



EXPERIMENTAL INVESTIGATIONS OF SURFACTANT PRECIPITATION AND MITIGATION IN SALINE ENVIRONMENT

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Abstract— Surfactant precipitation in high-salinity conditions is a major challenge for applications such as enhanced oil recovery (EOR). This study experimentally examined the precipitation behaviour of the anionic surfactant sodium dodecyl sulphate (SDS) in aqueous solutions containing monovalent (Na^+) and divalent (Ca^{2+} , Mg^{2+}) ions and the potential application of an enzymatic (greenzyme) additive as a mitigation. The brines were prepared using single salts (NaCl , CaCl_2 , MgCl_2), binary mixtures ($\text{NaCl}+\text{CaCl}_2$, $\text{CaCl}_2+\text{MgCl}_2$, $\text{NaCl}+\text{MgCl}_2$), and a ternary mixture ($\text{NaCl}+\text{CaCl}_2+\text{MgCl}_2$) at varied concentrations (10%, 50%, 100%). Surfactant-salt mixtures were prepared by adding SDS at 0.5 and 1.0 wt.% to each brine, and precipitation was assessed visually and via electrical conductivity measurements. The key findings show that SDS remained soluble in low to moderate NaCl brine salinity but precipitated only at extreme salinity of 100% NaCl brine, whereas even low salinity of CaCl_2 caused rapid SDS precipitation in all cases, forming insoluble calcium-dodecyl sulphate. MgCl_2 however had minimal effect, with no visible precipitation under all conditions, reflecting the comparatively weaker binding of Mg^{2+} to SDS. In mixed-salt solutions, the presence of Ca^{2+} dominated and synergistically enhanced precipitation effects throughout. Addition of 1.0 wt.% greenzyme as a mitigation agent completely prevented SDS precipitation in all single, binary, and ternary salt solutions as indicated by restored conductivity levels and absence of visual precipitate. It however had little effect in Ca^{2+} rich solutions, but at higher concentration of 2.0 wt.%, greenzyme completely prevented SDS precipitation in all solutions. These results demonstrate that divalent ions, especially Ca^{2+} strongly influence SDS instability in brines, and greenzyme offers an effective, eco-friendly method to stabilize the surfactants in harsh environments. These findings have important implications for designing salt-tolerant surfactant formulations in EOR and industrial processes.

Keywords— Surfactant; Precipitation; Salinity; Greenzyme; Sodium Dodecyl Sulphate, Brine

I. INTRODUCTION

Surfactants are amphiphilic molecules that above their critical micelle concentration (CMC), self-assemble into micelles and dramatically reduce interfacial tension between immiscible liquids [1, 2]. This ability to reduce interfacial tension result in lowering of capillary forces and mobilisation of trapped oil makes surfactants invaluable in enhanced oil recovery (EOR) and other applications where fluids of different types must be emulsified or mobilised [3, 4]. In aqueous environments, the behaviour and solubility of anionic surfactants such as sodium dodecyl sulphate (SDS) are strongly influenced by dissolved salts [5, 6]. Monovalent salts like sodium chloride (NaCl) typically screen electrostatic repulsion between negatively charged headgroups, reducing the CMC and promoting micellization [6]. However, at very high NaCl concentrations a “salting-out” effect can occur due to competition for water and decreased solvent quality, reduce surfactant solubility, thereby leading to precipitation [7].

The impact of multivalent cations on anionic surfactants is much more severe. Divalent ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) can bind strongly to the anionic headgroups, neutralising charge and forming insoluble complexes (“soaps”) that precipitate [8, 9]. In particular, SDS readily reacts with Ca^{2+} to form calcium dodecyl sulphate, a solid that precipitates out of solution even at moderate salt concentrations [10]. This precipitation not only depletes the active surfactant but also can cause operational problems such as pore plugging and equipment fouling [9]. This is because natural brines (e.g. formation water, seawater) are complex mixtures of ions, the combined effects of monovalent and multivalent salts on surfactant stability can be highly nonlinear [11, 12]. For example, mixed NaCl and CaCl_2 solutions often produce greater precipitation than single salts due to competitive and synergistic binding [11, 13]. The high ionic strength from multiple salts also compresses the electrical double layer, further destabilising micelles [14].

Practical EOR applications have consistently found that high salinity especially when accompanied by high hardness (Ca^{2+} , Mg^{2+}) dramatically reduces surfactant effectiveness [15]. Elevated salinity raises the CMC, shrinks micelle size, and ultimately leads to partial or full precipitation of surfactant



[16]. This limits the ability of surfactant floods to lower oil–water interfacial tension and it can also result in pore plugging [3, 17]. Given these challenges, considerable research has focused on developing salt-tolerant surfactant systems and additives. Mixed surfactant formulations and nanoparticles have also been explored to enhance salt tolerance, but another promising approach is the use of enzymes as “green” additives [13, 18].

Enzyme-based agents, including commercial products like greenzyme, offer a novel mitigation strategy. Enzymes are biocatalysts that can potentially alter surfactant molecules or the solution environment to prevent precipitation [19-21]. For instance, some enzymes can hydrolyse or modify surfactant functional groups, making them more water-soluble or preventing the formation of insoluble ion pairs [22]. Early studies of enzyme-assisted EOR suggest that enzymatic additives can improve chemical stability and oil mobility in salty brines [19, 23]. The relatively low toxicity and biodegradability of enzymes make them attractive as environmentally friendly alternatives to harsh chemical stabilisers [24, 25].

Despite this promise, there remain important knowledge gaps. Prior works have largely focused on single-salt effects or idealised surfactant mixtures, leaving uncertainty about real-world scenarios with mixed salts and moderate salinity [12, 26]. Moreover, detailed mechanisms of how an enzyme like greenzyme interacts with anionic surfactants in the presence of multivalent ions are not well understood. This study aims to fill these gaps by systematically investigating SDS precipitation behaviour in single, binary, and ternary salt solutions and by evaluating the ability of greenzyme to mitigate surfactant precipitation under harsh salinity conditions. The results will improve understanding of ion-surfactant interactions in complex brines and assess the viability of enzymatic stabilisation strategies for practical EOR and industrial fluid systems.

II. MATERIALS AND METHODS

A. Materials –

Surfactant and salts: Analytical-grade sodium dodecyl sulphate (SDS) surfactant was used as the model anionic surfactant. The salts used were high-purity sodium chloride (NaCl), calcium chloride (CaCl₂), and magnesium chloride (MgCl₂). These salts represent common monovalent and divalent ions found in natural and industrial brines. Distilled water was used as the solvent for all solution preparation.

Enzymatic agent: A commercial enzyme prepared from DNA of selected oil-eating microbe extract known as greenzyme was obtained from Biotech Processing Supply, Dallas Texas. Greenzyme has active H⁺ and OH⁻ sites that make it highly diffusive in water and its molecular weight is between 80,000 and 90,000 g/mol [27]. It has high salinity tolerance and has been reported for applications in oil recovery [19, 20]. A stock greenzyme concentration solution was used as received for all experiments.

B. Experimental methods –

Stock salt solutions were prepared by dissolving measured quantities of each salt in distilled water. Specifically, 85.500 g/L of NaCl, 61.720 g/L of CaCl₂, and 18.506 g/L of MgCl₂ stock solutions were prepared by stirring each salt to full dissolution. Working brine solutions were then prepared from these stocks by dilution to final concentration levels of 10%, 50%, and 100%. The compositional breakdown of the three brines used is presented in Table 1. Single-salt brines of 10%, 50%, and 100% were prepared for each salt. For double-salt brines (NaCl+CaCl₂, NaCl+MgCl₂, CaCl₂+MgCl₂), the appropriate masses of each salt were combined and dissolved together, then diluted to 10% and 50% of the total concentration. A triple-salt brine was made by mixing all three salts and similarly diluting the stock solution.

Table 1: Brine compositional breakdown

Salt	10% (g/L)	50% (g/L)	100% (g/L)
NaCl	8.550	42.750	85.500
CaCl ₂	6.172	30.860	61.720
MgCl ₂	1.851	9.253	18.506
Total	16.573	83.863	165.726

The SDS was added to each prepared brine to form surfactant–salt mixtures. Two SDS concentrations were tested: 0.5 wt.% and 1.0 wt.%. These levels are well above the SDS CMC (~0.2 wt.%) to ensure micellization [28]. For each salt solution (single, double, triple at 10%, 50%, 100%), the required amount of SDS was added. All the solutions were prepared at ambient temperature (~25°C). The mixture was then immediately observed for any cloudiness or precipitate formation. Visual observation and photographs were taken within minutes of mixing since SDS precipitation with multivalent ions tends to occur rapidly [11]. The conductivity of each surfactant–salt solution was measured after equilibrium (approximately 1 hour after mixing) to assess the ionic content remaining in solution. A decrease in conductivity relative to the salt-only solution indicates ion binding by SDS (i.e. precipitation of ionic complexes). All measurements were done in triplicate to ensure reproducibility. To evaluate the effect of the enzyme, greenzyme was added to selected SDS–salt mixtures that showed precipitation. Two enzyme concentrations were tested: 1.0 wt.% and 2.0 wt.%. Enzyme was added to the salt solutions before the SDS was added, and the solutions were checked for precipitation and conductivity was measured. The visual observations were recorded as either “precipitate” or “no precipitate” for each condition and the conductivity data were compared across all conditions to quantify the extent of precipitation. A significant drop in conductivity upon adding SDS indicates ion removal by precipitate; recovery of conductivity upon adding greenzyme indicates mitigation. All key results were evaluated qualitatively and quantitatively in the context of ion-specific interactions.

III. RESULTS AND DISCUSSIONS

A. Results –

The summary of the results of the single salt solutions of NaCl is presented in Figure 1. The conductivity results show a monotonic increase in conductivity as NaCl salinity increases from 10% to 100% for all brines with and without SDS. This behaviour is expected since conductivity is primarily governed by the concentration and mobility of ions in solution and increase in NaCl concentration introduces more Na^+ and Cl^- ions, thereby increasing ionic strength and electrical conductivity. The NaCl only solution however consistently shows the highest conductivity compared to the SDS containing brines. The presence of SDS in NaCl solution however reduces the number of freely mobile ions, leading to lower conductivity compared to NaCl alone. This reduction in freely mobile ions in SDS containing brines can be attributed to micelle formation effect and/or ion pairing. At concentration above the critical micelle concentration (CMC), SDS molecules aggregate into micelles and some sodium counterions become associated with the micelle surface thereby reducing their mobility. Also, electrostatic interactions between Na^+ and the dodecyl sulphate anion (DS^-) will result in reduction of the number of free charge carriers, slightly lowering conductivity.

At low and moderate salinities of 10% and 50% respectively, the two concentrations of SDS (0.5 wt.% and 1.0 wt.%) demonstrated high stability has evidenced by absence of any visible precipitation. Only in the highest salinity of 100% NaCl solution did SDS shows instability with white precipitate being visibly seen in the brines at both 0.5% and 1.0% SDS concentrations. At very high salinity, several effects destabilize SDS such as electrostatic screening, salting-out effect and micelle collapse/aggregation [6, 9]. When greenzyme was added, there was no precipitation at 100% salinity at both concentrations and conductivity slightly increases relative to SDS-only systems. Greenzyme likely stabilizes the surfactant system through one or more mechanisms such as ionic interaction modification, steric stabilisation and hydration enhancement.

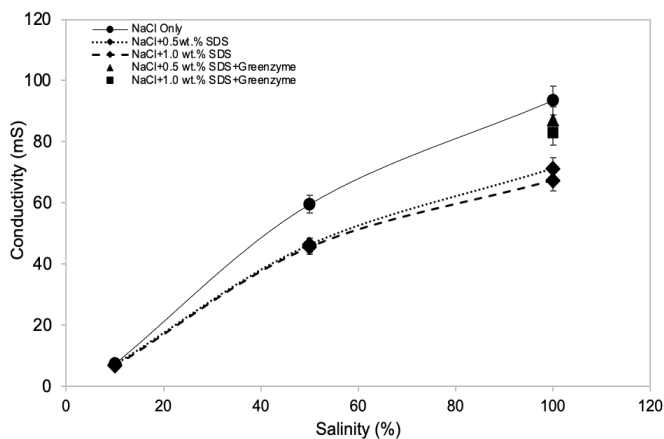


Figure 1: Conductivities of NaCl brines with and without SDS and greenzyme.

The summary of the results of the single salt solutions of CaCl_2 brine is presented in Figures 2 and 3. The CaCl_2 brines had the strongest effect on SDS. In 10%, 50%, and 100% CaCl_2 solutions, both 0.5 wt.% and 1.0 wt.% SDS immediately precipitated, forming a dense white solid in every case (Figure 2). The precipitate formation was very fast and prolonged, reflecting the well-known affinity of Ca^{2+} for SDS [8]. The conductivity plot shows that conductivity increases with increasing CaCl_2 salinity from 10% to 100%. This trend is expected because increase in CaCl_2 concentration introduces more Ca^{2+} and Cl^- ions in the solution resulting in higher conductivity. The Ca^{2+} ions carry double positive charge thereby contributing strongly to electrical conductivity. So, the CaCl_2 only solution consistently shows the highest conductivity values across the salinity range. When SDS was however added (both 0.5 wt.% and 1.0 wt.%), the conductivity decreases relative to the CaCl_2 only solution. The decrease in conductivity occurs due to strong interactions between Ca^{2+} ions and SDS anions (DS^-) resulting in formation of insoluble calcium dodecyl sulphate (Eq. 1), which removes ions from the solution and lower the conductivity compared to CaCl_2 brine alone.



Figure 2: Visual observation of precipitation of CaCl_2 brines with SDS.

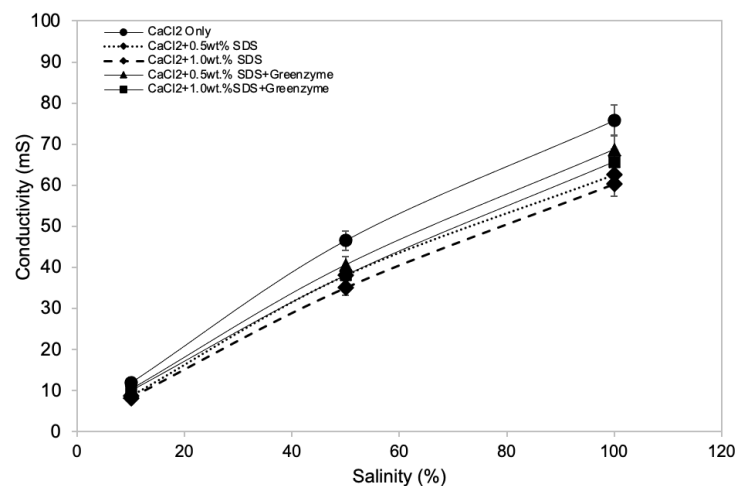


Figure 3: Conductivities of CaCl_2 brines with and without SDS and greenzyme.



This interpretation is fully supported by visual observations, which show precipitation at all salinity levels for SDS without greenzyme. The conductivity curves for 0.5 wt.% and 1.0 wt.% SDS are very similar, indicating that both concentrations exceed the critical aggregation threshold under these conditions. Once precipitation occurs, additional surfactant does not significantly alter the conductivity trend. When 1 wt.% greenzyme was introduced, the conductivity increases slightly relative to SDS-only brines, but precipitation still occurs at all salinity levels. This suggests that 1 wt.% greenzyme was insufficient to counteract the strong Ca^{2+} -SDS interaction. So, at this concentration, greenzyme provides minimal stabilization but at higher concentration of 2 wt.%, precipitation disappears completely across all salinity levels. This observation strongly suggests that greenzyme acts through a concentration-dependent stabilization mechanism. The slightly higher conductivity values observed in greenzyme containing brines suggest that ionic mobility was partially restored. This confirms that greenzyme improves surfactant stability in Ca^{2+} -rich brines.

The results of the single salt solutions of MgCl_2 brine are presented in Figure 4. The conductivity plot shows a linear increase in conductivity with increasing MgCl_2 salinity (10–100%). This behaviour reflects the expected relationship between ionic concentration and electrical conductivity, where increasing MgCl_2 concentration increases the number of charge carriers in solution due to dissociation of MgCl_2 into Mg^{2+} and Cl^- ions, increased ionic strength and enhanced charge transport within the solution. Although Mg^{2+} is a divalent ion, the conductivity values are lower than those observed in the CaCl_2 system, which may reflect differences in ionic mobility and hydration behaviour. When SDS was added at 0.5 wt.% and 1.0 wt.%, the conductivity values decrease slightly compared with the MgCl_2 only solution. This reduction in conductivity can be attributed to micelle formation effects and/or ion-surfactant association. These interactions are weak and insufficient to cause precipitation possibly because the system remains chemically stable. The visual observations confirm that no precipitation occurs at any salinity level for both surfactant concentrations. This indicates that SDS remains soluble and forms stable micellar structures in MgCl_2 brines under the experimental conditions. This stability suggests that Mg^{2+} does not bind SDS as strongly as Ca^{2+} under these conditions [7, 9]. The conductivity curves for 0.5 wt.% and 1.0 wt.% SDS are very close, indicating that both concentrations exceed the CMC of SDS and increasing surfactant concentration mainly increases micelle number or size, rather than changing ionic conductivity significantly. Thus, surfactant concentration has limited influence on conductivity once micelles dominate the system.

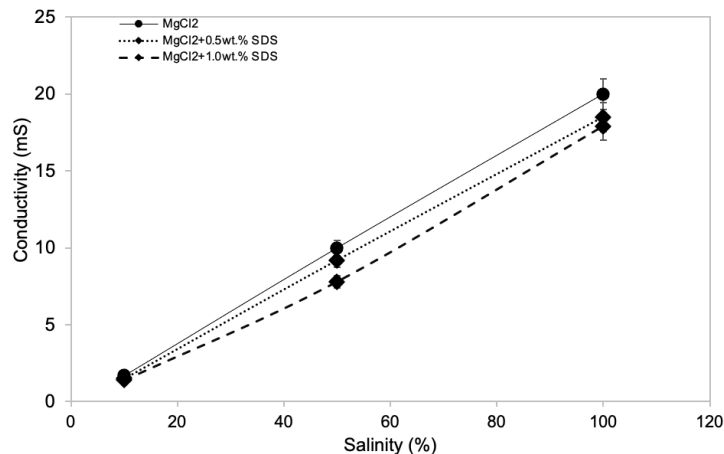


Figure 4: Conductivities of MgCl_2 brines with and without SDS.

Figures 5 and 6 present the results of binary salt solutions using $\text{NaCl} + \text{CaCl}_2$ brines. The conductivity plot shows that conductivity increases with increasing salinity for the $\text{NaCl} + \text{CaCl}_2$ system, but at very high salinity level the conductivity was immeasurable. This trend reflects the increasing concentration of Na^+ , Ca^{2+} , and Cl^- ions in solution because the brines contain both monovalent and divalent ions and the conductivity values were influenced by higher mobility of these ions. Consequently, the $\text{NaCl} + \text{CaCl}_2$ brine without surfactant exhibits the highest conductivity values. When SDS was added at 0.5 wt.% and 1.0 wt.%, conductivity decreases relative to the brine-only system. This reduction arises primarily from interactions between Ca^{2+} ions and the sulphate head group of SDS as illustrated in Eq. 1. Formation of calcium dodecyl sulphate precipitates removes both surfactant molecules and ions from the solution, thereby reducing the number of mobile charge carriers responsible for electrical conductivity. This interpretation was confirmed by the visual observations, which show precipitation occurring at all salinity levels in the absence of greenzyme. The conductivity curves for 0.5 wt.% and 1.0 wt.% SDS are very similar, indicating that increasing surfactant concentration does not significantly alter the conductivity trend. This suggests that once the precipitation begins, additional surfactant primarily contributes to more precipitate formation rather than increased micelle formation. When 1.0 wt.% greenzyme was however added to the brines, the precipitations of both 0.5 wt.% and 1.0 wt.% SDS were eliminated across the salinity range. This demonstrates that greenzyme effectively stabilizes the surfactant system even in the presence of Ca^{2+} ions.

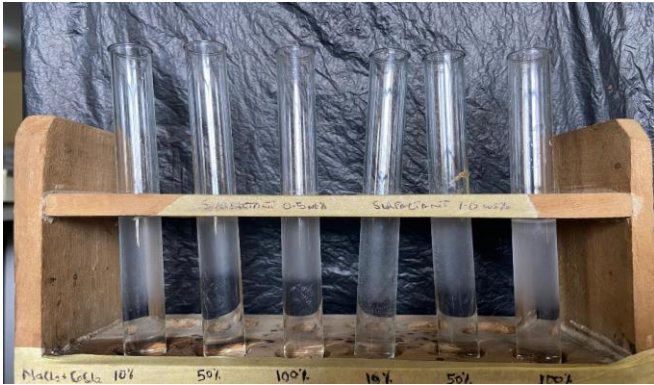


Figure 5: Visual observation of precipitation of NaCl+CaCl₂ brines with SDS.

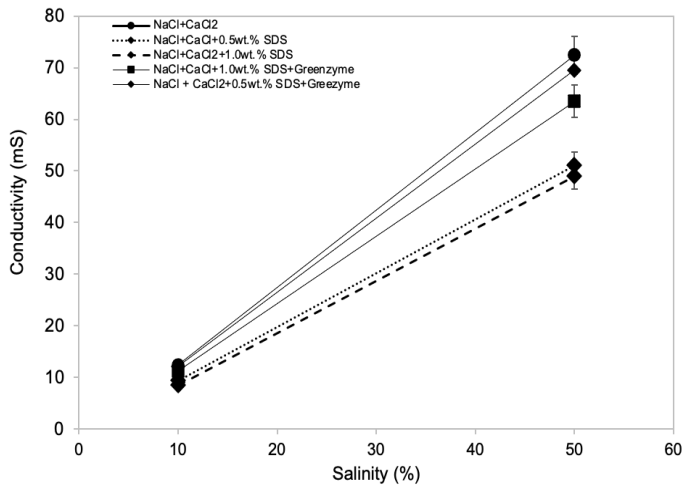


Figure 6: Conductivities of NaCl+CaCl₂ brines with and without SDS.

The results of binary salt solutions using CaCl₂+MgCl₂ brines are presented in Figures 7 and 8. Like previous results, the conductivity results show that conductivity increases with increasing salinity in the CaCl₂+MgCl₂ brine system. This trend reflects the increasing concentration of divalent cations (Ca²⁺ and Mg²⁺) and chloride ions in the solution, which enhances ionic strength and charge transport. Among all systems, the CaCl₂+MgCl₂ brine without surfactant exhibited the highest conductivity, indicating that ions remain freely mobile in the absence of surfactant-ion interactions. When SDS was however introduced, conductivity decreases relative to the brine-only system. This behaviour is consistent with surfactant-ion interactions and precipitation processes, which reduce the number of mobile ions in solution. Visual observations indicate that precipitation occurs at all salinity levels for both surfactant concentrations (0.5 wt.% and 1.0 wt.%) when no greenzyme was present.

This behaviour closely resembles the CaCl₂-only system, suggesting that Ca²⁺ ions dominate the interaction with SDS even in the presence of Mg²⁺. The precipitation mechanism can be described by the formation of insoluble calcium dodecyl sulphate salts given in Eq. 1. Although Mg²⁺ was also present in the brine, its strong hydration shell limits direct

interaction with the surfactant head groups. Consequently, calcium ions remain the primary driver of surfactant precipitation in the mixed system. Similar to previous systems, the conductivity curves for 0.5 wt.% and 1.0 wt.% SDS show only minor differences. This suggests that increasing surfactant concentration does not significantly alter system behaviour once precipitation occurs. In such conditions, additional surfactant molecules primarily contribute to further formation of insoluble calcium-surfactant complexes, rather than increasing micelle concentration. When 1 wt.% greenzyme was introduced, precipitation still occurs across all salinity levels. This indicates that the amount of greenzyme present was insufficient to effectively compete with Ca²⁺ ions for interaction with SDS but when higher concentration of 2 wt.% was used, the precipitation was eliminated for both concentrations of surfactant across all salinity levels. This result demonstrates that the greenzyme exhibits concentration-dependent stabilization capability, with a threshold concentration required to effectively mitigate surfactant precipitation in high-hardness brines.

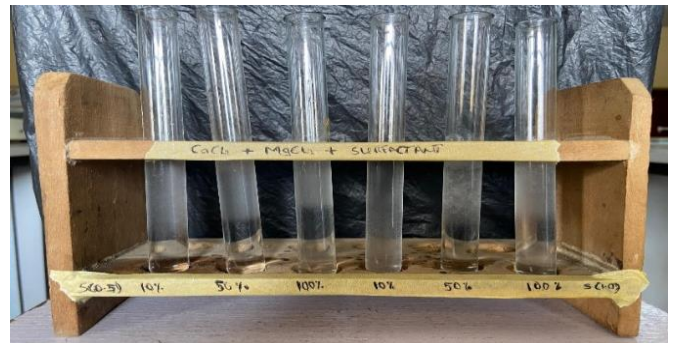


Figure 7: Visual observation of precipitation of CaCl₂ + MgCl₂ brines with SDS.

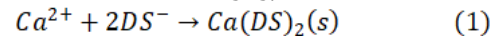
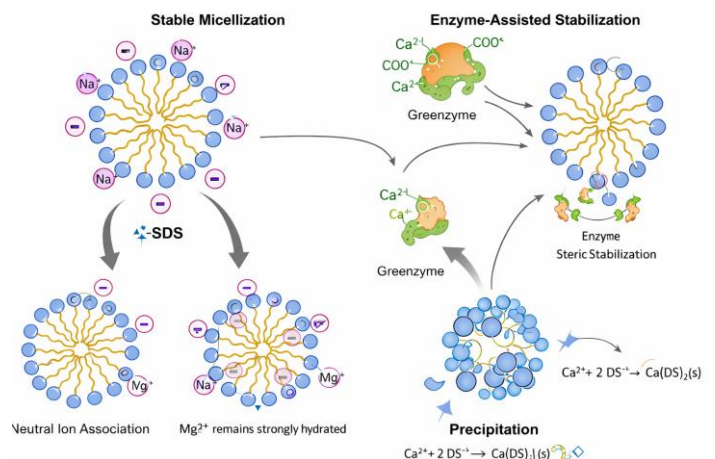


Figure 8: Conductivities of CaCl₂+MgCl₂ brines with and without SDS.

The results of binary salt solutions using NaCl+MgCl₂ brines are presented in Figure 9. The conductivity results show



a steady increase in conductivity with increasing salinity for the NaCl+MgCl₂ brine system. This trend reflects the increasing concentration of ionic species, including Na⁺, Mg²⁺, and Cl⁻ ions, which contribute to electrical conductivity. The NaCl+MgCl₂ brine without surfactant exhibits the highest conductivity values, indicating that ions remain freely mobile in solution. When SDS was introduced, the conductivity decreases slightly, which can be attributed to micelle formation and partial counterion association. Above the critical micelle concentration, SDS molecules aggregate into micelles, and a fraction of sodium counterions becomes associated with the micelle surface. This reduces the number of free ions available for electrical conduction, resulting in slightly lower conductivity values relative to the brine-only system. Visual observations indicate that no precipitation occurs at all salinity levels when 0.5 wt.% SDS was used, but with the application of 1.0 wt.% SDS, precipitation was observed at 100% salinity level. This suggests that SDS remains stable in NaCl+MgCl₂ brines at moderate salinity levels. This stability can be explained by the relatively weak interaction between Mg²⁺ ions and the sulphate head group of SDS. Magnesium ions possess a strong hydration shell due to their high charge density and small ionic radius. This hydration layer reduces the likelihood of direct binding between Mg²⁺ ions and the surfactant head groups, thereby preventing formation of insoluble surfactant salts. In addition, the presence of Na⁺ ions contribute primarily to electrostatic screening of micelles rather than precipitation reactions, further supporting surfactant stability at moderate salinity.

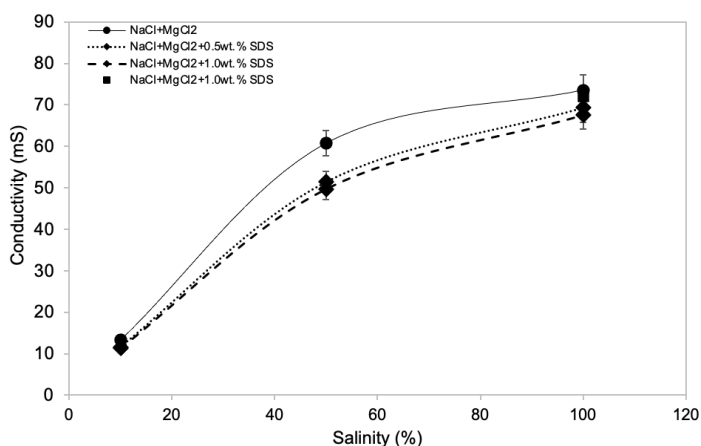


Figure 9: Conductivities of NaCl+MgCl₂ brines with and without SDS.

At the highest salinity level (100%), precipitation occurs in the system containing 1.0 wt.% SDS, while the lower surfactant concentration remains stable. This behaviour likely reflects the combined effect of high ionic strength and surfactant concentration, which can promote aggregation and salting-out of surfactant molecules. At extreme salinity, electrostatic repulsion between surfactant head groups becomes significantly reduced due to compression of the electrical double layer, allowing micelles to grow and aggregate. The resulting aggregation can eventually lead to phase separation or precipitation, particularly at higher

surfactant concentrations where intermolecular interactions are stronger. When greenzyme was introduced into the system, precipitation was completely eliminated. This observation indicates that greenzyme effectively stabilizes the surfactant system under extreme ionic conditions. Greenzyme molecules may adsorb onto surfactant aggregates, creating steric barriers that prevent micelle aggregation and precipitation. Other possibility is alteration of interaction between Mg²⁺ ions and surfactant head groups by greenzyme molecules. Greenzyme may also increase the hydration stability of surfactant head groups, thereby maintaining surfactant solubility even at high ionic strength.

The results of ternary salt solutions using NaCl+CaCl₂+MgCl₂ brines are presented in Figures 10 and 11. The conductivity results show a systematic increase in conductivity with increasing salinity for the NaCl+CaCl₂+MgCl₂ brine system. This trend reflects the increasing concentration of dissolved ions, including Na⁺, Mg²⁺, Ca²⁺, and Cl⁻, which collectively contribute to electrical conduction. The ternary brine without surfactant exhibits the highest conductivity values, indicating that ions remain freely mobile in the absence of surfactant-ion interactions. Upon the addition of SDS, conductivity decreases slightly relative to the brine-only system. This reduction can be attributed to micelle formation and partial counterion association, which decreases the number of freely mobile ions contributing to electrical conductivity. Visual observations reveal that precipitation occurs at all salinity levels for both concentrations of surfactant (0.5 wt.% and 1.0 wt.%) when no greenzyme was present. This behaviour indicates that SDS is highly unstable in the ternary brine system, despite the presence of Na⁺ and Mg²⁺ ions that individually showed relatively good compatibility with SDS in previous experiments.

The dominant factor responsible for this instability is the presence of Ca²⁺ ions, which strongly interact with the sulphate head groups of SDS to form insoluble calcium dodecyl sulphate complexes. This process removes both surfactant molecules and ions from solution, thereby reducing ionic mobility and contributing to the observed decrease in conductivity relative to the brine-only system. The conductivity curves for 0.5 wt.% and 1.0 wt.% SDS are very similar, indicating that surfactant concentration has only a minor influence on system behaviour once precipitation occurs. Under these conditions, increasing surfactant concentration primarily results in increased formation of insoluble calcium-surfactant complexes, rather than enhanced micelle formation. When 1.0 wt.% greenzyme was introduced, precipitation persists across all salinity levels, indicating that the enzyme concentration was insufficient to prevent the strong interaction between Ca²⁺ ions and SDS molecules. When the concentration was increased to 2 wt.%, the precipitation was eliminated across the entire salinity range for both surfactant concentrations. This result further demonstrates that greenzyme exhibits concentration-dependent stabilization capability, requiring a threshold

concentration to effectively mitigate surfactant precipitation in complex brine systems containing multiple ionic species.



Figure 10: Visual observation of precipitation of NaCl+CaCl₂+MgCl₂ brines with SDS.

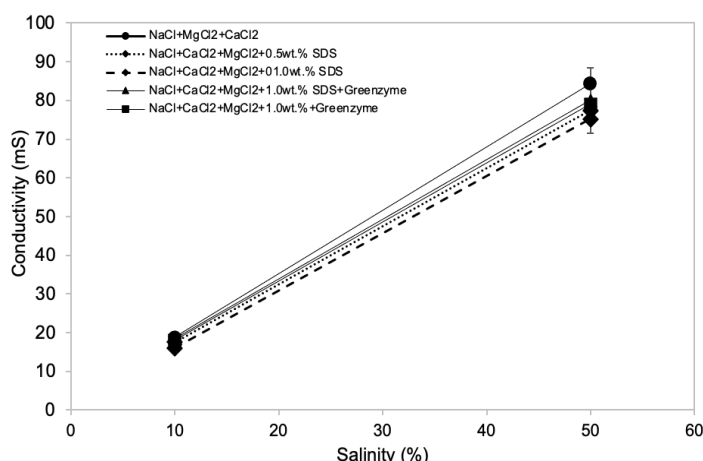


Figure 11: Conductivities of NaCl+CaCl₂+MgCl₂ brines with and without SDS.

B. Discussions of results –

The experimental results demonstrate clear ion-specific effects of brine compositions and salinities on SDS stability. Conductivity measurements for the three single brine systems (NaCl, CaCl₂, and MgCl₂) showed a consistent increase in conductivity with increasing salinity, reflecting the higher concentration of dissolved ionic species in solution. As expected, the brine-only systems exhibited the highest conductivity values, since all ions remained freely mobile in the absence of surfactant interactions. However, the magnitude and behaviour of conductivity varied with cation type, reflecting differences in ionic charge, hydration properties, and interactions with the surfactant. In particular, the CaCl₂ system generally exhibited higher conductivity values than MgCl₂, likely due to differences in ionic mobility and ion–water interactions [19]. These variations highlight the importance of cation chemistry in determining the electrochemical behaviour of saline surfactant systems.

The addition of sodium dodecyl sulphate (SDS) to the brines led to a reduction in conductivity relative to the corresponding brine-only systems across all brine compositions. This behaviour can be attributed to two primary mechanisms namely micelle formation and ion–surfactant interactions. Above the critical micelle concentration (CMC), SDS molecules aggregate to form micelles, with hydrophobic alkyl chains oriented inward and sulphate head groups exposed to the aqueous phase. During this process, sodium counterions become partially associated with micelle surfaces, reducing the number of freely mobile ions contributing to electrical conduction. Electrostatic interactions between the sulphate head groups of SDS and dissolved cations can further influence ionic mobility, particularly in systems containing divalent ions such as Ca²⁺ and Mg²⁺. These interactions become increasingly significant in high-salinity systems where ionic strength is elevated.

In NaCl brines, SDS remained stable at low and moderate salinity levels, with precipitation occurring only under extreme salinity conditions. This is consistent with literature findings that monovalent ions (Na⁺) primarily influence surfactant systems via electrostatic screening, not precipitation [15]. At high salinity, screening reduces head-group repulsion, leading to micelle growth, aggregation, and eventual salting-out. The results show no precipitation of SDS in MgCl₂ brines, even at high salinity. This behaviour can be explained by the strong hydration shell surrounding Mg²⁺ ions. Magnesium has a small ionic radius and high charge density, which results in strong binding with surrounding water molecules. This hydration shell prevents direct interaction between Mg²⁺ ions and the sulphate head groups of SDS, thereby limiting the formation of insoluble magnesium surfactant complexes. Consequently, Mg²⁺ ions exert a relatively weak destabilizing effect on SDS compared with other divalent cations [7, 9].

In contrast, CaCl₂ brines exhibited severe surfactant incompatibility, with precipitation occurring at all salinity levels investigated. Calcium ions interact strongly with the sulphate head groups of SDS, forming insoluble calcium dodecyl sulphate complexes according to the reaction in Equation 1. The result of the study is consistent with previous studies that show the SDS is prone to precipitation in Ca²⁺ ion solution [10]. The formation of this insoluble salt removes both surfactant molecules and ions from solution, reducing ionic mobility and resulting in decreased conductivity relative to the brine-only system [8, 9]. These results confirm that calcium ions represent the primary destabilizing species in SDS systems.

The behaviour observed in binary brine mixtures further supports the dominant role of calcium ions. In the NaCl+CaCl₂ brines, precipitation occurred across all salinity levels despite the presence of sodium ions. This indicates that even small concentrations of Ca²⁺ ions can dominate surfactant interactions, overriding the stabilizing effects of monovalent ions. Similarly, precipitation occurred in the CaCl₂+MgCl₂ system, demonstrating that magnesium ions do not sufficiently suppress the strong Ca²⁺–surfactant interactions responsible for precipitation. In contrast, the NaCl+MgCl₂ system exhibited relatively stable surfactant behaviour, with



precipitation occurring only at extreme salinity conditions for higher surfactant concentrations. This further confirms the weaker destabilizing effect of Mg^{2+} ions compared with Ca^{2+} . Also, the ternary $NaCl+MgCl_2+CaCl_2$ brine exhibited severe surfactant precipitation across all salinity levels in the absence of enzyme additives. This behaviour reflects the dominant influence of calcium ions, which interact strongly with SDS even in the presence of other ionic species [11, 14]. The results therefore demonstrate that calcium hardness influences surfactant compatibility in complex reservoir brines.

The addition of greenzyme revealed a concentration-dependent stabilization effect across calcium-containing systems. At low enzyme concentrations, precipitation persisted, indicating insufficient inhibition of calcium-surfactant interactions. However, increasing the greenzyme concentration resulted in complete mitigation of surfactant precipitation, even in highly saline and complex brine systems. The stabilization mechanism may involve complementary processes of complexation of Ca^{2+} ions, steric stabilization of surfactant aggregates and enhanced hydration of surfactant head groups [22]. The hypothesised mechanisms of SDS-ions-enzyme interactions are illustrated in Figure 12. These findings suggest that enzyme-assisted formulations may provide an effective strategy for improving surfactant stability in high-hardness reservoir environments.

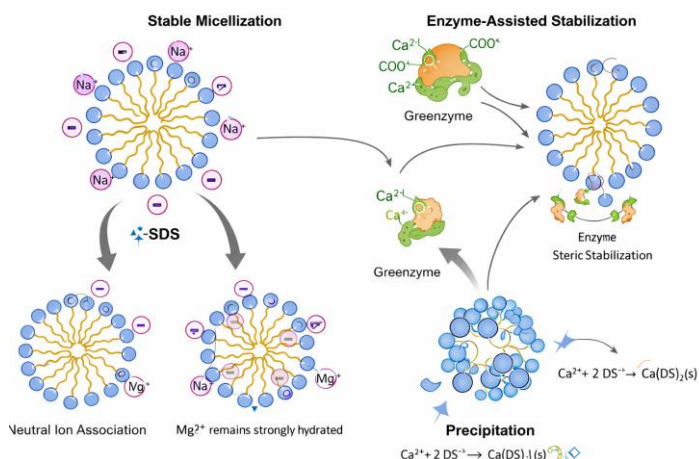


Figure 12: The mechanistic diagram of SDS-ions-enzyme interactions

The results of this study demonstrate that brine composition is a more critical factor than total salinity alone in determining surfactant stability. While SDS is compatible with sodium- and magnesium-dominated brines, the presence of calcium ions leads to rapid surfactant precipitation. These findings highlight the importance of formation water characterisation and hardness control in surfactant flooding applications. The use of enzyme additives such as greenzyme may represent a promising environmentally friendly approach for mitigating hardness-induced surfactant precipitation in chemical enhanced oil recovery processes [19, 20, 23]. Although all the tests were conducted at ambient condition (25°C), the results of this studies demonstrate surfactant stability potential of enzyme in varied salinity conditions.

Further studies will be conducted on effect of temperature variation on the stability of surfactant under similar conditions.

IV.CONCLUSION

This study provides a comprehensive investigation of SDS behaviour in single, binary, and ternary brine systems representative of reservoir formation waters. The results demonstrate that surfactant stability is strongly controlled by ion-specific interactions, with calcium ions playing a dominant role in surfactant destabilization. The key findings include:

1. Conductivity increased with salinity in all systems, while the presence of SDS reduced conductivity due to micelle formation and counterion association.
2. The SDS was stable at low to moderate salinity levels of NaCl, with precipitation occurring only at extreme salinity. Also, SDS exhibited high stability across all salinity levels of $MgCl_2$. On the contrary, a severe surfactant precipitation occurred at all salinity levels of $CaCl_2$ due to the formation of insoluble calcium dodecyl sulphate complexes.
3. In binary and ternary brines, Ca^{2+} ions dominated surfactant behaviour, overriding the stabilizing effects of Na^+ and Mg^{2+} and leading to precipitation even at low concentrations. In calcium-free brines, partial surfactant destabilization was observed at extreme salinity, indicating that ionic strength alone can induce aggregation and precipitation.
4. The addition of greenzyme demonstrated a strong concentration-dependent stabilization effect, completely mitigating precipitation in high-hardness brines at sufficient concentration. The observed stabilization effect of enzyme is hypothesised to be related to calcium ion complexation, steric stabilization, and enhanced hydration of surfactant aggregates. Further investigations would however be required for final conclusion.

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Table 2: Summary of the visual observation results of all the brines.

Surfactant	Enzyme (1wt.%)	10%	50%	100%	Comment
NaCl					
0.5	NO	No Precipitation	No Precipitation	Precipitation	Precipitate at only 100%
1.0	NO	No Precipitation	No Precipitation	Precipitation	Precipitate at only 100%
0.5	Yes	--	--	No Precipitation	Precipitation mitigated
1.0	Yes	--	--	No Precipitation	Precipitation mitigated
CaCl₂					
0.5	No	Precipitation	Precipitation	Precipitation	All concentration affected
1.0	No	Precipitation	Precipitation	Precipitation	All concentration affected
0.5	Yes	Precipitation	Precipitation	Precipitation	Greenzyme ineffective
1.0	Yes	Precipitation	Precipitation	Precipitation	Greenzyme ineffective
0.5	Yes (2 wt.%)	No Precipitation	No Precipitation	No Precipitation	Precipitation mitigated
1.0	Yes (2 wt.%)	No Precipitation	No Precipitation	No Precipitation	Precipitation mitigated
MgCl₂					
0.5	No	No Precipitation	No Precipitation	No Precipitation	stable
1.0	No	No Precipitation	No Precipitation	No Precipitation	stable
NaCl + CaCl₂					
0.5	No	No Precipitation	No Precipitation	No Precipitation	stable
1.0	No	Precipitation	Precipitation	Precipitation	All concentration affected
1.0	Yes	No Precipitation	No Precipitation	No Precipitation	Precipitation mitigated
CaCl₂ + MgCl₂					
0.5	No	Precipitation	Precipitation	Precipitation	All concentration affected
1.0	No	Precipitation	Precipitation	Precipitation	All concentration affected
0.5	Yes	Precipitation	Precipitation	Precipitation	All concentration affected
1.0	Yes	Precipitation	Precipitation	Precipitation	All concentration affected
0.5	Yes (2 wt.%)	No Precipitation	No Precipitation	No Precipitation	Precipitation mitigated
1.0	Yes (2 wt.%)	No Precipitation	No Precipitation	No Precipitation	Precipitation mitigated
NaCl + MgCl₂					
0.5	No	No Precipitation	No Precipitation	No Precipitation	Stable
1.0	No	No Precipitation	No Precipitation	Precipitation	Precipitation at 100%
1.0	Yes	-	-	No Precipitation	Greenzyme fully mitigates
NaCl + CaCl₂ + MgCl₂					
0.5	No	Precipitation	Precipitation	Precipitation	All concentration affected
1.0	No	Precipitation	Precipitation	Precipitation	All concentration affected
0.5	Yes	Precipitation	Precipitation	Precipitation	All concentration affected
1.0	Yes	Precipitation	Precipitation	Precipitation	All concentration affected
0.5	Yes (2 wt.%)	No Precipitation	No Precipitation	No Precipitation	Precipitation mitigated
1.0	Yes (2 wt.%)	No Precipitation	No Precipitation	No Precipitation	Precipitation mitigated