ABSTRACT

Corrosion processes are accountable for numerous losses mainly in the industrial scope. It is a constant and continual problem; often difficult to get rid of it completely, the best way to tackle it is prevention. Mild steel (MS), because of adequate mechanical properties, ease of availability and fabrication and economic consideration, has found applications in a variety of industries such as petroleum production, refining, chemical processing, automotive and power and water generation. However, MS has the disadvantage of poor resistance to corrosion in contact with aggressive acid solutions. Mineral acids e.g., HCl and H₂SO₄ are widely used as industrial acid cleaner such as in the removal of rust in metal finishing industries, steel pickling, acid descaling, pickling acid and in acidization of oil well at elevated temperatures up to 60°C. The pickling and acid cleaning solutions are highly corrosive and may cause extensive corrosion damage to the unprotected MS. In order to mitigate the adverse consequences of the corrosive solutions and to retard MS corrosion, addition of several additives or corrosion inhibitors in small concentration is a very guaranteeing and insightful approach. The corrosion inhibitors are the chemical substances which retards the corrosion rate when present in the corrosive system at a suitable concentration. They work at the interface of the corrosive media and the metal surface. Both organic and inorganic compounds have been substantially used as excellent inhibitors but the use of inorganic compounds is generally avoided due to their bio-toxicity and environmental hazardness. In this connection, organic compounds incorporating electron rich functional groups along with π-electrons display much better corrosion inhibition efficiency (IE). Organic compounds containing hetero atoms such as N, O, S and P in their aromatic ring or long carbon chain have been widely used as potential corrosion inhibitor in acid solutions. Presence of the hetero atoms and π-electrons on the double bond and aromatic ring in these compounds determines both the efficiency and adsorption mechanism as their presence favours the adsorption of the inhibitors on the metal surfaces. These compounds prevent corrosion by blocking the active corrosion sites either by getting adsorbed, or by forming a protective layer or an insoluble complex on the metal surface. The inhibitive action of these compounds depends mainly on some physico-chemical properties of the inhibitor such as the functional groups, steric factors, aromaticity, electron density at the donor atoms, p-orbital character of donating
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electrons, structure of molecule, corrosion environment, and the charge and nature of the metal. Basically, the adsorption process is constituted of two dependent steps; molecules of inhibitor are transferred from the bulk aqueous media to the double-layer and then adsorbed onto the corroding surface; resulting in construction of a protective layer. These inhibitors may adsorb on the metal/acid solution interface by the following ways: electrostatic interaction between protonated inhibitors and already adsorbed chloride ions or donor–acceptor interactions between the π-electrons of aromatic ring and vacant d orbital of surface Fe atoms or by the interaction between unshared electron pairs of hetero-atoms and vacant d orbital of Fe surface atoms.

The environmental consideration has led to the research of a range of environmentally benign organic compounds as effective corrosion inhibitors. In recent years, the exploration for new eco-friendly compounds as potential inhibitors has encouraged the evaluation of different amino acids and their derivatives as safe inhibitors for corrosion of different metals in various aggressive media. Amino acids form a class of non-toxic, water soluble organic compounds and are naturally occurring, biodegradable, relatively cheap, and produced with high purity greater than 99%. They have been exploited as corrosion inhibitors by a number of investigators. In general, they contain two ionisable functional groups with opposite chemical nature: the amine group with basic property and the carboxyl group with acid property. The sulphur containing amino acids and amino acids with longer hydrocarbon chains have shown greater inhibition effect. Additional groups or groups which increase electron density on alpha amino group also increase the IE. However, the employment of single amino acids have the limitation of high amount of usage and low to moderate IE. Attempts have already been made to further enhance the corrosion inhibition performance of amino acids by incorporating substances having synergistic effect such as halide additives, metal ions etc., or by exploring amino acid derivatives as corrosion inhibitors. A combination of inhibitors is likely to provide multiple effects required for effective corrosion inhibition. Synergism is one of the most important effects in the inhibition process and serves as the basis for most of the modern corrosion inhibiting formulations. Synergistic inhibition, which is an improved performance of a mixture of inhibitors compared with the individual inhibitors in preventing the corrosion of metals, has proved to be an effective method
to improve the inhibition performance or to decrease the required dosage of the inhibitor and to diversify the application of the inhibitor in acidic media.

Surfactants have effectively been used as corrosion inhibitors and have the ability of influencing the properties of surfaces and interfaces. However, the influence of surfactants on the corrosion inhibition behavior of other organic compounds is very scanty. Amino acids interact with the surfactants to form a complex structure and help to adhere to surface, thus covering larger surface area and offers great promise in corrosion inhibition. The binding of surfactants to amino acids depends upon the structure, molecular weights, interaction time and charge densities.

The work presented in the thesis deals with the corrosion inhibition behavior of amino acids and their derivatives in acidic medium. The work was planned to understand the inhibition behavior of some selected amino acids [L-cysteine (CYS), L-tyrosine (TYR)], amino acid derivatives [L-Phenylalanine methyl ester hydrochloride (PMEH), a glycine derivative, N-benzylidine-2((2-oxo-2-(10H-phenothiazine-10yl)ethyl)amino) acetohydrazide (BPAA) and amino acid ionic liquid surfactants [glycine propyl ester lauryl sulphate (GlyC₃LS), glutamic acid propyl ester lauryl sulphate (GluC₃LS)] separately and in combination with very low concentration of surfactants [sodium dodecyl sulfate(SDS), cetyl pyridinium chloride (CPC), triton X-100 (TX)] on MS in 1 M HCl solutions. The aim of the addition of low concentration of surfactants was to synergistically improve the corrosion inhibition effect of amino acids/amino acid derivatives with minimum compromise on their green nature. The behavior of MS in presence of inhibitive formulation was examined by using gravimetric, Potentiodynamic polarization measurement (PDP) and Electrochemical impedance spectroscopy (EIS). 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 gravimetric. Other techniques like UV-visible spectroscopy, fourier transform infrared (FT-IR) spectroscopy and quantum chemical calculations, using Density Functional Theory (DFT), were also used. Corrosion attack morphologies on MS was observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).
The breakup of the work contained in various chapters is as follows:

**Chapter-I**

This chapter is dedicated to general introduction. The general introduction is divided into two sections. The first section deals with fundamentals of corrosion and includes the definition of corrosion and its importance, mechanism of corrosion, forms of corrosion and corrosion prevention and control methods. The second section of the introduction focuses on the corrosion inhibitors and their types, toxicity of corrosion inhibitors, environment friendly or green corrosion inhibitors, exhaustive literature survey on amino acids and their derivatives as green corrosion inhibitors and synergism consideration in corrosion inhibition. 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 three decades. 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 deals with the experimental details which highlights materials and methods used during the experimental work. The chapter also includes the procedure of synthesis of amino acid derivatives. The details of techniques which have been undertaken to investigate the inhibition behavior of investigated inhibitors have also been explained in this chapter.

**Chapter-III**

The work presented in this chapter deals with the corrosion inhibition performance of sulphur containing amino acid L-cysteine (CYS) as environmentally safe corrosion inhibitor for MS in aerated and unstirred 1 M HCl solution, in the
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The corrosion IE of CYS was determined by using gravimetric, PDP and EIS. In order to evaluate the protective layer formed in the presence of CYS and also to establish the functional groups of CYS responsible for binding on the MS surface, FT-IR study was carried out. The surface morphology of corroded MS specimens was studied by SEM. The mode of adsorption of inhibitor molecules on MS surface was also elucidated by determination of thermodynamic/kinetic parameters. The effect of the addition of very small SDS, CPC, and TX, respectively on the corrosion inhibition behavior of CYS was also studied. The inhibition performance obtained from experimental results was successfully verified by theoretical quantum chemical calculations.

CYS inhibited corrosion of MS to a considerable extent; the maximum IE being 85.62% at 30°C at 500 ppm concentration. which can be attributed to the adsorption of CYS on the MS surface. The IE increase with the increase in the inhibitor concentration up to 500 ppm but decrease with increasing temperature. The increased IE with the increase in CYS concentration indicates that more inhibitor molecules get adsorbed on the MS surface, thus leading to the formation of protective film. The decrease in IE with increasing temperature suggests possible desorption of absorbed CYS molecules at higher temperature.

The effect of the addition of very small concentrations of SDS, CPC, and TX respectively, on the corrosion inhibition behavior of CYS was also studied. IE of CYS is significantly increased in presence of all the three surfactants. The effect of surfactants on the corrosion inhibition behavior of CYS appears to be synergistic in nature; the effect of non ionic surfactant TX being more pronounced than CPC and SDS. CYS separately and in combination with surfactants acts as mixed type inhibitor. The change in impedance parameters indicated that CYS and CYS-surfactants molecules acted by accumulating at the metal/solution interface. SEM micrographs show a clearly different morphology in presence of CYS and CYS-surfactant additives. The adsorption of CYS separately and in presence of surfactants on MS surface obeyed Langmuir’s adsorption isotherm. The calculated thermodynamic parameters for adsorption reveal a strong interaction between the CYS and the MS surface. The results obtained by quantum chemical calculation
studies are consistent with the results of the gravimetric as well as electrochemical measurements.

**Chapter-IV**

This chapter deals with the inhibition effect of L-tyrosine (TYR) and TYR mixed with SDS/CPC on MS corrosion in aerated and unstirred 1 M HCl at temperatures 30, 40, 50 and 60°C. The various techniques employed during the study include: gravimetric analysis, EIS, PDP measurements, SEM, EDS, FT-IR, UV-visible spectroscopy and theoretical quantum chemical calculations using DFT. Thermodynamic/kinetic parameters were calculated to elaborate the adsorption and corrosion inhibition mechanism of the inhibitor.

The concentration of TYR was varied between 10-200 ppm, whereas that of CPC or SDS was fixed at 5 ppm. TYR inhibits the corrosion rates of MS to a considerable extent, which can be attributed to the adsorption of TYR on the MS surface. The value of IE is both concentration and temperature dependent. The increase in TYR concentrations causes an increase in IE till it reaches a maximum value of 72.34% at 100 ppm concentration at 30°C, a further increase in TYR concentration resulted in a little lowering of the IE due to desorption of some of the molecules. However, an increase in temperature resulted in the lowering of IE at all the studied concentrations, suggesting physical adsorption. The weak Vander Waal’s forces responsible for such type of adsorption tend to diminish at elevated temperatures.

IE of TYR is synergistically enhanced on adding SDS/CPC at all concentrations. The change in impedance parameters indicated that TYR and TYR-SDS/CPC molecules acted by adsorption at the MS/solution interface. Distinctively different surface morphologies for uninhibited and inhibited MS specimens verified the formation of adsorbed protective covering at the MS surface. TYR alone and in combination with SDS/CPC acts as mixed type inhibitor and adsorbed on the MS surface in accordance with the Langmuir adsorption isotherm. IE of TYR or TYR mixed with SDS/CPC obtained by gravimetric, EIS and PDP measurements are in good agreement and find support from theoretical quantum chemical parameters.
Chapter-V

This chapter deals with the corrosion inhibition behavior of a non toxic derivative of amino acid L-phenylaniline, namely L-phenylalanine methyl ester hydrochloride (PMEH) alone and in combination with SDS on MS in 1 M HCl in the temperature range of 30-60°C. The techniques used are gravimetric measurements, PDP measurement, EIS, UV-visible and theoretical quantum chemical calculations. Corrosion attack morphologies was observed by SEM and EDX to verify the results qualitatively.

The obtained results revealed that PMEH is a good inhibitor for the corrosion of MS in HCl solution. The IE increased with the inhibitor concentration up to 400 ppm 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.

Corrosion attack morphologies as observed by SEM and EDX verify qualitatively the results obtained by gravimetric as well as electro-chemical methods. The results obtained from all the techniques are in good agreement.

Chapter-VI

This chapter presents the investigation of an environmentally benign compound, a glycine derivative N-benzylidine-2((2-oxo-2-(10H-phenothiazine-10yl)ethyl)amino) acetohydrazide (BPAA), as potential corrosion inhibitor for MS in 1 M HCl solution at temperatures 30, 40, 50 and 60°C. The investigation is accomplished by employing the techniques such as PDP, EIS, gravimetric, UV-Visible spectrophotometry, FT-IR spectroscopy, SEM, EDX and theoretical calculations using DFT. As an alternate strategy to enhance the inhibitive effect of the inhibitor, the corrosion inhibition performance of BPAA in the presence of surfactant additives SDS and CPC at quite lower concentration was also studied. Thermodynamic and activation parameters were calculated and discussed.

The IE of BPAA increased with the increase in the inhibitor concentration. The increase in the concentration of inhibitor caused an increased adsorption of
BPAA molecules on the electrode surface, which increased the availability of electron donors (O, S and N) and phenyl rings leading to the formation of a protective layer and hence an increase in the IE. The highest IE was obtained at 100 ppm of BPAA, a further increase in inhibitor concentration resulted in a decrease in IE. This is attributed to desorption of the BPAA molecules from the MS surface after reaching an optimum value. IE increased with increasing electrolyte temperature from 30-60°C at all the inhibitor concentrations. This is suggestive 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 of the inhibitor. In addition, at high temperatures desorption of water molecules from the steel surface is more favored leaving larger steel surface area available for the adsorption of the inhibitor molecules. The maximum IE of 95.55% at 100 ppm is obtained at 60°C. The inhibition performance of the studied inhibitor is synergistically improved by adding small amount of SDS (5 ppm) and CPC (5 ppm) to the aggressive acid solution with better inhibition in case of BPAA in combination with CPC.

The order of IE acquired from experimental results is successfully verified by theoretical quantum chemical calculations.

**Chapter-VII**

In this chapter, amino acid ionic liquid surfactants (AAILs) i.e., glycine propyl ester lauryl sulphate (GlyC₃LS) and glutamic acid propyl ester lauryl sulphate (GluC₃LS) were synthesized and investigated as efficient inhibitor MS corrosion in 1 M HCl solution at different concentrations and temperatures (30, 40, 50 and 60°C) by using gravimetric, PDP, EIS, SEM/EDX and quantum chemical calculations by DFT. The adsorption equilibrium constant ($K_{ads}$) and standard free energy of adsorption ($\Delta G_{ads}^\circ$) were also calculated and discussed.

The inhibiting performance of both the AAILs was temperature and concentration dependent. IE increases with the increase in temperature, which is indicative of chemical mode of adsorption of inhibitors on MS surface, as well as with increase in concentration with maximum IE of 98.54% for GlyC₃LS at 100 ppm and 99.81 for GluC₃LS at 100 ppm. Polarization studies revealed the mixed-type nature of
both AAILSs. EIS studies indicated the formation of adsorbed protective film by AAILSs molecules on the MS surface to form pseudo-capacitive interface. The adsorption of GlyC₃LS and GluC₃LS obeyed Langmuir adsorption isotherm model with mixed adsorption mechanism involving both physical- and chemisorption. FT-IR spectroscopic analyses confirmed the presence of chemical interactions between the inhibitors and MS surface. Detailed investigation of the surface morphology of the MS specimens was carried out by using SEM and EDX, to affirm the existence of an adsorbed protective film on the MS surface which shield it from the direct attack of acid. Quantum chemical calculations were performed for determining the mechanism of corrosion inhibition and results obtained corroborates with the results obtained from other techniques.

**Chapter-VIII**

This chapter presents overall conclusions from the thesis and future plan of work. The studied amino acids/amino acid derivatives act as good inhibitor for MS corrosion in 1 M HCl solution. The IE of inhibitors synergistically increased in presence of small concentration of surfactants. Among the studied inhibitors amino acid ionic liquid surfactants were found to be the best inhibitors for MS corrosion in 1 M HCl solution at comparatively lower concentrations. The order of IE at a particular concentration (100 ppm), as obtained by gravimetric measurements, is as follows: CYS < PMEH < TYR < BPAA < GlyC₃LS < GluC₃LS.

In future, it is proposed to evaluate the corrosion inhibition effect of studied amino acid/amino acid derivatives-surfactant mixture for other active metals/corrosive environments. It is also proposed synthesize some water soluble amino acid-biopolymer composites and study as corrosion inhibitors.