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Review Article

EXPLORING THE PROTECTIVE EFFECTS OF SURFACTANTS AGAINST CORROSION: A CRITICAL REVIEW

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ABSTRACT

Corrosion is the spontaneous chemical or electrochemical reaction of metal with its surrounding environment. There have been ongoing worries about how corrosion affects the strength and stability of metal surfaces. Chemical corrosion inhibitors are often used in manufacturing and processing activities to prevent the deterioration of materials. Surfactants are a highly affordable, readily available, and environmentally friendly choice for corrosion inhibitors. This article outlines surfactants' capacity to prevent corrosion on various metal surfaces. The properties of multiple surfactants and their possible applications for corrosion inhibitors have also been discussed. This review article also explores additional factors, such as how varying levels of surfactants contribute to the mechanisms behind corrosion inhibition.

Keywords: Aggregation, anti-corrosive material, critical micelle concentration, surfactants

INTRODUCTION

Corrosion is the spontaneous deterioration of a material, predominantly metals, caused by chemical or electrochemical interactions with its surrounding environment, often resulting in structural weakening or failure (Malik *et al.*, 2011). This process is primarily driven by the reaction of metals with atmospheric oxygen, water, acids, salts, or other environmental agents, with the most prevalent example being the oxidation of iron in the presence of water and oxygen to form iron oxide, commonly known as rust. For instance, rust as the corrosion on metal is shown in Fig. 1.

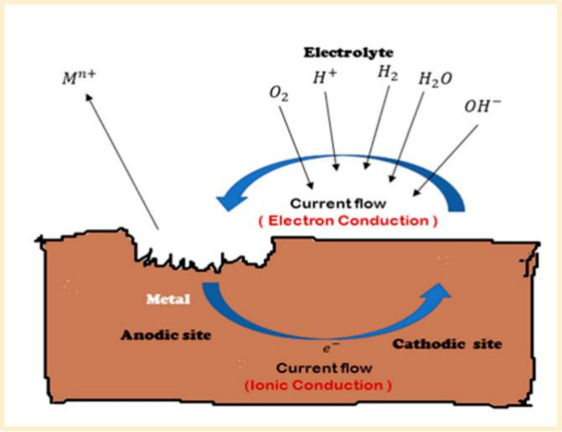

Figure 1. Corrosion on metal (Bijapur *et al.*, 2023)

Corrosion presents substantial issues across multiple sectors, including infrastructure and industry, and its negative impacts on material quality and longevity are well established. The use of surfactants in corrosion control has emerged as a potential option, giving novel solutions to attenuate its negative effects. Surfactants, recognized for their surface-active qualities, have shown great promise in building protective barriers, suppressing corrosive processes, and extending the life of materials exposed to severe conditions (Song *et al.*, 2023). The purpose of this critical review is to look into surfactants' varied role in corrosion prevention and control. This analysis offers a thorough understanding of surfactant corrosion protection by clarifying the underlying mechanisms, analyzing the many types of surfactants, and assessing their efficacy across different applications and conditions. First, we will look at the fundamental principles controlling the interaction of surfactants and corroding surfaces (Lone *et al.*, 2023). Understanding the molecular mechanisms by which surfactants adsorb on metal surfaces, change surface energies, and influence corrosion kinetics is critical for developing effective corrosion inhibitor techniques. Following that, we will look at the wide range of surfactants used in corrosion prevention, including standard anionic, cationic, and non-ionic surfactants as well as more specialized amphiphilic compounds designed for particular uses. We hope to identify the many functionalities and applications of surfactants in corrosion control by assessing their chemical structures, surface activities, and compatibility with different substrates (Bashir *et al.*, 2017; D'Souza *et al.*, 2015).

Surfactant blockers are classified into four separate categories: (a) inorganic inhibitors; (b) organic inhibitors; (c) surfactant-based inhibitors; and (d) mixed-material inhibitors. Surface active agents are composed of compounds with a polar water-attracting "head" connected to a non-polar water-repelling "tail". The capability of surfactant molecules to hinder processes in water can be attributed to either physical (electrostatic) attachment or chemical bonding to a metal interface. The effect is driven by the electrical charge present on the exterior of the solid material and the alteration in free energy that occurs when a chain of carbon and hydrogen atoms is transferred from water to the outer layer of the solid material (Ramezanzadeh *et al.*, 2018).

Surface active agent inhibitors offer numerous benefits, such as high effectiveness, low cost, minimal adverse effects, and simple production. These substances that hinder the activity of surface active agents provide these advantages (Migahed & Al-Sabagh, 2009). Additionally, investigating how surfactants adhere to metal surfaces is crucial for electrochemical studies related to bonding, smooth operation, and cleaning. The most efficient anti-corrosion agents for the specified applications are the ones that form protective films. Surfactants are now extensively used across various industries, including the petroleum sector because they can significantly influence surface and interface properties.

Furthermore, we will investigate the synergistic effects of surfactants with various corrosion inhibitors and coating technologies, focusing on their function in improving corrosion resistance and extending the service life of vital infrastructure, industrial equipment, and consumer items. Although surfactant inhibitors are important corrosion inhibitors, little attention was in the literature (Musa *et al.*, 2009). The main inhibition process involves binding the surfactant's active group to the metal's exterior. This involvement is crucial for preventing corrosion. A surfactant's involvement capacity is often linked to its tendency to create micelles. This study offers a concise overview of surfactants employed as corrosion inhibitors. By integrating insights from recent advances in surfactant chemistry, corrosion science, and materials engineering, this study seeks to give researchers, engineers, and industry stakeholders a complete overview of the state-of-the-art in surfactant-based corrosion inhibition. Finally, our research aims to spur additional innovation and collaboration in exploiting surfactants' protective potential to solve the pervasive difficulties faced by corrosion in the modern world (Tan *et al.*, 2024).

Surfactants and Their Types with Corrosion Inhibitors

Surfactant substances are amphipathic, meaning they have both water-attracting and water-repelling areas. Surfactants have an extended hydrocarbon chain and a tiny ionic or polar group at the end. The characteristics of these functional groups determine whether surface active agents are ionic (either cationic or anionic), zwitterionic, or nonionic. Figure 2 illustrates a typical surfactant in a schematic diagram.

Surfactants can be used as corrosion inhibitors to reduce the electrochemical activity of a metal surface. Some types of surfactants that can be used as corrosion inhibitors include.

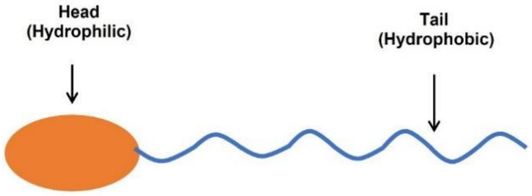

Figure 2. Surfactant containing hydrophilic head and hydrophobic tail

Anionic surfactants

These surfactants contain a negatively charged hydrophilic group, such as sulfate (SO^{4-}) or carboxylate (COO^{-}) ions. The anion is the active surface component; anionic surfactants are utilized more frequently compared to other types. Globally, about 10 million tons of surfactants are produced each year, with roughly 60% being anionic types. Their widespread use can be attributed to their ease of production and low cost. Negatively charged surfactants are commonly used in cleaning products, where alkyl and alkyl aryl chains within the C_{12}-C_{18} spectrum provide optimal cleaning efficacy (Belhaj *et al.*, 2020). Among the most commonly utilized counter ions are sodium, potassium, ammonium, calcium, and alkyl amines with added protons. Sodium and potassium increase the ability of substances to dissolve in water, and this improved water solubility enhances the ability of substances to dissolve in oil. Amine and alkanolamine offer solubility in both oils and water. These surfactants have a negatively charged functional group and can form a complex with a counter ion. Examples include sodium stearate $CH_3(CH_2)_{16}COO\text{-}Na+$, sodium dodecyl sulphate $CH_3(CH_2)_{11}SO_4^{-}Na^{+}$, sodium dodecyl benzene sulphonate $CH_3(CH_2)_{11}C_6H_4SO_3^{-}Na^{+}$.

Cationic surfactants

Unlike anionic surfactants, cationic surfactants have a positively charged hydrophilic category, such as an ammonium (NH^{4+}) ion. In positively charged surfactants, the active agents at the surface are the positively charged ions. Quaternary ammonium salts constitute the primary chemicals within this category. Typically, cationic surface active agents use nitrogen atoms to provide the positive charge, with amines and quaternary ammonium compounds being frequently utilized (Belhaj *et al.*, 2020). Amines function as surfactants only when they are protonated, which means they are not effective in alkaline conditions. Quaternary ammonium compounds are unaffected by changes in pH. Similarly, non-quaternary cations are very sensitive to the presence of polyvalent anions (Sachin *et al.*, 2019). These surfactants have a positive charge and can be adsorbed on materials with a negative charge. They can be used to protect the surface of carbon steel from corrosion. Examples of cationic surfactants are benzalkonium chloride (BZlC), cetylpyridinium chloride (CPC), benzethonium chloride (BZT), etc.

Nonionic surfactants

These surfactants lack charged groups and mostly feature polar functional groups in their hydrophilic part, such as hydroxyl (-OH) or ether (-O-) groups. Nonionic surfactants have no electrical charge on their surface and are made up of a non-polar segment, usually a polyether or polyhydroxy unit. In the broad category of non-ionics, the polar group consists of a polyether made of ethylene oxide units, which result from the chemical reaction of ethylene oxide (Cacua *et al.*, 2019). The term 'poly' isn't quite precise. Surfactants, like dispersants, usually contain between five and ten oxyethylene units in their polar chain, though some might have longer chains. The water-soluble part of these compounds may feature hydroxyl groups or a polyoxyethylene chain. In this segment, ethylene oxide compounds are primarily bonded to alkyl phenolic compounds and fatty alcohol derivatives. Example of non-ionic surfactants (Massarweh & Abushaikha, 2020) are polyoxyethylene alcohol $C_nH_{2n+1}(OCH_2CH_2)_mOH$, Alkylphenol Ethoxylate $C_9H_{19}–C_6H_4–(OCH_2CH_2)_nOH$.

Zwitterionic surfactants

Aside from standard classification, there are amphiphilic molecules that obscure the distinction between surfactants and other chemicals. Zwitterionic surfactants have two charged entities of varying sizes. The positive charge usually comes from ammonium, while the negative charge can come from various sources, with carboxylate being the most commonly used (Musso & Holovko, 2011). Zwitterions are also known as 'amphoterics'. An amorphic surfactant transitions from cationic to anionic as pH increases. The molecule is only zwitterionic within a specific pH range, as neither the acidic nor basic sites are permanently charged. The charge of genuinely amorphic surfactants changes with pH, affecting their characteristics including foaming, wetting, and detergency. All of these qualities are highly dependent on the solution pH. Perfluorinated hydrophobic surfactants have multiple applications, including fire extinguishers, electroplating, and water-repellent fiber coatings (Sah *et al.,* 2024). Examples of such surfactants are dodecyl betain $C_{12}H_{25}N+(CH_3)_2CH_2COO^-$, lauramidopropyl betain $C_{11}H_{23}CONH(CH_2)_3N+(CH_3)_2CH_2COOC$.

Gemini surfactants

Gemini surfactants are dimeric compounds consisting of two hydrophobic chains and two hydrophilic heads linked by a spacer positioned near the head groups (Mangat & Kaur, 2015). They exhibit a lower threshold for micelle formation, enhanced efficiency in forming micelles, and greater capacity for solubilizing substances compared to their traditional (monomeric) counterparts. Additionally, they can reduce the water's surface tension and the oil-water boundary tension by factors of 10 to 100. This behavior largely depends on the specific characteristics of their components (heads, hydrophobic chains, and spacers), so their synthesis mainly involves modifying the type and length of these components (Abdel-Gaber *et al.*, 2020). Some examples of Gemini surfactants are N,N'-hexadecyl-N,N,N',N'-tetramethyl-1,6-hexanediammonium bromide $[(CH_3)_2N+\text{-}(CH_2)_{16}\text{-}N+(CH_3)_2]Br_2^-$ (El Sayed *et al.*, 2019). Sulfate-Based Gemini Surfactants: Dodecyl sulfate Gemini surfactant.

Surfactants are categorized into various types depending on their water-attracting groups (Aslam *et al.*, 2021). Fig. 3 shows different types of surfactants and their hydrophobic and hydrophilic parts.

Micellization and Corrosion Inhibition

In solvents with a polar nature such as H_2O, surface-active agents with both water-attracting and water-repellent components aggregate to form a micelle. The hydrophobic tails group in the center, while the hydrophilic heads extend outward into the surrounding water, forming a barrier that keeps the water-repelling parts isolated from the water. Micelles can be seen as stationary spherical groups of surfactant molecules arranged in a specific manner (Sheokand *et al.*, 2024). However, micelles are in a state of constant flux with surfactant monomers in the surrounding solution, with surfactant molecules frequently swapping between the micelles and the bulk solution. Micelles are tiny structures created by the clustering of surface-active molecules with both hydrophilic and hydrophobic properties (which can be ionic, non-ionic, zwitterion, or Gemini types) (Wang *et al.*, 2024). The micelles exist in a state of thermodynamic equilibrium, with surfactant molecules swiftly exchanging between individual aggregates, generally for durations ranging from 0.01 to 0.001 seconds. As surfactant concentration increases, micelles are formed (Fig. 4).

Micelles are continuously disassembling and reassembling. Since a micelle's outermost part has a lower dielectric value over the water in its bulk, it resembles a highly concentrated electrolytic mixture. The polarization of the micellar portion is less severe than that of water-based and charged micelles even showing polarity similar to ethanol alone in the stern region (Saulnier *et al.*,1996). The size and shape of a micelle are influenced by factors such as the amount of monomers and the aggregation count. In water-based solutions, surfactant aggregation numbers usually range between 10 and 100. The aggregation number is important for corrosion because a higher value corresponds to a smaller surface area per molecule. As the aggregation number increases, surface polarity decreases. The Hydrophilic-Lipophilic Balance (HLB) of a surfactant is a key physical property that indicates how effectively it functions to prevent corrosion. A lower HLB value indicates that the surfactant has greater oil solubility, whereas a higher HLB value implies that it has increased water solubility. Fig. 5 illustrates how the opposing forces within the double layer neutralize the electric charge in ionic micelles. The innermost layer next to the surface is known as the Stern layer, which can also be referred to as the Stern plane (Mirgorod *et al.*, 2019). In this area, the charge-balancing ions are tightly bound, inhibiting any heat-induced movement, and they travel along with the suspended particle when subjected to an electric force. Based on the most widely recognized theory, this layer also contains the head portions of surfactant compounds. The remaining part of the double layer is known as the diffuse layer (Gouy-Chapman layer), where the ions disperse into the surrounding solution because of their thermal movement. The central region diameter is approximately the full span of the stretched alkyl chain. The core can be described as being divided into a pair of sections: the central core and the external core. The external layer consists of approximately the first four methylene groups. An additional definable zone inside micelles, referred to as the palisade layer or mantle, surrounds the hydrophilic heads. According to the Hartley model, the total size of a micelle is approximately twice the size of the bottom layer (White *et al.*, 2007).

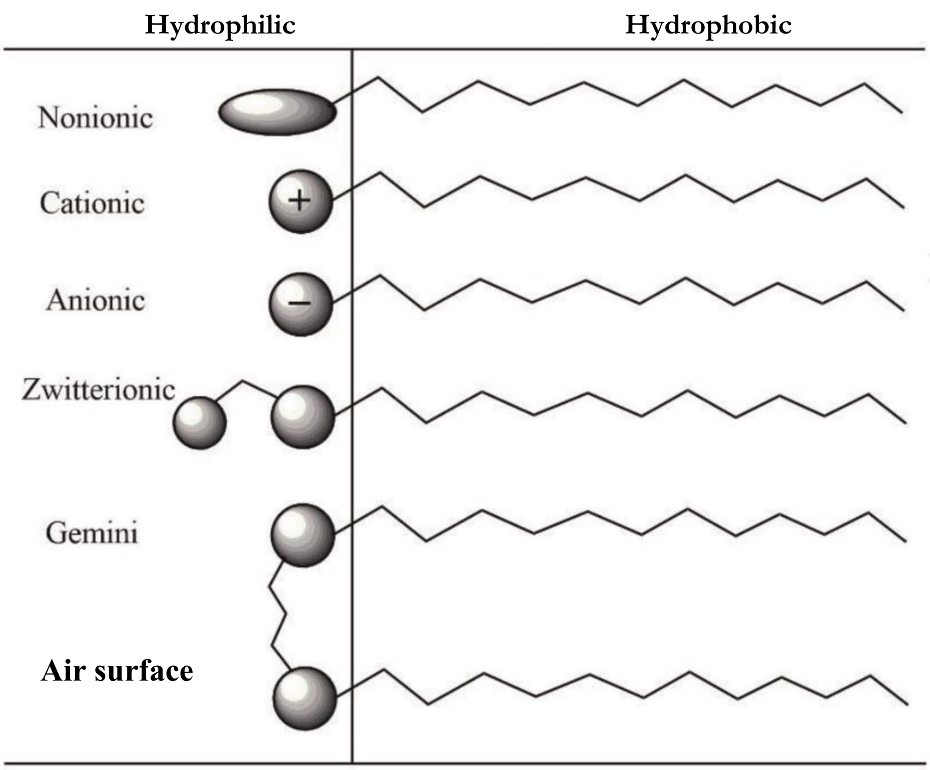

Figure 3. Different types of surfactants: Their hydrophobic and hydrophilic parts (Mandal, 2023).

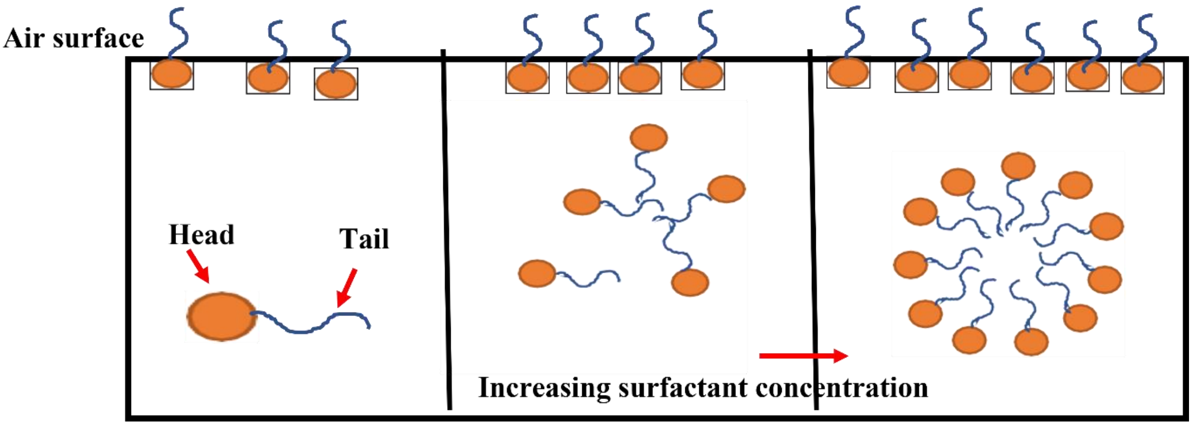

Figure 4. A schematic representation of micelle formation as surfactant concentration increases.

The form and dimensions of micelles are influenced by the design of the surfactant molecules and the electrical charge of their polar groups. Surfactants can aggregate into different structures depending on their concentration in the solution and their molecular configuration. The structures can encompass planar bilayers, spherical vesicles, and elongated, thread-like formations, among others (Mirgorod *et al.*, 2019).

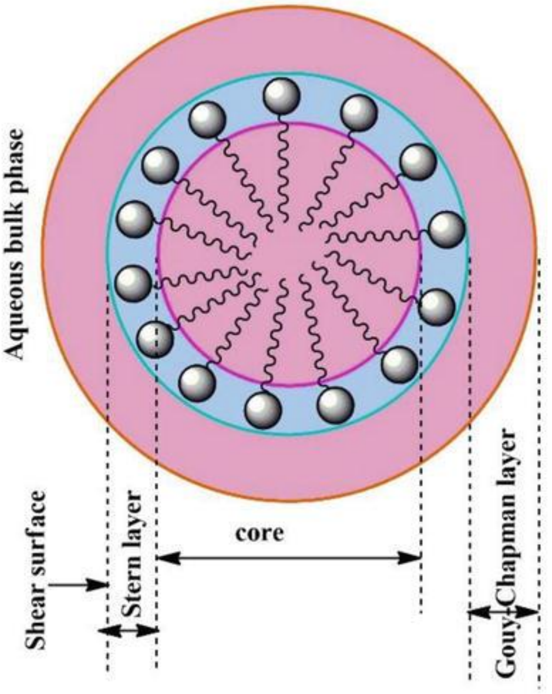

Figure 5. **Diagram of a standard charged micelle illustrating the position of the hydrophilic head, surfactant tail, and the positive ions (Mandal, 2023)**

Surfactants' ability to reduce surface tension and form self-assembled structures like micelles, bilayers, and adsorption films makes them crucial in corrosion inhibition. Surfactants are suitable for corrosion prevention. Surfactants adhere to metal surfaces, creating a protective barrier that inhibits contact between corrosive agents (e.g., oxygen, water, or chloride ions) and the metal (Song *et al.*, 2023). Surfactants form stable monolayers or micelles that shield the metal surface. Many surfactants are biodegradable and non-toxic, offering sustainable alternatives to conventional corrosion inhibitors. Surfactants are used in diverse industries, including oil and gas, marine, and construction, where metal corrosion is a significant challenge (D'Souza *et al.*, 2015).

In-Depth Analysis: Advancements in the understanding and application of surfactants have revealed the following mechanisms that contribute to corrosion inhibition: Ionic surfactants (e.g., cationic or anionic) form bonds with metal surfaces via electrostatic attraction, while nonionic surfactants adsorb through van der Waals forces or hydrogen bonding. Adsorbed surfactant layers act as barriers, suppressing both oxidation (anodic reaction) and reduction (cathodic reaction) processes that drive corrosion (Ramezanzadeh *et al.*, 2018). Combinations of surfactants and other inhibitors enhance corrosion resistance. For example, surfactants improve the dispersibility of nanoparticles or polymers, resulting in more effective protective coatings. The hydrophobic tail of surfactants repels water, limiting moisture interaction with the metal surface. Micelles formed by surfactants can encapsulate and isolate corrosive agents, such as chloride ions, preventing them from reaching the metal surface. Research has also shown that the performance of surfactants depends on their concentration, structure, and compatibility with the operating environment (e.g., pH, temperature, and electrolyte composition) (Migahed & Al-Sabagh, 2009).

Novel Insights: Recent advancements in surfactant technology and their mechanisms of corrosion inhibition have yielded several innovative findings. Customizing surfactant molecular structures (e.g., chain length, functional groups) improves adsorption strength and protective layer stability. Naturally derived surfactants, such as biosurfactants from microorganisms, show promise due to their high efficiency and environmental compatibility. Incorporating surfactants into self-healing polymeric coatings allows for automatic repair of micro-cracks, maintaining corrosion resistance over extended periods (Malik *et al.*, 2011). Surfactants combined with nanomaterials, like graphene or metal oxide nanoparticles, exhibit enhanced anticorrosion properties due to synergistic effects. Advanced modeling techniques provide insights into surfactant adsorption mechanisms, enabling the prediction of corrosion inhibition performance in specific environments. These advancements point to a future where surfactants play an increasingly vital role in corrosion management, offering sustainable, efficient, and customizable solutions for protecting metals in various industries (Kilo *et al.*, 2021).

Surfactants have revolutionized corrosion science by filling gaps in understanding interfacial interactions, offering environmentally friendly alternatives, and providing enhanced performance in complex environments (Shahi *et al.*, 2024). Their multifunctionality, adaptability, and compatibility with modern materials science pave the way for innovative and sustainable corrosion management solutions, meeting both scientific and industrial demands.

Aggregation plays a significant role in surfactant adsorption and corrosion inhibition (Zhu & Free, 2015). A model for predicting the corrosion inhibition efficiency of pure surfactants and mixed surfactants in aqueous media was developed and validated by Ning *et.al*, 2016. To develop a comprehensive model for predicting corrosion inhibition, a Langmuir adsorption (LA) sub-model was merged with a critical micelle concentration (CMC) prediction sub-model. The derivation of the model was demonstrated using an example involving mixed homologous benzalkonium chlorides (C_nCl) in aqueous media containing NaCl, and its validity was tested across multiple pure and mixed surfactant systems.

At varied NaCl concentrations, $C_{12}Cl$ and $C_{16}Cl$ mix equally with varying molar fractions of $C_{14}Cl$. Fig. 6 shows the data and model comparison, demonstrating the cmc model's broad applicability. This corrosion inhibition prediction model offers a potential way for evaluating the effectiveness of various surfactants in metal corrosion inhibition under a variety of aqueous media conditions (Ning *et al.*, 2016).

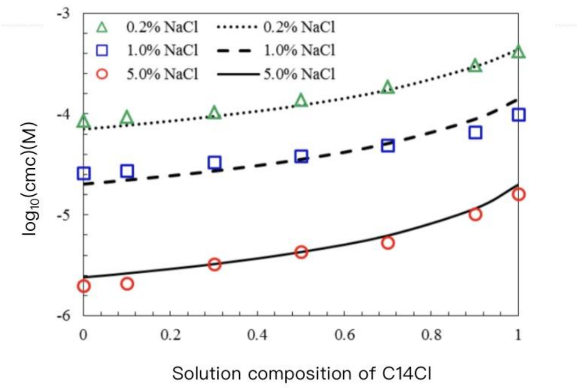

Figure 6. CMC versus solution composition of $C_{14}Cl$ in a ternary mixed $C_{12}Cl$, $C_{14}Cl$, and $C_{16}Cl$ in aqueous solution, where $C_{12}Cl$ and $C_{16}Cl$ are equal-molar mixture. Solid and dashed lines reflect model predictions, whereas symbols represent experimental data (Ning *et al.,* 2016)

Surfactants are known to have CMC. The CMC is the point at which the surfactants transition from their initial solvated molecular state in a solution. The characteristics of surfactant solutions undergo a sudden change at this concentration. The CMC is affected by various factors that depend on the characteristics of the surfactant and the surrounding aqueous environment. Among these important variables, the ion concentration of the solution is what causes the CMC value to shift to its fundamental worth of clean water.

As a result, the critical micelle concentration (CMC) plays a crucial role in determining surfactant efficiency in preventing corrosion. Under conditions below the critical micelle concentration (CMC), individual surface active agent particles generally adhere to open surfaces. The clustering at the surface reduces the cohesive forces, which helps in preventing deterioration. Beyond the critical micelle concentration, several monolayers (Fig. 7) cover the exterior, forming a protective coating over the metal interface. Thus, if more surface-active agent is introduced into the liquid beyond the critical micelle concentration, micelles or multiple strata adhering to interfaces will form. Consequently, the cohesive force at the liquid's surface and the concentration of the corrosive flow remains relatively constant above the critical micelle concentration (CMC). An effective surfactant blocker either clusters or adheres with minimal amounts. Alternatively, surface active agents with a low critical micelle concentration are favored due to their effective binding at lower levels.

The prevention of corrosion by surface active agent compounds is linked to their ability to form aggregates both at interfaces and within mixtures. To comprehend how surfactants inhibit corrosion, it is crucial to understand the factors influencing their aggregation and the state of these aggregates on metal surfaces. Surfactants generally tend to gather at boundaries and within mixtures. The degree of surface active agent clustering is possible to be evaluated by observing a reduction in the interfacial tension at the boundary between air and water. Heat plays a crucial role in both practical applications and theoretical considerations in biochemical reactions. The corrosion rate of iron and steel, like other chemical reactions, increases with temperature, especially in media where hydrogen evolution accompanies corrosion, such as when steel corrodes in acids. A study (Pumera, 2005) examined how temperature affects the corrosion behavior of aluminum in acidic environments with and without anionic surfactant concentrations. It is evident that corrosion efficiency rises with higher surfactant concentrations and falls as the temperature increases. This suggests that as the temperature rises, the adsorption of the corrosion inhibitor on the metal's exterior decreases, leading to faster degradation of the metal.

Mechanism

The process of preventing corrosion is intricate and depends on the formation of one- or multi-layered protective coatings on the metal's exterior. The protective characteristics of the outer layer are influenced by various factors, including the interaction between corrosion-resistant agents and the underlying material, the integration of the agents into the outer layer, chemical reactions, voltage differences, and the concentration of the agents, temperature, and the characteristics of the relevant surface, among others. The initial phase of how surfactants work as corrosion inhibitors in harsh environments involves the attachment of surfactant compounds to the metal's exterior. The process of adsorption is influenced by factors such as the metal's characteristics and its electrical charge, the surfactant's molecular composition, and the nature of the corrosive electrolyte. The attachment of these surface-active agent particles onto the metal is described by this equation:

Surfactant (in solution) + nH_2O (adsorbed) = Surfactant (adsorbed) + nH_2O (in solution)

Here, n represents the number of water molecules displaced from the metal surface per unit of surfactant used. The value of n is determined by the surfactant molecule's cross-sectional region in comparison to the water molecule. Surfactant molecules adsorb because their ability to interact energy with the metal surface is greater compared to that of water molecules. As a result, the inhibitory action of surfactants is attributed to surfactant compounds adsorbing to the metal interface through their functional groups. The rate at which adsorption occurs is typically fast, so the active metal surface is safeguarded against harsh conditions. The prevention of corrosion depends on how effectively surfactant substances adhere to the deteriorating surface, which is directly proportional to their ability to aggregate into micelles. The CMC is a crucial factor in evaluating the effectiveness of a corrosion prevention agent. As the surfactant concentration increases below the CMC, the particles begin to cluster at the boundary, reducing the cohesive forces at the surface. When the CMC is exceeded, the metal surface becomes covered by a single layer of surfactant agents, which blend to form micelles or multiple layers. Consequently, the surface tension and rate of metal deterioration remain constant. Gemini surfactants exhibit complex adsorption behavior on metal surfaces due to their combination of water-repellent and water-attracting groups. Fig. 8(a) illustrates the surfactant's behavior of adhering as individual particles at very low concentrations of the agent. Fig. 8(b) illustrates the surfactant's mechanism of forming hemimicelles at an intermediate concentration, the hemimicelle state within the surfactant. Fig. 8(c) illustrates the surfactant's mechanism of the development of multiple layers at very elevated concentrations of the inhibitor.

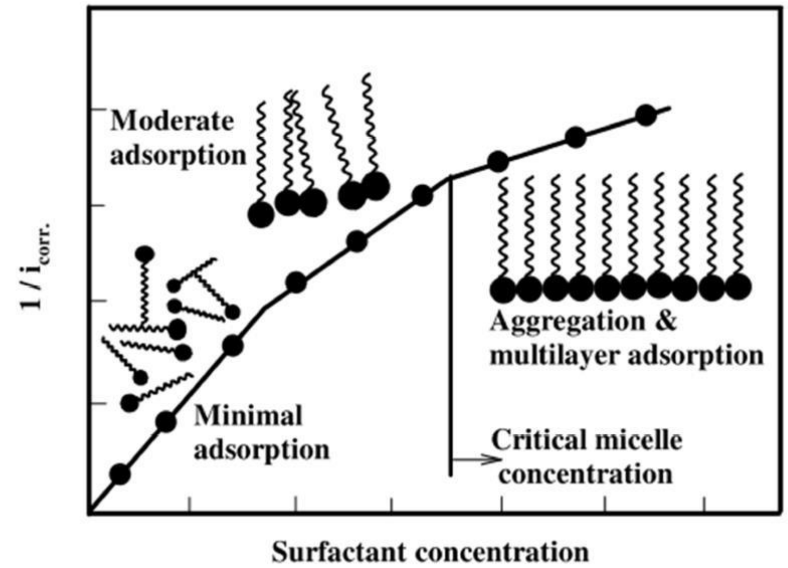

Figure 7. Impact of surface active agent levels regarding corrosion prevention (Malik *et al.*, 2011).

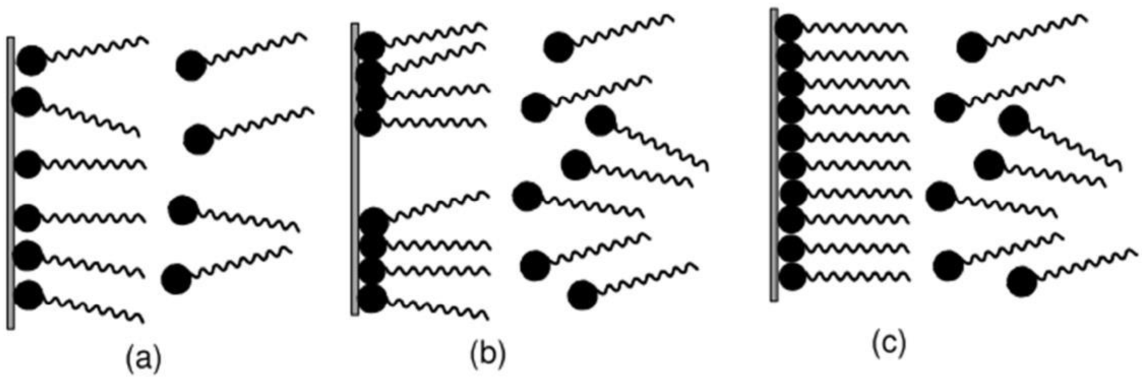

Figure 8 . Diagrammatic illustrations of the surfactant adsorption on a steel surface (Malik, *et al.,* 2011).

The diagrammatic illustrations of the surfactant adsorption process on a steel surface include: (a) the attachment of a single particle at a low concentration, (b) the appearance of hemi-micelles occurs at elevated concentrations, (c) the development of multiple layers at very elevated concentrations of the inhibitor.

Figure 9 shows how some anionic surfactants adsorb (a) Sodium octyl sulfate, (b) Sodium salt of decyl sulfate (c) Sodium dodecyl sulfate (d) Sodium salt of hexadecyl sulfate, and (e) Dodecylbenzene sulfonate, accordingly) (Elewady *et al.,* 2008). The sequence of effectiveness in inhibiting is as follows: (a) < (b) < (c) < (d) < (e). The larger molecular dimensions and increased electron concentration at the areas where molecules adhere could contribute to the higher corrosion inhibition efficiency.

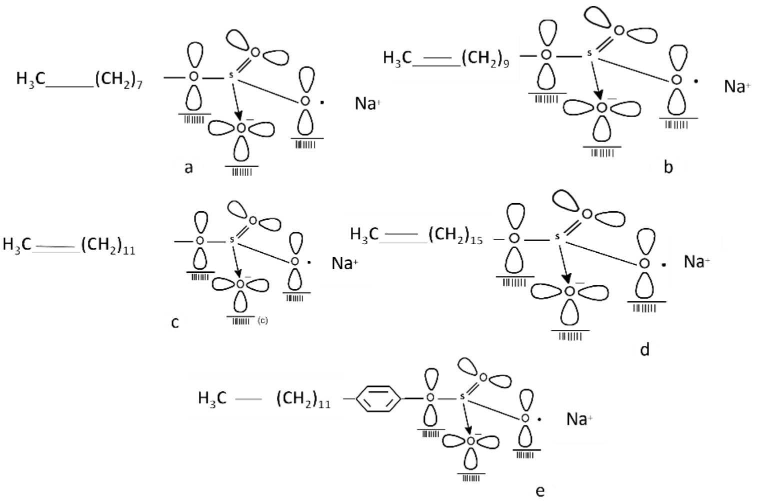

Figure 9. A diagrammatic depiction of how anionic surfactants adhere to surfaces(Malik *et al.*, 2011).

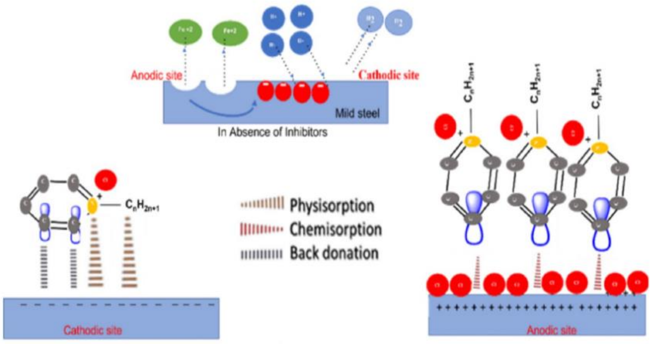

Figure 10. Mechanism of surfactant adsorption on the metal surface (Yadav, *et al.*, 2024)

In Fig. 10, the mechanism the protonated pyridinium group and carbon chain of CPC adsorb onto the MS surface, inhibiting iron dissolution. At anodic sites, iron undergoes e^-loss to the environment or acidic medium, resulting in rust formation on the metal surface, while at cathodic sites, the hydrogen evolution reaction is suppressed. This confirms the coexistence of anodic and cathodic sites on the metal surface, as illustrated in the upper section of Fig. 10. The multimodal inhibitory mechanism of CPC on metal is elaborated further on Fig. 10 (Yadav *et al.*, 2024). CPC molecules adsorb onto the metal surface and self-aggregate into surfactant micelles depending on their concentration. Chemisorption occurs between the π-orbital e^- of the pyridinium ring in CPC and the anodic site, while physisorption arises from the interaction of the nitrogen's π-orbital e^- in the CPC functional group with the cathodic site. Furthermore, back donation between the cathodic site and the π-π orbital e^- of the pyridinium ring in CPC enhances the interaction. These long-range interactions effectively cover the metal surface, as depicted in Fig. 10.

Surfactants as Corrosion Protectors

Surfactants as anti-corrosion agents are a highly investigated topic in the corrosion fields of science and engineering. The promising potential of surfactants for use as rust-preventing agents has been thoroughly explored in recent years. Surfactants are known to interact with each other at surfaces and in solutions, forming aggregates (Free, 2002). The techniques involving adsorption are crucial for preventing corrosion, and the main role of the surfactant's active component is to adhere to the metal surface.

Finding out that surfactant molecules adsorb to metallic surfaces and inhibit corrosion is often connected to their tendency to form micelles (D'Souza *et al.*, 2015). Therefore, gaining a clearer insight into how surfactant molecules adhere to metal surfaces and their role in preventing corrosion is crucial for both theoretical and practical purposes. To prevent corrosion, inhibitors should be continuously introduced into the systems (Pon-On *et al.*, 2008). Several studies have used surfactants to decrease steel corrosion in acidic conditions. Adding surfactants to an acidic environment is a cost-effective and efficient method for preventing rust on metallic materials. The capability of surfactants to dissolve organic substances and affect various electrical processes in water was demonstrated in the 1950s. Over the last two decades, research has concentrated on designing electrochemical interactions using surfactants and describing aggregates using electrochemical means. This research focuses on controlling electrostatic catalysis through its minuscule structures. Studies show that surfactants may neutralize electrochemically generated ion radicals through columbic and hydrophobic interactions (Alagta *et al.*, 2008). Surfactants were incorporated into this scientific area to provide a new and advantageous aspect to the discoveries. The impact of surfactants on altering electrode surfaces has been underexplored in research. Researchers studying surfactants in micelle systems have recently concentrated on understanding or utilizing the aggregates that develop on the electrode surface. Surfactant particles typically gather at the boundary between two distinct phases, such as the interface between gas and liquid, immiscible liquids, or an electrolyte and a liquid. The presence of surfactants on electrodes can significantly affect electrochemical processes in these systems (Bentiss *et al.*, 2009).

Surfactants are used in various applications, serving as emulsifiers and dispersants. Their diverse and particular applications are thoroughly detailed in the research studies that have thoroughly documented the catalytic effects in chemical processes within micellar and polymeric environments (Rahal *et al.*, 2018). Surface-active agent clusters assist in dispersing chemicals, a typical occurrence involving electricity and chemical reactions. In the field of electroanalytical chemistry, gelatin, and Triton X-100 were frequently utilized to minimize the observed flow effect at the dropping mercury electrode (DME) before Heyrovsky developed polarography (Li *et al.*, 2019). The initial significant research on the influence of surface-active agents emerged within the realm of organic electrochemical science. SDS was shown to effectively prevent the deterioration of copper in acidic environments. The electrochemical analysis showed that SDS served as a potent anodic inhibitor at lower anodic excess voltages, with the inhibitor adhering according to a Langmuir adsorption model . In the context of measuring weight loss, SDS was identified as an effective suppressant of nickel in acidic environments. As the concentration of SDS increased, the surface active agent's ability to inhibit nickel improved. Recent findings have revealed that the primary reason for enhanced corrosion prevention is the attachment of negatively charged surfactants, like SDS, to an aluminum surface.

Micelles made from extended-length quaternary ammonium bromides, such as CTAB, have been found to prevent the corrosion of steel. As long as the concentration exceeds the CMC, the corrosion inhibition becomes more effective with an increase in the length of the alkyl chain of the surfactant. del Río et al. (2024) recently shown that CTAB has a positive influence on electrochemical film development. They explained that the CTAB-promoted layer improved the energy conversion efficiency of solar cells sensitive to dye. In Fig. 11 (a) and (b), the top-down SEM images of heat-treated TiO2, both with and without CTAB, show that each film consists of groups of nearly round, non-aligned, irregularly interconnected, and sparsely assembled tiny units. On the other hand, films produced via precipitation from digested TiCl4 mixtures typically yield rod-like components (Wang *et al.*, 2012). Regardless of whether TiCl3 or TiCl4 was used as the precursor, the top-down SEM photographs captured were almost identical. However, the simultaneous inclusion of CTAB significantly enhanced the layer depth (Goldraich *et al.*, 1997), as indicated by Fig. 11 (c) and (d). This suggests that the surfactant has a beneficial impact on the electro-deposition process.

According to Bashir *et al.* (2017) cetyl pyridinium chlorides (CPC), a cationic surfactant, demonstrated significant efficacy in preventing corrosion of low carbon steel in a 1M H_2SO_4 solution, with protective rates reaching as high as 97%. El Achouri and colleagues developed Gemini surface-active agents called 1,2-ethanediyl bis-(dimethylalkylammonium bromide) and studied their effectiveness in inhibiting iron degradation in hydrochloric acid. They discovered that such substances act as effective inhibitors of iron rusting, achieving their highest level of effectiveness near the critical micelle concentration of those substances. Utilizing surfactants in acidic environments frequently turns out to be the most effective and cost-efficient method for preventing rust on metals. The primary way corrosion inhibitors function is by forming a layer that sticks to the metal surface, thereby offering protection. Liu and colleagues demonstrated that a polyaniline-4-dodecyl-phenol complex (PANI-DDPH) without doping functions effectively serves as a rust prevention agent. They also found that the surfactant enhances the moisture-based bond with the metal surface and the coating.

Gemini surface active agents have garnered significant interest recently due to their inclusion of a pair of water-attracting groups and a pair of water-repelling groups within a single compound. These clusters are connected by either a rigid or flexible spacer, unlike conventional surfactants, which typically have only one water-attracting component and one water-repelling component. These molecules are more effective in reducing surface tension and forming micelles. Gemini surfactants possess unique advantages over conventional single-chain surfactants, including lower critical micelle concentrations (CMCs), enhanced wetting properties, and superior effectiveness in reducing the surface tension of water. Farhat and his team studied three specific gemini surfactants: N-hexane-diyl-1,2-ethane-bis ammonium bromide (HEAB), N-dodecane-diyl-1,2-ethane-bis ammonium bromide (DDEAB), and N-hexadecane-diyl-1,2-ethane-bis ammonium bromide (HDEAB). D'Souza *et al.* (2015) examined to establish them as unique anti-corrosion agents for mild steel in 20% formic acid. Electrochemical tests were employed to assess the inhibitory efficiency of these Gemini surface active agents. Scanning electron microscopy was used to explore surface adsorption processes. The SEM in Fig. 12 indicates that each of the Gemini surface active agents acts as a protector against rust for mild steel. The effectiveness of suppression is related to the sequence of the critical micelle concentrations (CMCs) of these substances (Jia *et al.*, 2019).

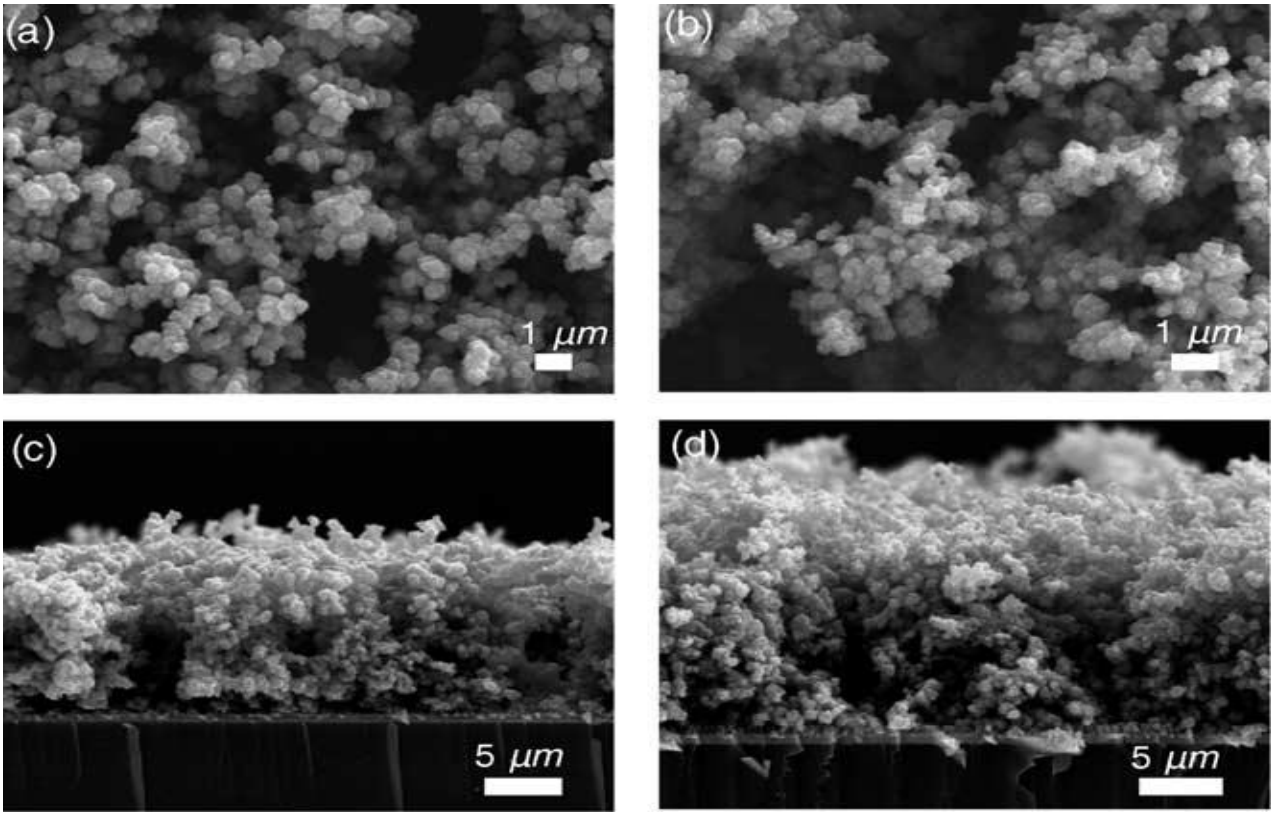

Figure 11. The FE-SEM pictures of the electrically deposited and tempered TiO2 film, made from TiCl4, show basic and horizontal views: (a, c) the absence of CTAB and (b, d) the presence of it (Malik *et al.*, 2011).

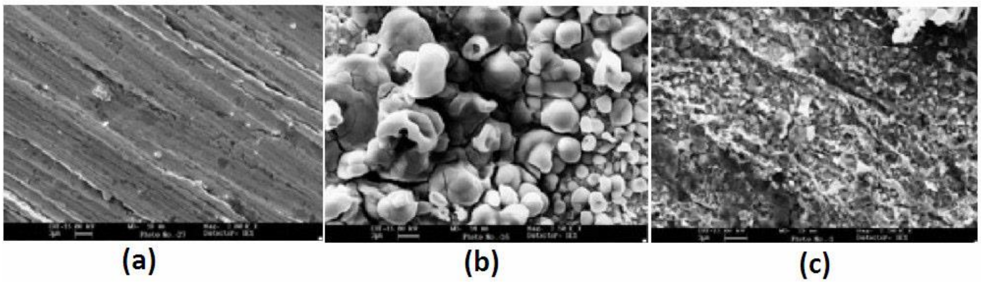

Figure 12. The way Gemini surfactants attach to the surface of mild steel (Malik *et al.,* 2011).

Electrochemical studies revealed that the inhibitors bind to the air-water interface and form a protective layer on the metal surface. All the inhibitors discussed effectively prevent corrosion through an adsorption mechanism, which follows Langmuir's adsorption isotherm. Additionally, Scanning Electron Microscopy (SEM) shows that the coated metal surfaces appear smoother compared to the unprotected metal surfaces due to the formation of the protective layer (Prélot & Zemb, 2005).

Fayomi *et al.* (2017) investigated the effects of the eco-friendly surfactant alkyl polyglucoside (APG) on the deterioration of carbon steel with a designation of 907 when exposed to ambient seawater. They employed voltage-current curve analysis and performed mass-loss tests in their study. The research shows that the eco-friendly surface active agent APG can lessen the degradation of 907 carbon steel in stagnant, untreated seawater. By combining APG with calcium gluconate and zinc sulfate, the effectiveness of rust prevention increased significantly, even with a much smaller quantity of APG used. APG, calcium gluconate, and zinc sulfate demonstrated a notable combined effect. The rust-preventive agent inhibited reactions at both the anode and the cathode, indicating it is a combined-mode inhibitor. The corrosion-protective agent may function as a substance that adheres to surfaces, forming a layer over the metal. The primary role was achieved by the absorbing film. Brij 56, an uncharged surface active agent, or Pluronic P123, which is a type of triblock copolymer, guided the deposition of porous nickel layers onto foam nickel substrates. The technique showed a 30- to 35-fold increase in the area of three-dimensional structures. This enhancement is beneficial for various applications including chemical sensors, energy storage devices, and power generators. By using a water-soluble solution of nickel(II) acetate combined with the liquid crystallized templates Brij 56 and Brij 78, metallic nickel was electrodeposited. In comparison to samples developed without the use of a tailoring electrolytic solution, it was discovered the total electrochemically reachable surface area of this nickel sheet was 100 times larger. Di dodecyl benzyl triethyl ammonium chloride (CS) is a new cationic surfactant chemical that (Loginova *et al.*, 2021) have studied. It effectively inhibits carbon steel corrosion. Wang *et al.* (2012) investigated how surfactants affect electroplating by cleaning metallic surfaces and speeding up hydrogen production at the electrode. It is common practice to use fatty alcohol ethoxylates and sulfates, and occasionally alkyl benzene sulfonates as well. The advantageous effects of fluorosurfactants in electroplating were especially important due to their chemical durability. Surfactants were utilized in the electroplating enterprise due to their numerous advantageous advantages (Goldraich *et al.*, 1997). By altering the crystal structure of the coated metal, the final plate becomes brighter, and the liquid's cohesive forces are reduced. The reduced surface cohesion of the liquid makes it easier for air pockets to detach from the electrode, thereby preventing problems like scouring and pinhole formation. This also cleans the metal surface before plating, such as when using nickel baths for plating. The most effective deposits are achieved when the surface tension is minimized, which can be accomplished by adding surfactants.

Uchida and collaborators have secured a patent for a gold–tin alloy coating solution that does not use cyanide. The invention includes a mixture containing gold chloride, a mixture containing tin chloride, and other components. The bath also includes a polymeric cationic surfactant or agent that enhances the luster and reflow characteristics of the coating. Surface-active agents can reduce or remove the need for smoothing (removing imperfections from the surface) when applying Ag, Au, and Cu using a basic solution of double cyanide compounds, a process that is typically necessary to achieve a shiny, refined finish. Agents that reduce surface tension impact the reduction of polarization in coatings applied through electroplating and affect the efficiency of the deposition processes. Surfactants can affect the polarization characteristics at the cathode and influence the uniformity of the surface, as well as impact the size of the crystals, their growth rate, and how well the crystals adhere to both the underlying material and each other. Parekh *et al.* (2011) have developed an innovative metal coating method that uses nonionic surfactants to create high-quality nickel films. This method results in coatings with greater consistency, smaller particle sizes (below 100 nanometers), and enhanced hardness as measured by the Vickers scale, surpassing the quality of coatings produced by traditional electroplating techniques that do not incorporate surfactant. Surfactant solutions are important for electrodes covered with mineral layers. Naturally occurring clays, which are structured with layers of aluminosilicate materials that exchange cations, can absorb cationic surfactants. The surfactants create a double-layer or partial micelle layer on the surface of the clay particles. Clay colloids treated with surfactants can absorb non-polar substances. The process of coating pyrolytic graphite (PG) with a 500 nm-thick layer of colloidal sodium bentonite has produced clay-modified electrochemical (CMEs). The CMEs absorbed Tris(2,2'-bipyridyl) cobalt (II) ions both with and without the presence of CTAB micelles (Suib, 1988). It showed distinct cyclic voltammetry reduction signals at -1.2 V for Co(II) and at -1.5 V for Co(I). Abdel-Gaber *et al.* (2020) created layers of tetraalkylammonium surfactant films inserted among particulate clay sheets, which were utilized as barriers with controlled passage. Rahal *et al.* (2018) examined the effects of negatively charged surfactants, including sodium dodecyl sulfonate (DSASS), sodium dodecyl benzene sulfonate (DBSASS), and sodium dodecyl sulfate (SDS), on aluminum surfaces. It was demonstrated that surfactants play a crucial role in inhibiting corrosion. When the amount of surfactants reaches their CMC, aluminum exhibits the highest level of adsorption, minimal weight loss, and the most robust corrosion resistance. Additionally, adsorption rules align with the Langmuir equation when using a direct adsorption mode, with the hydrophilic component oriented towards the aluminum interface and the hydrophobic component oriented towards the surrounding medium. Various surface-active agents that act to prevent rusting also have antimicrobial characteristics. Using electrochemical impedance spectroscopy (EIS), Malik *et al.* (2011) investigated the effects of sodium dodecyl sulfate (SDS), polysorbate 80, and sodium oleate, with cetyltrimethylammonium bromide (CTAB) on copper degradation. It was found that the combined action of positively charged ammonium ions and bromide ions was the reason CTAB was an effective agent. (Maayta & Al-Rawashdeh, 2004) measured the rates at which carbon steel corrodes, both with and without SDS and zinc ions in water. Research has been conducted on the effects of ethanol, n-butanol, and sodium dodecyl sulfate (SDS) in suppressing nickel corrosion. Researchers Abd-El-Rehim and colleagues discovered that within the temperature range of 10-60° C, the deterioration of Al alloy in 1M HCl is slowed down by the adhesion of the negatively charged surface active agent SDS to the metal's surface, while still maintaining the fundamental corrosion process.

The effect of SDS on copper corrosion was examined with and without benzotriazole, using techniques such as EIS and analysis of surface tension properties. Rahal *et al.*, 2023 and colleagues assessed the effectiveness of SDS in preventing the degradation of carbon steel submerged in a sodium chloride solution with a concentration of 60 mg/l, both with and without Zn^{2+} present. The FTIR spectrum has shown that the film contains a complex of iron and SDS, as well as zinc hydroxide.

Abdel-Gaber *et al.* (2024) investigated the effectiveness of different inhibitors in preventing corrosion of Al alloy (AA 6351) in a 0.01 molar NaCl solution. The substances analyzed include sodium salts of N-dodecanoyl-N-methylglycine (NLS), dodecyl sulfate (LS), N-dodecanoyl-N-methyltaurine (NLT), and dodecylbenzene sulfonate (DBS). The creation of hemimicellar gathering, which induces blocker adsorption from the metal/solution interface at greater levels, has been identified as the cause of the synergism and antagonistic effects of sodium dodecylbenzene sulfonate along with hexamethylene tetramine in preventing of simple steel corrosion (Hosseini *et al.*, 2003). Malik *et al.* (2011) research demonstrates how the addition of zinc (II) ion to rainfall impacts the interaction between HEDP and SDS in order to prevent carbon steel from deteriorating. Their tasks include: (i) assessing the antimicrobial and inhibition efficacy of the SDS-Zn2+ system concerning the deterioration of carbon steel in a 120 mg/l chloride solution; (ii) investigating the antimicrobial efficacy of N-cetyl-N, N,N-trimethylammonium bromide [CTAB] and N-cetyl pyridinium chloride [CPC] in the presence of the blocking system and their impact on the IE of the SDS-Zn^{2+} system; (iii) utilizing FTIR and UV spectra for examining the protective layer on carbon steel; (iv) employing polarization potential examinations and AC impedance inspection to comprehend the biological aspects of corrosion inhibition; and (v) suggesting an appropriate method for deterioration inhibition. Corrosion protection can be compared using different types of surfactants as shown in Table 1.

Table 1. Comparison of corrosion protection using different types of surfactants

PSA surfactants (cationic benzene sulphonamide surfactants)	1. Experimental results showed that PSA surfactants had an inhibition capacity of 92.8–97.0%, indicating that removing the CN group significantly improved their corrosion inhibition efficiency.	1. Shalabi *et al.* (2024).
Cationic surfactants	1. Cationic surfactants have a positive charge and adsorb to materials with a negative charge. They can be used to protect carbon steel surfaces.	1. Shalabi *et al.* (2024).
	2. Cetyltrimethylammonium chloride proved to be an effective inhibitor for aluminum corrosion. Similarly, cationic surfactants derived from dimethylaminopropylamine were utilized as corrosion inhibitors for carbon steel in 1.0 M HCl, with their effectiveness increasing proportionally with both the inhibitor concentration and the length of the hydrophobic chain.	2. Al-Rawashdeh & A.K. Maayta (2005).
	3. 1-Dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide demonstrated excellent corrosion inhibition for carbon steel in a 7 M H3PO4 solution.	3. Shaban *et al.* (2015).
	4. Modified vanillin Schiff bases, as cationic inhibitors, effectively reduced carbon steel corrosion in 1 N HCl.	4. Hegazy (2015). Negm *et al.* (2011).
Anionic surfactants	1. Anionic surfactants have a negative charge on their hydrophilic end, which helps them suspend and lift soils in micelles. Examples of anionic surfactants include alkyl sulfates, sulfonates, carboxylates, and betaines. Surfactants can inhibit corrosion by reducing the electrochemical activity of a metal surface. This can be done by reducing the rate of ion transport across the metal-solution interface, or by reducing the rate of anodic or cathodic reactions.	1. Farahmand *et al.* (2018).
	2. The three anionic surfactants studied—Diisononyl phthalate, Sodium lauryl sulfate, and N-oleyl-1,3-propane-diamine—demonstrated strong corrosion inhibition for carbon steel in an HCl medium.	2. Assem *et al.* (2018).
	3.Examples of anionic surfactants, such as octyl sulfate sodium salt, decyl sulfate sodium salt, dodecyl sulfate sodium salt, hexadecyl sulfate sodium salt, and dodecyl benzene sulfonate, have been shown to act as effective corrosion inhibitors for aluminum in a hydrochloric acid medium.	3. Elewady *et al.* (2008).
	4. The novel anionic surfactant, 4-Tert-Octyl Phenol Ethoxylate Phosphate, exhibited excellent corrosion inhibition for carbon steel in an HCl medium.	4. Fouda *et al.* (2020).

	5. The anionic surfactant p-myristyloxy carbonyl methoxy p'-sodium carboxylate-azobenzene effectively inhibited the corrosion of mild steel in a 1 M sulfuric acid solution.	5. Migahed *et al.* (2004).
Gemini surfactants	1. Gemini surfactants work well to prevent corrosion in stainless and carbon steel. Gemini surfactants prevent metals from corroding in organic and mineral acids. In seawater, Gemini surfactants prevent metals from corroding.	1. Brycki & Szulc (2021).
	2. Anti-corrosion properties of Gemini surfactants on Aluminum in 1.0 M HCl medium were investigated. Then efficiency has found in 47.13 %.	2. Shaban *et al.* (2021).

CONCLUSIONS

a. Surfactants as Corrosion Preventers: Surfactants are highly efficient and environmentally friendly agents for preventing corrosion.

b. Adhesion and Micelle Formation: Surfactant molecules have a strong tendency to adhere to interfaces and form micelles.

c. Interfacial Applications: This property makes surfactants useful in various interfacial structures.

d. Anti-Corrosion Suitability: Their unique properties make them particularly effective as anti-corrosion agents on metal surfaces.

e. Industry Benefits: Novel anticorrosion properties of surfactants can help address corrosion issues, reducing material and financial losses in industries.

FUTURE PERSPECTIVES

This review paper has significant advancements in the use of surfactants as corrosion inhibitors, but there remains a vast potential for further research aimed at enhancing their effectiveness. Additionally, future studies could focus on expanding their applicability by exploring the following aspects.

Novel Surfactant Formulations

Developing and testing novel surfactants, particularly those made from sustainable and biodegradable materials, is essential. This approach would enhance corrosion protection while also addressing the environmental issues associated with conventional surfactants.

a) Molecular-Level Understanding:
Advances in computational chemistry and simulations of molecular dynamics could provide deeper insights into how surfactants interact with metal surfaces. This understanding could lead to the design of more efficient surfactant-based inhibitors tailored to specific environments.

b) Synergistic Effects with Other Inhibitors:
Future research could explore the synergistic effects of surfactants in conjunction with various other corrosion inhibitors, including both organic and inorganic compounds. By pursuing this strategy, it may be possible to develop multi-functional corrosion protection systems that offer improved efficacy.

c) Field Applications and Long-Term Studies:
Although laboratory research has demonstrated encouraging outcomes, there is a need for long-term field studies to evaluate the real-world effectiveness of surfactant-based corrosion inhibitors under various environmental conditions. Furthermore, it is essential to assess the economic viability of applying these inhibitors on a large scale.

d) Smart and Responsive Surfactants:
The development of smart surfactants capable of reacting to environmental changes, such as pH, temperature, or the presence of corrosive agents, has the potential to provide a flexible and adaptive method for corrosion protection. These responsive surfactants could be engineered to activate only when needed, thereby extending the lifespan of protective coatings.

e) Regulatory and Safety Considerations:
As surfactants are introduced into various industrial applications, addressing regulatory requirements and safety standards is essential. Future work should include evaluating the potential health and environmental effects of new surfactant formulations to confirm they meet international regulatory standards.

While significant progress has been made in understanding the protective effects of surfactants against corrosion, there is still room for innovation. Continued interdisciplinary research and collaboration between academia and industry will be essential to unlock the full potential of surfactants as effective and sustainable corrosion inhibitors.

AUTHOR CONTRIBUTIONS

MKA, SC, and CKY: Contributed to the design of the draft, collected the review paper, and conceptual framework development; APY and AB: Responsible for figures designed, involved in reviewing and editing the manuscript.

CONFLICT OF INTEREST

There are no conflicts of interest to declare.

DATA AVAILABILITY STATEMENT

All the data are included in the manuscript and are available for the readers.

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