (CMC), reducing its ability to form strong, cohesive films. In seawater, SDS outperforms CTAB but still shows diminished foam performance relative to distilled water. Interestingly, while CO_2 has lower solubility in seawater due to the ionic strength and presence of competing dissolved species, the effect of CO_2 on foam destabilization is paradoxically more significant in seawater, not due to higher dissolution, but because of interactions among ions, surfactants, oil, and pH-sensitive CO_2 species. For instance, divalent ions like Mg^{2+} and Ca^{2+} can screen the negative charges on SDS molecules, weakening the electrostatic repulsion and accelerating bubble coalescence. Additionally, oil again plays a destabilizing role by penetrating the foam structure and thinning the film.

Fig. S13 illustrates how varying the proportion of distilled water (from 1% to 20%) in a seawater-based system affects foam half-life and total foam stability. The results demonstrate a clear enhancement in foam stability as the percentage of distilled water increases. Both half-life and total stability increase gradually at low concentrations (1–5%), but a marked rise is observed between 10% and 20%, indicating a nonlinear or exponential improvement in foam behavior.

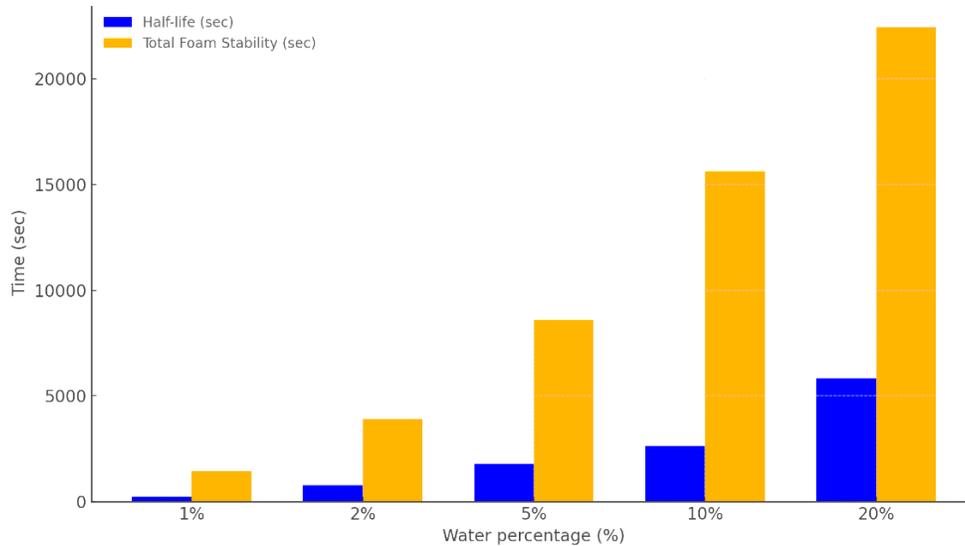


Fig. S13. Comparison of foam half-life and total foam stability at different distilled water percentages (1%–20%) mixed with seawater during the foam generation process.

This trend can be explained by the progressive reduction in ionic strength as more distilled water is introduced into the system. At low distilled water contents (1–2%), the high concentration of dissolved salts (e.g., NaCl, $MgCl_2$, $CaCl_2$) from seawater weakens the foam film, leading to shorter half-life and rapid foam collapse. However, as the percentage of distilled water increases, the destabilizing ionic interactions diminish, and surfactant molecules are better able to organize at the gas-liquid interface, forming more robust and longer-lasting foams.

Fig. S14 presents a comparative evaluation of foam stability, both half-life and total stability, for lignin-based systems under air injection across a concentration range of 100, 500, 1000, and 2000 ppm. The systems examined include lignin in distilled water, lignin + CTAB (at optimized concentration of 500 ppm), and combinations of seawater and heptol.

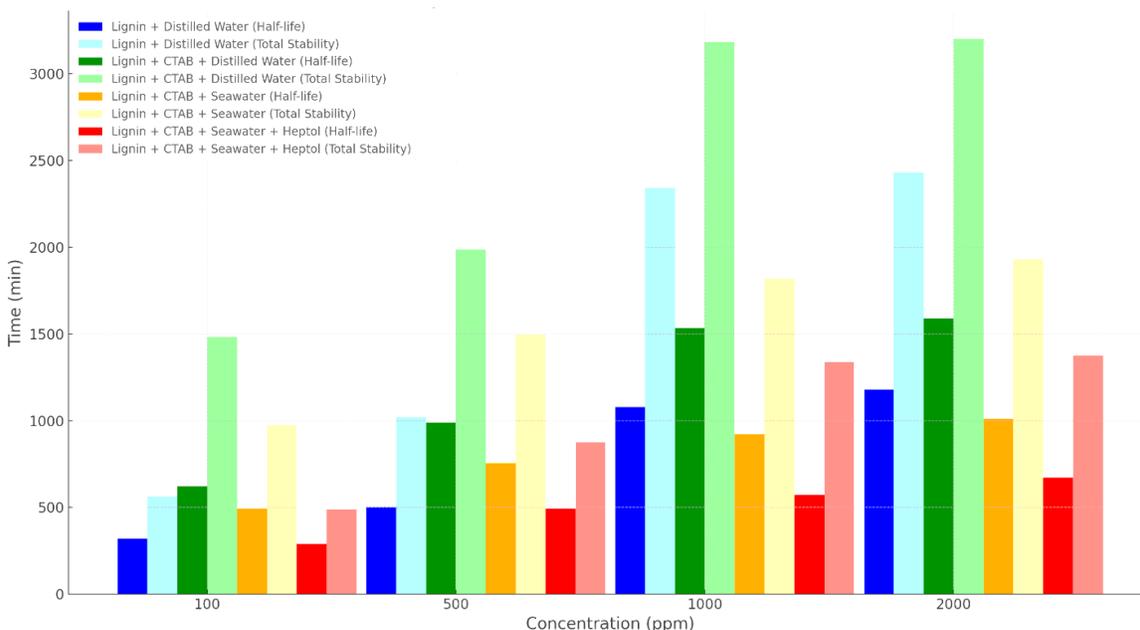


Fig. S14. Comparative analysis of foam stability (half-life and total stability) at various lignin concentrations (100–2000 ppm) in systems containing distilled water, seawater, heptol, and CTAB (500 ppm) under air injection.

The results indicate that lignin in distilled water alone shows a steady increase in both foam half-life and total foam stability with increasing lignin concentration. This is attributed to lignin's surface-active behavior, which enhances film strength at the air–liquid interface and supports foam formation. Upon the addition of CTAB at 500 ppm, a significant increase in foam stability is observed, especially in distilled water. CTAB, a cationic surfactant, complements lignin by reducing surface tension and reinforcing the foam film. The synergistic effect is evident across all lignin concentrations, with the most pronounced enhancement seen at 1000 and 2000 ppm, where both foam half-life and total stability exceed 3000 minutes in some cases. In seawater-based systems, foam stability is lower than in distilled water due to the presence of salts that interfere with surfactant assembly, as previously explained. Nevertheless, the addition of CTAB (500 ppm)

improves foam properties compared to lignin alone in seawater, indicating that even under ionic conditions, surfactant-lignin interactions remain partially effective.

When heptol is introduced into the system (lignin + CTAB + seawater + heptol), a notable decline in foam half-life and stability is observed. This is due to oil spreading at the gas-liquid interface, displacing surfactant-lignin structures and leading to rapid foam collapse. The destabilizing effect of heptol overrides the benefits of surfactant addition, showing the sensitivity of foam systems to hydrocarbon phases. Overall, the best foam performance is achieved with lignin + CTAB + distilled water, confirming the effectiveness of lignin-CTAB synergy in non-ionic environments. Foam performance follows this order: lignin + CTAB + distilled water > lignin + distilled water > lignin + CTAB + seawater > lignin + CTAB + seawater + heptol.

Fig. S15 (See supplementary data) compares foam stability in terms of half-life and total stability for different concentrations (100, 500, 1000, and 2000 ppm) of lignin + SDS in distilled water, seawater, and seawater mixed with heptol in the presence of air. The foam stability was measured under different conditions, including the presence of distilled water, seawater, and a mixture of seawater and heptol. As the concentration increases, the foam's half-life of lignin + SDS + distilled water (blue bars) increases consistently. At 2000 ppm, the half-life reaches around 504 minutes, indicating that lignin combined with SDS in distilled water provides a long-lasting foam structure. The total stability (light blue bars) follows the same trend, increasing with higher concentrations, with a maximum of about 1072 minutes at 2000 ppm. This demonstrates the effectiveness of distilled water in maintaining foam stability over time.

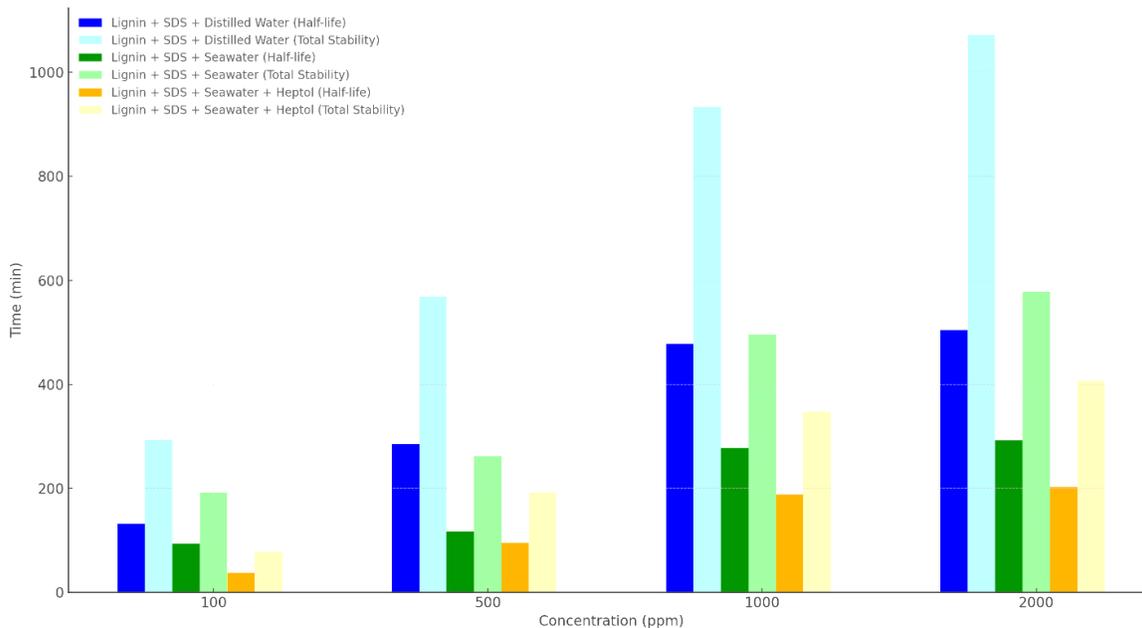


Fig. S15. Comparative analysis of foam stability (half-life and total stability) at various lignin concentrations (100–2000 ppm) in the presence of SDS in systems containing distilled water, seawater, and seawater with heptol under air injection.

In seawater, the foam's half-life (green bars) is lower than in distilled water. The maximum half-life at 2000 ppm is around 292 minutes, which is significantly lower than in distilled water. The total foam stability in seawater (light green bars) is also lower than in distilled water, reaching about 578 minutes at 2000 ppm. Seawater negatively impacts foam stability due to the presence of dissolved salts such as NaCl, $MgCl_2$, $CaCl_2$. These ions interfere with the surfactant's ability to

stabilize the foam, resulting in shorter half-life and lower overall stability. The addition of heptol, a hydrocarbon oil, significantly reduces the foam's half-life (orange bars). At 2000 ppm, the half-life drops to around 202 minutes, the lowest observed among all conditions. Similarly, the total foam stability (light orange bars) is also reduced, reaching about 407 minutes at 2000 ppm, which is considerably lower than in distilled water or seawater alone. The presence of heptol, a hydrophobic compound, greatly diminishes foam stability. Heptol disrupts the foam structure by breaking the film between bubbles, causing the foam to collapse more quickly. This shows that oil contamination in seawater can severely affect foam performance.

Therefore, the foam stability in distilled water is superior to seawater, as shown by both the half-life and total stability values. This is due to the lack of dissolved salts and impurities in distilled water, which allows the surfactant molecules to effectively stabilize the foam. In all cases, increasing the concentration of lignin + SDS improves both the half-life and total stability of the foam. However, the impact of the medium (distilled water, seawater, or seawater + heptol) plays a crucial role in determining the foam's overall performance. Overall, lignin + SDS in distilled water shows the best performance in terms of both half-life and total foam stability.

Fig. S16 represents the comparative analysis of foam stability (both half-life and total stability) across different lignin systems with distilled water, seawater, CTAB surfactant, and heptol oil at various concentrations under CO_2 injection. CO_2 affects the foam stability differently compared to air due to its solubility in water, which lowers the pH and alters the polymer's properties.

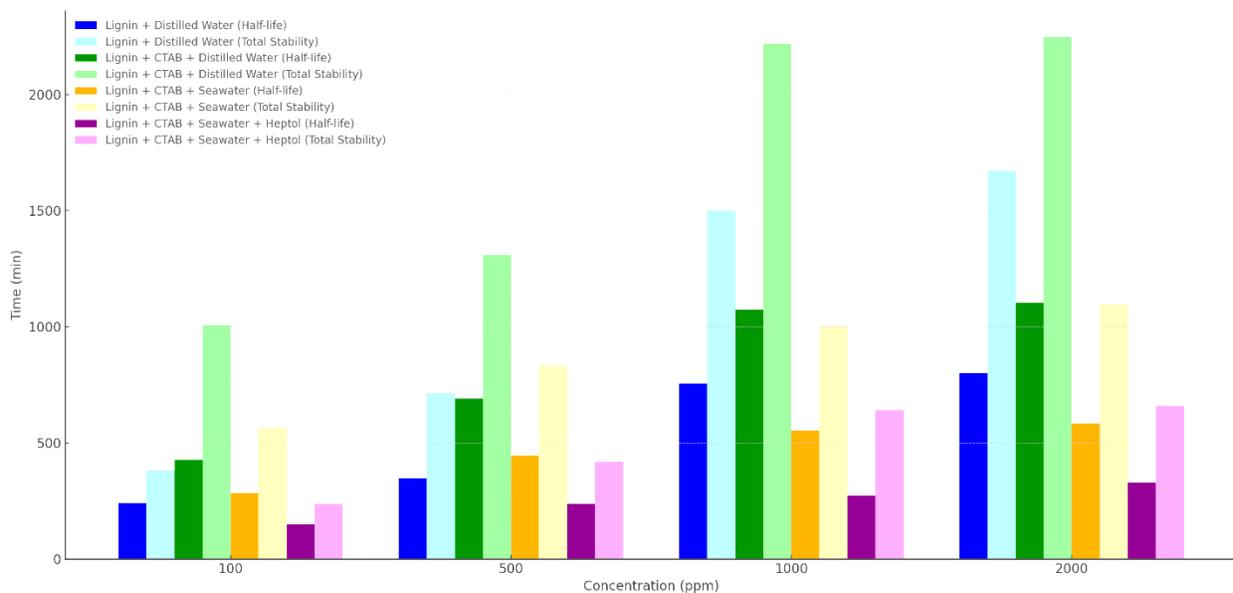


Fig. S16. Comparative evaluation of foam half-life and total foam stability for lignin systems under CO_2 injection, incorporating various concentrations (100, 500, 1000, and 2000 ppm) in the presence of distilled water, seawater, CTAB (at optimal concentration of 500 ppm), and heptol.

The foam stability, both half-life and total stability in the presence of lignin and distilled water (blue and light blue bars), generally increases as the concentration of lignin rises from 100 to 2000 ppm. Half-life starts at 241 minutes for 100 ppm and rises to 801 minutes at 2000 ppm. Total stability follows a similar trend, starting at 383 minutes at 100 ppm and increasing to 1673 minutes at 2000 ppm. The steady increase indicates that in the absence of additional surfactants or seawater, lignin in distilled water behaves as a foaming agent, enhancing foam stability as its concentration increases. The combination of CTAB surfactant with lignin in distilled water produces a significant increase in foam stability compared to lignin alone. Half-life (green bar) starts at 427 minutes at 100 ppm and rises to 1102 minutes at 2000 ppm, while total stability (light green bar) rises from 1005 minutes to 2248 minutes. This considerable improvement is attributed to the strong foaming properties of CTAB, which synergizes with lignin to extend both the half-life and overall foam

stability. The foam remains stable for longer periods at higher concentrations of CTAB. The introduction of seawater decreases foam stability when compared to distilled water with the same lignin and CTAB concentrations. Half-life (orange bar) begins at 285 minutes at 100 ppm and increases to 585 minutes at 2000 ppm. Total stability (light orange bar) reaches its maximum at 1098 minutes for 2000 ppm, which is lower than the corresponding distilled water system. The presence of seawater likely interferes with foam formation due to its ionic content (salt), reducing the overall foam stability. However, the presence of CTAB still helps stabilize the foam, albeit less effectively than in distilled water. Last but not least, The addition of heptol further diminishes foam stability in comparison to the other systems, both in terms of half-life and total stability. Half-life (purple bar) ranges from 148 minutes at 100 ppm to 330 minutes at 2000 ppm, while total stability (light purple bar) shows a maximum of 660 minutes at 2000 ppm. Heptol, as an oil, likely disrupts the foam structure and accelerates foam collapse, even in the presence of lignin and CTAB. This results in lower foam stability, as observed in the reduced half-life and total stability compared to the other systems.

Thus, The combination of lignin + CTAB in distilled water demonstrates the best foam stability across all concentrations, indicating the synergy between the natural polymer lignin and the surfactant in a low-ionic environment. The introduction of seawater causes a noticeable decrease in foam stability, which is further exacerbated by the presence of heptol oil. The salt content in seawater likely disrupts the foam structure, while the oil phase destabilizes the foam further, leading to lower half-life and total stability.

Fig. S17 shows the foam stability using SDS surfactant instead of CTAB. This bar chart illustrates the foam stability (both half-life and total stability) for lignin mixed with SDS in three different environments: distilled water, seawater, and seawater with heptol, under CO₂ injection. The analysis is conducted at varying concentrations (100, 500, 1000, and 2000 ppm), comparing the impact of each mixture on foam behavior. The trends are similar to those with CTAB, but the foam stability is generally lower when using SDS. This is due to the anionic nature of both SDS and lignin, leading to electrostatic repulsion between the two and reducing their ability to stabilize the foam. In contrast, CTAB, a cationic surfactant, interacts more effectively with the anionic lignin, resulting in better foam stability. The foam stability in terms of half-life increases with higher concentrations of lignin + SDS in distilled water, with the half-life rising from 86 min (100 ppm) to 329 min (2000 ppm). The total foam stability similarly improves significantly, peaking at 681 min for 2000 ppm. This trend indicates that SDS in distilled water promotes strong foam stability due to effective surfactant action without additional complex elements, such as seawater salts or oil. Foam stability in seawater is generally lower than in distilled water, with half-life ranging from 51 min (100 ppm) to 172 min (2000 ppm). This reduction is due to the presence of salts in seawater, which hinder the foaming capacity and foam lifetime, weakening the effect of SDS. The total stability follows a similar trend as the half-life but is considerably reduced when compared to distilled water. The highest total stability in seawater is 306 min at 2000 ppm. The decrease is attributed to the negative interaction between SDS and seawater salts, which reduce the effectiveness of the foam.

The foam stability further decreases in the presence of both seawater and heptol. The half-life ranges from 17 min (100 ppm) to 91 min (2000 ppm), indicating that the presence of heptol (a non-foaming oil) significantly diminishes foam stability. Heptol reduces the foam-forming ability of SDS by destabilizing the surfactant films. The total stability shows a steep reduction, reaching only 182 min at the highest concentration of 2000 ppm. The oil phase (heptol) interferes with foam stability, reducing both the foam lifetime and overall stability due to the increased drainage and faster foam collapse. For all systems, increasing the concentration from 100 ppm to 2000 ppm improves foam stability. However, the positive effect of higher concentrations is most noticeable in distilled water, with reduced benefits in seawater and even more so when heptol is present.

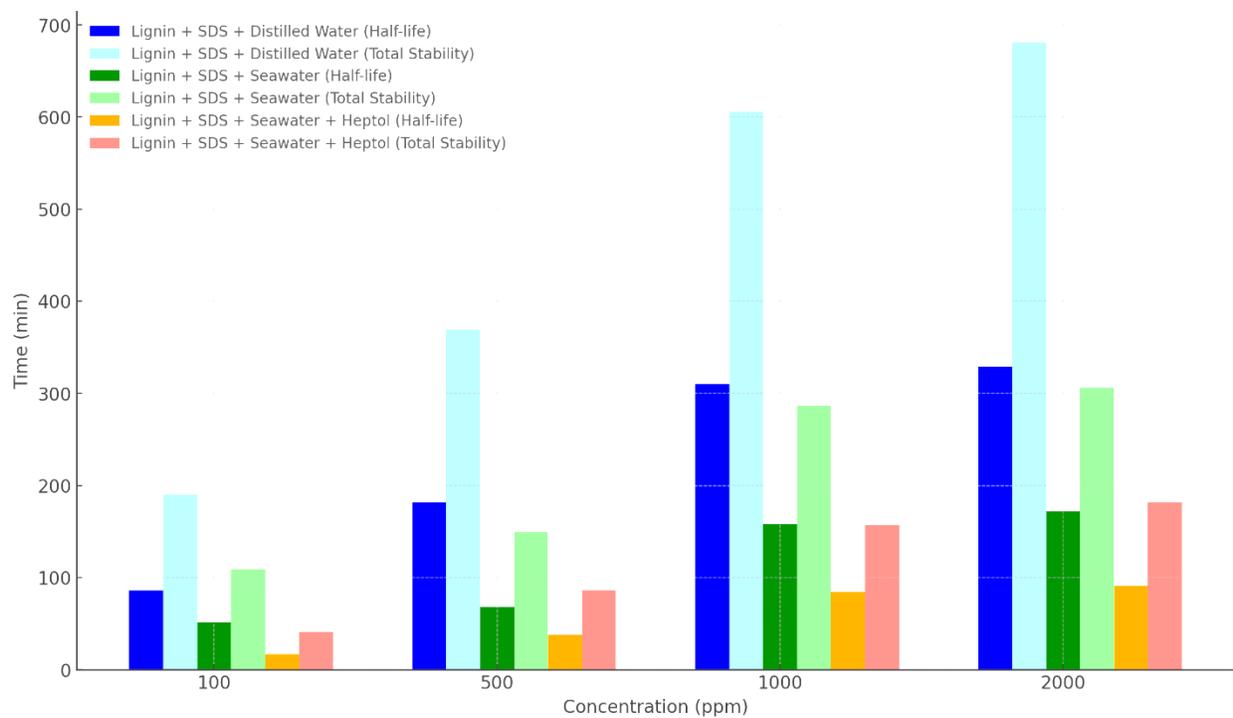


Fig. S17. Comparative evaluation of foam half-life and total foam stability for lignin systems under CO₂ injection, incorporating various concentrations (100, 500, 1000, and 2000 ppm) in the presence of distilled water, seawater, and seawater with heptol, using SDS surfactant (at optimal concentration)

Table S1 summarizes the comparative foam performance of lignin-based systems under both air and CO₂ injection at different lignin concentrations (100–2000 ppm). The table clearly illustrates the influence of gas type and fluid environment—including distilled water, seawater, CTAB, and heptol—on foam half-life and total stability. It is evident that air injection generally results in longer half-life and total stability values compared to CO₂ injection, particularly in distilled water environments. Furthermore, systems containing CTAB consistently exhibit improved foam performance, while the presence of heptol leads to noticeable reductions in stability.

Table S1 Comparison of foam half-life and total foam stability for lignin-based systems under air and CO₂ injection at various lignin concentrations (100–2000 ppm). The systems include different fluid environments: distilled water (DW), seawater (SW), and mixtures containing CTAB (at optimal concentration) and heptol.

Type of gas	Measurement	Half-life (min)	Half-life (min)	Half-life (min)	Half-life (min)	Total stability (min)	Total stability (min)	Total stability (min)	Total stability (min)
	Lignin Concentration (ppm)	100	500	1000	2000	100	500	1000	2000
Air	Lignin + Distilled water	321	500	1078	1180	563	1020	2342	2430
	Lignin + CTAB + Distilled water	620	988	1532	1588	1482	1984	3183	3202
	Lignin + CTAB + Seawater	493	755	923	1010	974	1498	1818	1932
	Lignin + CTAB + Seawater + Heptol	289	492	573	672	487	874	1337	1375
CO ₂	Lignin + Distilled water	241	348	754	801	383	714	1502	1673
	Lignin + CTAB + Distilled water	427	691	1072	1102	1005	1308	2218	2248
	Lignin + CTAB + Seawater	285	447	553	585	564	835	1004	1098
	Lignin + CTAB + Seawater + Heptol	148	238	273	330	237	419	642	660

Table S2 (See supplementary data) provides a comprehensive comparison of foam half-life and total foam stability for lignin-based systems using SDS as a surfactant under both air and CO₂ injection. The systems include distilled water (DW), seawater (SW), and seawater combined with heptol. Foam stability was evaluated across four lignin concentrations (100, 500, 1000, and 2000 ppm). From the table, it is evident that air-injected systems generally exhibit higher foam stability compared to CO₂-injected systems under similar conditions. In both gas environments, the presence of SDS significantly improves foam performance in distilled water, but its effectiveness decreases in saline conditions and is further reduced when heptol is present. As the lignin concentration increases, both half-life and total stability of foam improve, with the most stable foam observed in the SDS + DW system under air injection at 2000 ppm lignin. Conversely, the lowest foam stability occurs in CO₂ + SDS + SW + heptol systems, where the combined effects of salinity, oil, and CO₂-induced destabilization result in poor foam performance

Table S2 Comparison of foam half-life and total foam stability for lignin-based systems under air and CO₂ injection at various lignin concentrations (100–2000 ppm). The systems include different fluid environments: distilled water (DW), seawater (SW), and mixtures containing SDS (at optimal concentration) and heptol.

Type of gas	Measurement	Half-life (min)	Half-life (min)	Half-life (min)	Half-life (min)	Total stability (min)	Total stability (min)	Total stability (min)	Total stability (min)
	Lignin Concentration (ppm)	100	500	1000	2000	100	500	1000	2000
Air	Lignin + Distilled water	321	500	1078	1180	563	1020	2342	2430
	Lignin + SDS + Distilled water	132	285	478	504	293	568	933	1072
	Lignin + SDS + Seawater	93	117	278	292	192	262	496	578
	Lignin + SDS + Seawater + Heptol	38	95	188	202	78	191	348	407
CO ₂	Lignin + Distilled water	241	348	754	801	383	714	1502	1673
	Lignin + SDS + Distilled water	86	182	310	329	190	369	606	681

Lignin + SDS + Seawater	51	68	158	172	109	149	287	306
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Lignin + SDS + Seawater + Heptol	17	38	84	91	41	86	157	182
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