Corrosion problem is one of the main concerns for energy and material loss during the service life of many engineering structures. The direct cost of corrosion is about 4.2% of the gross national products (approximately $100 billion in USA and around €200 billion in Europe). Mild steel (MS), which is widely used in the petroleum industry, automobile bodies, construction of buildings and pipes and fabrication of weaponry, is liable to bear different kinds of corrosion attack due to exposure to various corrosive environments. Their service life can be lengthening by the surface treatments. Among these treatments, employment of corrosion inhibitors is preferred.

The chemical inhibitors have widely been employed in the protection and mitigation approaches for inhibiting corrosion. The corrosion inhibitors are the chemical substances which work at the interface of the corrosive media and the metal surface and retard the corrosion rate when present in the corrosive system at a suitable concentration. Both inorganic and organic compounds have been substantially used as excellent inhibitors. Though, various corrosion inhibitors are nitrogen or sulphur based compounds, containing inherent toxic properties. As such their usage is against modern safety regulation for the industrial chemicals with severe criticism.

Organic corrosion inhibitors are generally used as replacements for inorganic compounds in the control of dissolution of the metals in aqueous media. The huge interest in this class of compounds has continued to grow in the last decade as naturally occurring and some synthetic compounds as well as their products meet the environmental requirements for safe product application with good corrosion inhibiting potential and infinitesimally small/reduced or zero pollution risk. The presence of heteroatoms and π-electrons in their molecular structure favour their adsorption on the metal substrate. Among the variety of organic compounds used as corrosion inhibitors, surfactants (having one head group and one hydrophobic group) have gained wide acceptance in the recent past, due to their ease of production, cost effectiveness and relatively high inhibition efficiencies. As a result, over the last few decades new surfactants molecules are being synthesized at relatively rapid pace. The inhibitory effect of the surfactants generally increases with increasing concentration and hydrophobic chain length up to critical micelle concentration (CMC); above CMC the inhibition effect remain almost constant. Non-ionic surfactants, which have no apparent charge on the head group, have notable lower critical micelle
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Concentrations (CMCs) in comparison to the analogous ionic surfactants. Non-ionic surfactants are reported to possess high inhibition efficiencies for corrosion of metals in various aggressive solutions. Generally, the surfactant having lower CMC value has greater adsorption capability. However, with increasing concern on environmental pollution and human health, the practice of the surfactants as corrosion inhibitor has been limited to some extent owing to their toxicity. The above fact has inspired the researchers for the search/development of less toxic, environmentally compatible surfactants with desired surfactant properties and hassled to various reports on the synthesis of gemini surfactants (with of two amphiphilic moieties joined at the level of, or close to, the head groups by a spacer group). Gemini surfactant exhibits higher functionalities such as low CMC value, high solubilisation value and interfacial activity than their monomeric counterpart. These gemini surfactants have attracted considerable interest as corrosion inhibitors for iron and steel in various corrosive medium and proved to be much superior as corrosion inhibitor compared to the monomeric counterpart and extremely efficient even at very low concentration. However, one of the limitations associated with gemini surfactants have been their non-biodegradable nature. Attempts have been made to convert non-biodegradable gemini surfactants into biodegradable eco-friendly compounds by introduction of cleavable ester bonds in their chemical structure or by synthesizing gemini surfactants from natural building blocks like simple sugars and amino acids. Though limited number of references are available dealing with corrosion inhibition studies of amino acid based surfactants, the cleavable ester bonded gemini and sugar based surfactants have yet not been exploited as corrosion inhibitor to the best of our knowledge.

In addition, the idea of implementation of synergism in corrosion inhibition studies is also of great importance as it helps in improvement in the inhibitive force of an inhibitor, decrease in the amount of inhibitor usage and diversifies the application of the inhibitor. Corrosion researchers have been exploring the possibilities of synergism in the complicated corrosive media as it plays an important role in theoretical research on corrosion inhibitors as well as in practical work where inhibition efficacy of many organic compounds having low to moderate efficiency can be enhanced. The cations and anions have been extensively evaluated for their possible synergistic effect with metal corrosion inhibitors. It is an established fact that addition of chemicals such as salts reduces the dose of surfactants thus cost of
application process. Generally, addition of salts additives in corrosive media has resulted in an increase in the inhibition effect of surfactants for MS corrosion. The principle focus of salt addition to surfactant is to maximise its adsorption while minimising the aqueous inhibitor concentration.

This study reports on three monomeric surfactant (i.e., two sugar based \( N \)-decyl-\( N' \)-glucosylethlenediamine designated as Glu (10) and \( N \)-doceyl-\( N' \)-glucosylethlenediamine designated as Glu (12) and one amino acid based \( N \)-dodecyl cysteine counterpart, designated as (C\(_{12}\)Cys)) and 7 gemini surfactants (i.e., three cationic gemini surfactants having ester linkage in the spacer namely, ethane-1,2-diylbis(\( N,N \)-dimethyl-\( N \)-dodecylammoniumacetoxy)dichloride designated as (12-E2-12), ethane-1,2-diylbis(\( N,N \)-dimethyl-\( N \)-tetradecylammoniumacetoxy)dichloride designated as (14-E2-14), ethane-1,2-diylbis(\( N,N \)-dimethyl-\( N \)-hexadecylammoniumacetoxy)dichloride designated as (16-E2-16); two ester based cationic pyridinium gemini surfactants namely, 4,4′-(propane-1,3-diyl) bis(1-(2-(tetradecyloxy)-2-oxoethyl) dipyridinium chloride designated as 14-Py and 4,4′-(propane-1,3-diyl) bis(1-(2-(hexadecyloxy)-2-oxoethyl) dipyridinium chloride designated as 16-Py; one sugar based gemini surfactant \( N,N' \)-dido decy1-\( N,N' \)-digluconamideethylenediamine, designated as Glu(12)-2-Glu(12) and one amino acid based gemini surfactant \( N,N' \)-dialkylcystine designated as 2(C\(_{12}\)Cys) as corrosion inhibitors for MS in 1M HCl/3.5% NaCl solutions. The techniques used are weight loss and electrochemical (PDP, EIS) measurements, spectroscopic (UV-vis, FT-IR), surface morphological studies (SEM/EDX/AFM), theoretical quantum chemical calculations and Monte Carlo simulations. The inhibitors are differed in their alkyl chain and functional groups. The investigations were done to test their inhibition ability and adsorption characteristics with MS. The study was also extended to investigate the adsorption isotherms, influence of temperature on the corrosion process and evaluation of some thermodynamic and activation parameters using the results of the gravimetric analysis. During the course of exploration of the adsorption behaviour of investigated compounds, which were completely novel corrosion inhibitors, inorganic (sodium iodide and potassium iodide) and organic (sodium salicylate) salts were added to some of the corrosion inhibition systems that gave rise to synergistic effects.
The breakup of the work contained in various chapters is as follows:-

**Chapter I**

This chapter is devoted to general introduction, which has been divided into three sections. Section I focuses on the basics of corrosion and corrosion control and includes definition of corrosion, cost of corrosion, different form of corrosion, electrochemical theory of corrosion and mitigation of corrosion. Section II deals with the corrosion inhibitors and their inhibition action and includes classification of corrosion inhibitors, green corrosion inhibitors and mechanism of inhibitive action of organic inhibitors. Section III focuses on surfactants as corrosion inhibitors and includes surfactants and their classification, gemini surfactants, exhaustive literature survey on gemini surfactants as corrosion inhibitors, synergism consideration in corrosion inhibition and scope and objectives of the present work. Except for some early pioneering research papers, the thesis include literature survey from the selected research papers, reviews and reports published on the subject during the last two decade. Special emphasis has been laid to the work which has direct or indirect bearing on the studies presented in this thesis. It might be possible that some results of the important studies have been left unquoted quite unintentionally, yet there was absolutely no intension to undermine those works.

**Chapter II**

This chapter is devoted to the experimental details, which highlights the materials and methods used during the experimental work. It includes the procedure of synthesis of monomeric and gemini surfactants, their characterization and details of techniques which were undertaken to investigate the corrosion inhibition behavior of synthesized surfactants.

**Chapter III**

The work presented in this chapter deals with the corrosion inhibition effect of three ester bonded cationic gemini surfactants (labelled as m-E2-m; where E2 is the diester group in gemini's spacer part and m = 12, 14, 16 the number of carbon atoms in alkyl tail) for MS in 1M HCl solutions at 30-60°C using weight loss measurements, electrochemical (PDP, EIS) studies, spectroscopic (UV-vis, FT-IR) studies, surface morphological (SEM, EDX) studies and quantum chemical calculations. The thermal behaviour and stability of m-E2-m was distinguished by thermo gravimetric (TG)
Abstract

analysis at elevated temperatures. Further, to maximise the adsorption of studied inhibitors while minimising the aqueous inhibitor concentration, the effect of sodium salicylate (NaSal) on inhibition effect of m-E2-m has also been examined.

The results of weight loss, potentiodynamic polarization and impedance spectroscopic measurements suggest that all the three studied gemini surfactants possess great inhibition efficiencies for MS in 1M HCl solution. Inhibition efficiency increases with increase in inhibitor concentration, solution temperature and hydrophobic chain length and followed the order: **16-E2-16 > 14-E2-14 > 12-E2-12**

The increase in inhibition efficiency with increasing gemini surfactants concentration indicates greater adsorption of inhibitor molecules forming a protective film at MS surface. The increase in inhibition efficiency with increasing solution temperature confirmed the ability of surfactants to inhibit steel corrosion in HCl at relatively high temperature and supports chemisorptions. The higher inhibition efficiency of 16-E2-16 compared to 14-E2-14 and 12-E2-12 is attributed to longer hydrophobic chain length. It is observed that the inhibition efficiency of mixed m-E2-m surfactants and NaSal is more than m-E2-m surfactants or NaSal alone. The order of percentage inhibition efficiency increase is: **NaSal+16-E2-16 > NaSal+14-E2-14 > NaSal+12-E2-12**

The adsorption of m-E2-m surfactants on MS surface in HCl solution obeys the Langmuir adsorption isotherm at all the temperatures. Thermodynamic and activation parameter like $\Delta G^\circ_{\text{ads}}$ and $E_a$ revealed that the spontaneous adsorption of m-E2-m on MS was mixed type and predominantly chemical in nature. The $\Delta H$ and $\Delta S$ values of adsorption and activation suggest that adsorption process was endothermic accompanied by a decrease in entropy. m-E2-m gemini surfactants are mixed-type inhibitors, according to results of corrosion potential obtained from potentiodynamic polarization. The decreasing values of $C_{\text{dl}}$ and increasing values of $R_{\text{ct}}$ obtained during EIS measurements, suggests formation of protective layer over the MS surface.

The UV-Visible and FT-IR results further confirmed the presence of the adsorbed m-E2-m films on MS surface. TG analysis showed that the surface inhibitor film possesses relatively higher thermal stability. SEM micrographs displayed clearly different morphology in presence of m-E2-m and confirmed the existence of an adsorbed protective film on the MS surface. Inhibition efficiency of inhibitors was
also explained by quantum chemical parameters, which agree well with the experimental data.

**Chapter IV**

The chapter deals with the anticorrosion performance of an amino acid (cystine)-based gemini surfactant designated as 2(C₁₂Cys), for MS in 1M HCl at temperatures 30-60°C. The techniques used are gravimetric measurements, electrochemical measurements (PDP and EIS), and surface assessment (SEM/EDX and AFM). The performance of 2(C₁₂Cys) has been compared with monomeric surfactant (C₁₂Cys). The anti-corrosion performances of 2(C₁₂Cys) and (C₁₂Cys) are correlated with quantum-chemical parameters and Monte Carlo simulations.

The inhibition efficiency (\(\eta_w\)) of (C₁₂Cys) and 2(C₁₂Cys) for MS corrosion in HCl solution at all studied temperatures indicated that \(\eta_w\) (%) enhanced with an increase in inhibitors concentrations as well as with an increase in temperature up to 60°C. The increase in inhibition efficiency with a rise in concentration and temperature is indicative of chemisorption, which is attributed to the interaction between the vacant, low-energy d-orbitals of Fe surface atoms and de-localized electrons of the -NH₂, -SH and -COOH of the inhibitors.

The studied inhibitors showed good inhibition efficiency and stability over a long period of immersion (48 h) for MS corrosion in acid solution. The \(\eta_w\) (%) of 2(C₁₂Cys) at optimum concentration of 2×10⁻³ mM at 60°C was found to be 94.2% whereas at near same concentration and temperature \(\eta_w\) (%) of (C₁₂Cys) was found to be only 74.3%.

PDP study suggested that the presence of (C₁₂Cys) or 2(C₁₂Cys) inhibited oxidation of Fe, and to a lower extent hydrogen evolution, implying that the both the studied surfactants act as mixed type corrosion inhibitors with a predominating anodic character. The values of \(R_{ct}\) for the (C₁₂Cys) or 2(C₁₂Cys) inhibited solutions rises with the concentration of inhibitors. This is related to the formation of a protective layer at the MS/acid interface. The \(C_{dl}\) values are observed to decrease with an increase in concentration of (C₁₂Cys) or 2(C₁₂Cys) which is attributed to the increase in the electrical double layer thickness and/or a drop in the local dielectric constant. AFM and SEM/EDX images are suggestive of smoother MS surface for (C₁₂Cys) or 2(C₁₂Cys) inhibited acid solution compared to uninhibited system. Experimental
findings are adequately supported by quantum chemical calculations and Monte Carlo simulations.

Chapter V

This chapter deals with the corrosion inhibition effect of a sugar based non-ionic gemini surfactant, $N,N'$-didodecyl-$N,N'$-digluconamideethylenediamine, designated as Glu(12)-2-Glu(12) for MS corrosion in 3.5% NaCl solution using PDP, EIS, weight loss, SEM, EDX, and AFM techniques. Effect of electrolyte temperature (temperature range 30-60°C) on corrosion inhibition of Glu(12)-2-Glu(12) has also been assessed and discussed. The associated activation energy of corrosion, enthalpy of activation, entropy of activation, and thermodynamic parameters such as equilibrium constant, standard free energy of adsorption, and entropy of adsorption were computed to elaborate the corrosion inhibition mechanism. Synergistic inhibition between Glu(12)-2-Glu(12) gemini surfactant and iodide ion (10 mM KI) in 3.5% NaCl solution has also been investigated by means of weight loss and electrochemical methods, and the possible synergistic mechanism has been proposed. DFT calculations was employed in an attempt to understand the adsorption of Glu(12)-2-Glu(12) molecules on MS surface at the molecular level.

With increase in Glu(12)-2-Glu(12) concentrations the corrosion rate decreases, which further decreases in presence of KI additive. This may be associated to the increased surface coverage of Glu(12)-2-Glu(12) at the MS/solution interface, which prevented the attack of 3.5% NaCl solution to MS surface and slowed down its dissolution. Glu(12)-2-Glu(12) in the presence of KI is observed to work more effectively. The inhibition efficiency is both concentration and temperature reliant and reaches 92.0 and 96.9% for Glu(12)-2-Glu(12) and Glu(12)-2-Glu(12)+KI, respectively at 60°C. Adsorption of Glu(12)-2-Glu(12) on the MS surface followed the Langmuir adsorption isotherm. Observing the high value of the adsorption equilibrium constant $K_{\text{ads}}$, it is evident that Glu(12)-2-Glu(12) is strongly adsorbed on the MS surface. The negative values of $\Delta G^\circ_{\text{ads}}$ suggest spontaneous adsorption of Glu(12)-2-Glu(12) on MS surface. The adsorption of Glu(12)-2-Glu(12) molecules on the MS surface in test solution is comprehensive type of adsorption although predominantly chemical in nature.
Abstract

It can be seen from PDP results that the addition of Glu(12)-2-Glu(12) causes slight shift in $E_{\text{corr}}$ towards more negative direction, qualifying it as typical mixed type inhibitor. Decreasing values of $C_{dl}$ (the double layer capacitance) in the inhibited acid solution, with an accompanying increase in $R_{ct}$ (charge transfer resistance) with respect to blank solution indicated the accumulation of protective Glu(12)-2-Glu(12) layer at the metal/solution interface. Formation of adsorbed protective layer due to binding of inhibitor with MS surface was assured by FT-IR results. The interactions of Glu(12)-2-Glu(12) with Fe$^{2+}$ to form a complex in 3.5% NaCl solution was also confirmed by UV-Visible spectroscopic measurements. AFM/SEM/EDX results revealed that in-homogeneity of MS surface was considerably homogenized by Glu(12)-2-Glu(12) giving a clear evidence of its adsorption on MS surface and the high protection it offers in 3.5% NaCl solution.

Quantum chemical calculations and MD simulation were applied to analyze the experimental data and elucidate the adsorption behaviour and inhibition mechanism of inhibitors. MD simulation showed a nearly parallel or flat disposition for Glu(12)-2-Glu(12) molecules on the MS surface providing larger blocking area to prevent the metal surface from corrosion. The proposed mechanism states that adsorption occurs by electrostatic interaction of the Glu(12)-2-Glu(12) with positively charged MS surface, as well as via the lone pair interaction with vacant d orbital of Fe$^{2+}$ on steel surface.

Chapter VI

This chapter deals with the corrosion inhibition performance of two ester based pyridinium gemini surfactants namely, 4,4’-(propane-1,3-diyl) bis(1-(2-(tetradecyloxy)-2-oxoethyl) dipyridinium chloride (14-Py) and 4,4’-(propane-1,3-diyl) bis(1-(2-(hexadecyloxy)-2-oxoethyl) dipyridinium chloride (16-Py) for MS corrosion in 1M HCl solution at temperatures 30-60°C. The techniques used are PDP, EIS and weight loss measurements. Surface analyses were carried out by using AFM, SEM, EDX and FT-IR techniques.

There is a decrease in the values of CMC with increasing number of carbon atoms in the alkyl chains of the gemini surfactants suggesting that the capability of micellization increases on increasing the length of the alkyl chain.
The increase in $\eta_w$ (%) with increasing concentration of inhibitors was due to increase in the surface coverage, which results in the lowering of metal dissolution in the aggressive media. 16-Py with higher hydrophobic chain length ($C_{16}$) in its molecules showed better inhibition performance than 14-Py ($C_{14}$). It is assumed that a longer chain length will lead to a more ordered film because of the increasing van der Waals interactions between the alkyl chains of the GS. In addition, longer chain will form a thicker film with fewer defects, which can offer greater protection to the MS surface. The adsorptive behavior of 14-Py and 16-Py on MS surface under all of the studied temperature was described well by Langmuir adsorption isotherm. Thermodynamic adsorption parameters show that 14-Py and 16-Py is adsorbed on MS surface by an endothermic, spontaneous process. Moreover, the calculated values of $\Delta G^\circ_{\text{ads}}$ reveal that the adsorption mechanism of tested inhibitors on MS surface is mainly due to chemisorption. The negative values of $\Delta S^*$ is suggestive of the fact that the process of adsorption of inhibitors is accompanied by a decrease in the entropy.

Tafel polarization results clearly revealed that studied inhibitors can be classified as mixed inhibitor with dominant cathodic effect. The EIS results indicated that the tested GS inhibitors acted by accumulating at the metal/acid solution interface.

The FT-IR results established the interactions between the inhibitors and MS. The surface analysis (AFM/SEM/EDX) revealed that the inhibitive behavior might be associated with the formation of an inhibitor layer on the MS surface, blocking the active sites.

Chapter VII

This chapter reports the results of the corrosion inhibition of the MS in 3.5% NaCl employing glucosamide surfactants $N$-alkyl-$N'$-glucosylethylenediamine, Glu (n), with the general formula $C_nH_{2n+1}NH(CH_2)_2NHCO(CHOH)_4CH_2OH$ ($n = 10, 12$). The corrosion inhibition performance have been conducted using a variety of techniques such as electrochemical (OCP, PDP and EIS), weight lost measurements along with surface analyses techniques (FT-IR, AFM, SEM and EDX). Effects of inhibitor concentration and temperature on inhibition action have also been looked into. The different molecular parameters like energy of frontier molecular orbitals (HOMO, LUMO) in energy optimised geometry, global hardness and softness, electronegativity, dipole moment and fraction of transferred electron have been
calculated using density functional theory (DFT) calculations and used to explore the corrosion inhibition performance of the compounds. The obtained results revealed that Glu (n) are good inhibitors for the corrosion of MS in NaCl solution.

The $\eta_w$ (%) increased with the inhibitor concentration as well as with rise in temperature, which is suggestive of chemical adsorption mechanism. The adsorption of inhibitor onto the MS surface was found to obey the Langmuir adsorption isotherm. The order of inhibition efficiency acquired from experimental results is successfully verified by theoretical quantum chemical calculations.

**Chapter VIII**

This chapter reports the major conclusions resulting from the present investigation and gives some suggestions for future work. Among the studied inhibitors 16-E2-16 and Glu(12)-2-Glu(12) were found to be the best inhibitor for MS corrosion in 1M HCl and 3.5% NaCl solution, respectively, at comparatively lower concentrations. The order of inhibition efficiencies for gemini surfactants in 1M HCl, as obtained by gravimetric measurements, is as follows: **16-E2-16 > 16-Py > 2(C_{12}Cys) > 14-E2-14 > 14-Py > 12-E2-12 > (C_{12}Cys)**. The order of inhibition efficiencies for gemini surfactants in 3.5% NaCl solution, as obtained by gravimetric measurements, is as follows: **Glu(12)-2-Glu(12) > Glu(12) > Glu(10)**. Inorganic (KI) and organic (NaSal) salts have been used as additives in very small amounts (10 mM) with some of the gemini surfactants to enhance their moderate inhibition efficiencies offered by them.

In future studies, it is proposed to evaluate the corrosion inhibition effect of studied gemini surfactants mixture for other active metals/corrosive environments. The studied surfactants may be used in preparation of inhibitor loaded conducting polymer based coatings for which virtually no reference is available. A combination of two or more surfactants may test for MS and other metals in the studied corrosive media.