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A review of amino acids used as corrosion inhibitors on iron metal/alloys in aggressive environments

ABSTRACT

Research into the use of safe and environmentally friendly corrosion inhibitors can pave the way for an understanding of their inhibition mechanisms in metallic alloy materials. This review seeks to present and discuss the research work reported in the literature on the use of amino acids and their derivatives as corrosion inhibitors for iron and its alloys in different aggressive solutions. This non-toxic, biodegradable and relatively cheap corrosion inhibitor has shown to be efficient as an inhibitor for metals/alloys in acidic, alkaline and neutral solutions depending on experimental conditions. Electrochemical and surface techniques were among the most often used techniques to evaluate the corrosion inhibition efficiency of amino acids. Highest values of inhibition efficiency can be obtained in the presence of ions as I^- and Br^- . This review presents and discusses most of the contributions made in literature on the use of amino acids and their derivatives as corrosion inhibitors for iron and its alloys.

Keywords: corrosion inhibitor, iron, metal, alloy, amino acid, computational methods.

1. INTRODUCTION

Corrosion can be defined as a spontaneous and irreversible weakening of metals or alloys which occurs by electrochemical or chemical reactions with the environment [1]. Corrosion causes enormous wastes of metallic materials which leads to enormous economic losses all over the world. It is a global problem, negatively affecting the growth of both developed and developing countries. Hence, it has drawn much academic and industrial attention [1–5]. Causes of corrosion include acids, bases, brines, oxygen, moisture/water, hydrogen sulfide, bacteria, carbon dioxide, etc. Many techniques of corrosion protection have been developed over time. A flow diagram of the available corrosion protection measures is presented by Verma et al. [2]. Among these, corrosion inhibitors are briefly discussed.

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2. BACKGROUND

Corrosion Inhibitors

The use of inhibitors is the most important method for protecting metals from corrosion, and many scientists are conducting research on this topic. New inhibitors are discovered often. In principle, inhibitors prevent the corrosion of metal by interacting with the metal surface via adsorption through donor atoms, π -orbitals, electron density and the electronic structure of the molecule [6–12]. In particular, $-NH_2$ and $-SH$ groups in the structures of inhibitors often act as reaction centres during the adsorption of the inhibitor. In this way, the inhibitors form an adsorbed protective film on the metal surfaces and protect the metals from the attacking acid solution [13–18]. The common corrosion inhibitors such as chromates [19], nitrite [20], and aromatic heterocyclic compounds [21] are environmentally threatening. The replacement of these inhibitors with new environment-friendly materials is crucial. Amino acids are nontoxic, biodegradable, relatively cheap and completely soluble in aqueous media. Much research has been performed as regards the inhibition effect of some amino acids on the corrosion of metals.

Amino acids as Inhibitors

An amino acid is a molecule that possesses at least one carboxyl (-COOH) group and one amino (-NH₂) group usually bonded to the same carbon atom (α - or 2-carbon). The other ligands of the α -carbon are -H and R- groups of different sizes, shapes, and chemical properties (side chain) [22]. In physiological terms, there are twenty different amino acids, which are used to build up proteins in all species from bacteria to humans [23].

Amino acids contain heteroatoms (e.g., S, N and O) and eventual conjugated π -electrons system on their molecular structures. This attribute has attracted the attention of researchers to explore their potential abilities to act as green corrosion inhibitors. The first tentative use of amino acid compounds as corrosion inhibitors for metals was reported by [24]. More recent reports such as [25 - 28], on the use of amino acids and even their derivatives have been published.

A thorough examination of literature has revealed that almost all tested amino acids compounds have exhibited the ability to act as ecofriendly inhibitors against metal corrosion in different mediums. However, there is no universal amino acid compound that is applicable to all or most of the metal/solution systems. Hence, the inhibition capability of these compounds depends on their molecular structure, concentration, corrosive medium, nature of the metal surface, hydrodynamic conditions in the system, pH of solution, etc. Whereas an amino acid can act as an effective corrosion inhibitor on a given metal at certain conditions, it can also accelerate the corrosion process at other operating conditions. Current research focuses on the use of newly synthesized derivatives of amino acids with higher corrosion inhibition efficiencies than their corresponding simpler/original compounds as corrosion inhibitors. It also incorporates an explanation of their inhibition mechanisms using quantum chemical calculation and/or simulation by molecular dynamics approach. A list of amino acids which have been researched as green corrosion inhibitors for iron and its alloys is presented in Table 1.

Characterization Techniques

Characterization and determination of corrosion inhibition effectiveness can be conducted in two different ways: experimental methods and Computational methods.

Experimental Methods

Potentiodynamic polarization (PDP) measurement: This method is one of the most used DC

electrochemical methods in corrosion measurements. It is based on the evaluation and analysis of the current produced by a variable potential in a working electrode. Here, a wide range of potential is applied to the test electrode. Subsequently, current is generated. The presentation of the potential in the function of current density (I) (or $\log I$) for each measured point results in the polarization curve. The polarization curve can be used to determine the corrosion potential and the corrosion rate of the metal in the given condition (Tafel slope). The advantage of this method is the likelihood of a localized corrosion detection, easy and quick determination of the corrosion rate, efficiency of the corrosion protection, etc. [29].

Cyclic Potentiodynamic Polarization (CPDP).

This is also widely used to determine resistance to localized corrosion or degradation rate in a short time [30]. It is performed like a potentiodynamic scan, but with an addition: the voltage is swept across a range but reversed back to the starting potential. This allows a return to the original potential. The surface is likely to be changed by the reactions during the scan, so often the data from the return voltage sweep do not superimpose upon the data from the forward sweep.

Electrochemical Impedance Spectroscopy (EIS) [31]. This technique is used to determine the impedance of a system in terms of the frequency of a variable potential. The analysis of EIS results relies on models with equivalent electrical circuits, with the most recurrent graphical representations of its results being Nyquist plots [32]. EIS shows more information, for example, mechanism and different resistance of the system.

Electrochemical Frequency Modulation (EFM):

This is a technique that enables the instantaneous determination of a corrosion rate, without previous knowledge of the Tafel parameters. The EFM approach requires only a small polarizing signal, and measurements can be completed in a short period. A unique advantage of the EFM technique is its ability of innate data validation control using causality factors. It can be used effectively for corrosion rate measurements under various corrosion conditions. [33].

Electrochemical Noise (EN): EN is a method that enables the determination of the phenomenon of metal corrosion at E_{OCP} without the need for any sort of external potential perturbation. Time-dependent statistical treatments of the random current and potential noise signals originating from the corrosion system can be used to calculate the corrosion rate, while corrosion mechanisms can be predicted based on the interpretation of certain spectral patterns obtained from frequency-dependent analysis of the noise signals [34 -39]

Linear polarization resistance (LPR) is a technique used to obtain the corrosion rate by determining the relationship between electrochemical potential and generated currents on charged electrodes [40].

Weight Loss Method (WL): This technique is based on the mass lost by the metal, which is directly monitored to get the corrosion rate. The loss of metal due to corrosion is measured by exposing the metal specimen of known area to the environment for a period of time and calculating the difference in weight before and after exposure [41].

Thermometric method: This is a temperature-based method for corrosion rate calculation. The temperature variation during the reaction of a metal test piece with a definite volume of a corroding solution is ascertained [42]. By the increase in temperature per unit of time, the reaction number (RN) and inhibition efficiency are calculated. [43].

Surface characterization is usually studied by means of spectroscopy and microscopy techniques. Some of these are;

Scanning Electron Microscope (SEM) provides a clear comparison between the metal surface with and without a corrosion inhibitor, as well as other morphological information [44, 45].

Atomic Force Microscope (AFM) obtains information regarding the shape of the metal surface for comparison purposes and topography imaging [46 -49].

X-Ray Photoelectron Spectroscopy (XPS) is recurrently used for oxidation states, stoichiometry, and electronic state determination [50 -53].

Fourier transform infrared (FTIR) spectroscopy is used to obtain information on the functional groups and vibrational modes on the corrosion inhibitors [54].

Ultraviolet–Visible (UV–VIS) spectroscopy helps to explain functional groups, electronic transitions, and optical band gaps.

Computational methods

Computational chemistry methods have been employed by researchers for the purpose of investigating and understanding how the molecular structure of amino acids affects inhibition efficiency. Investigations have been limited to amino acid molecules acting alone in vacuum or in aqueous phase/solution in its neutral, protonated, or unprotonated forms. These methods are briefly described.

Quantum chemical calculation methods:

(i) Semi-empirical methods: These serve as efficient computational tools which can yield fast quantitative estimates for a number of

properties. This may be particularly useful for correlating large sets of experimental and theoretical data, for establishing trends in classes of related molecules, and for scanning a computational problem before proceeding with higher-level treatments. However, there is a need to improve semiempirical methods with regard to their accuracy and range of applicability, without compromising their computational efficiency. Examples of semi-empirical methods include MNDO, AM1, PM3, etc. [55].

(ii) Ab initio Methods: The term ab initio indicates that the calculation is from first principles and that no empirical data is used. The simplest type of ab initio electronic structure calculation is the Hartree–Fock (HF), in which the instantaneous Coulombic electron-electron repulsion is not specifically considered, and only its average effect is included in the calculation [55].

(iii) The Density Functional Theory (DFT): This is used in the field of reaction chemistry, in explaining the science of solids and chemistry. It enables an understanding of the structure, properties, reactivity, and dynamics of atoms, molecules and clusters. Large systems involving many atoms or molecules are simulated on a regular basis using this method. [56]. The most important parameter in DFT is the electron density $\rho(r)$, in terms of which all the chemical quantities are expressed [57]. The main objective of DFT is, therefore, to replace the many-body electronic wave function with the electronic density as the basic quantity [58]. The structural parameters calculated through the electronic density ($\rho(r)$ concept) compare well with the parameters calculated by the Schrodinger equation in terms of the single electron wave function (ψ), where the latter can be applied [59]. Examples include B3LYP/6-31+G*, B3LYP/6-311G**, etc.

The inhibition of corrosion is, however, a complex phenomenon, which involves many competitive effects, such as the inhibitor-metal surface bonding (adsorption energy), the solubility of inhibitor, and the complexation of inhibitor with metallic ion in solution, etc. All these factors and others should be taken into consideration if such a phenomenon must be clearly understood. [60 – 67]

Molecular Dynamic (MD) simulation: MD simulation with periodic boundary conditions (which use the Metropolis Monte Carlo statistical method) is used to calculate the adsorption energy and to identify the adsorption configuration (with lower

energy) of several amino acid compounds on metal surfaces. This has been implemented by several authors [68–71]. MD simulation method has the advantage of reduced time consumption compared to quantum chemical methods. Frequently, during MD simulations, the COMPASS (Condensed phase Optimized Molecular Potentials for Atomistic Simulation Studies) ab initio force field is used to calculate the energy of all components of the system.

Quantitative-Structure Activity Relationship (QSAR): Various researchers [72–76] have found a relationship between the inhibition efficiency of amino acids compounds and their reactivity indicators by merging some reactivity indicators obtained from computational methods with statistical tools. This methodology is called Quantitative-Structure Activity Relationship (QSAR) [77–79].

The main steps of QSAR modeling process are reactivity indicators' selection, data splitting, training, and testing of the model. Frequently, simple and multi-linear regression are used to construct QSAR models [80–81].

Machine Learning Methods: This is a recent trend in recent works on amino acids developed from artificial intelligence. Examples include support vector machine [74] genetic function approximation [70] and artificial neural network [71]. Almost all these studies have been limited to the building of the QSAR models for the prediction of the inhibition efficiency of tested amino acids.

Recently, Taylor et al, 2015 [67] critiqued the investigation of inhibitor efficiencies through QSAR using electronic properties of the molecule because this approach has not taken into consideration factors such as concentration of inhibitor, temperature, solution flow, etc. This leads to the obscurity of these factors in the process of parameter fitting during the training step. Therefore, to build a predictive model for corrosion science and engineering, it is essential to consider the above-named factors. Such an approach is referred to as “Multiphysics Modeling” [67].

3. DISCUSSION

Factors affecting the inhibition ability of amino acid compounds

The efficiency of inhibitors depends on a number of factors and on the interplay between several competitive effects [82]. The major factors which influence the inhibition efficiency (IE) of amino acids include temperature, immersion time,

concentration of inhibitor, chemical nature of inhibitor, solution pH, hydrodynamic condition, aerated and deaerated condition, additive, chemical nature of metal and metal/alloy surface state. Few of these factors are discussed here.

Temperature plays a very important role in the IE of an inhibitor. The determination of the optimum temperature for the high IE of an inhibitor is very important in the selection of an inhibitor for a particular application. Table 1 presents such temperatures as investigated by some authors such as Zerfaoui et al., 2004b [83] and Amin et al., 2009a [84]. Immersion time can also play a decisive role in the prevention of corrosion. It has been reported that cysteine displayed a dual effect on the corrosion of galvanized steel [85, 86]; it acted as a corrosion inhibitor at short exposure time and as corrosion accelerator at long immersion time. However, some amino acids have shown an increase in their inhibition performance by increasing exposure time as reported in the case of alanine for nickel [87] and glutamine for mild steel [88]. Such phenomena can be attributed to the instability/stability of adsorbed amino acid film on the metal surface and its affinity to react with metallic ions in the solution. It is also pertinent to ascertain the optimal concentration for the effectiveness of an inhibitor. Some inhibitors perform excellently at very small concentrations [89] while others perform well at higher concentrations [90]. Hydrodynamic conditions (i.e., stagnant, or dynamic solution) can also affect the inhibition performance. Generally, in the presence of inhibitor, two opposite effects for hydrodynamic conditions can be pointed out, which influence its inhibition efficiency. First, the flow can increase mass transport of inhibitor molecules toward the metal surface and raise the inhibition efficiency, as noted in the case of methionine [91] and glutamine [92] for mild steel and aluminum respectively. Secondly, the highest shear stress resulting from flow speed can lead to the desorption of adsorbed inhibitor molecules from the metal surface, which reduces the inhibition efficiency. The same behavior was reported for low alloy steel when a series of amino acids were used. It is pertinent to know that little work appears to have been done on the effect of some of these factors on the inhibition performance of amino acid compounds. More research is, therefore, encouraged in these areas. These factors should also be considered when building predictive models using computational methods.

Recent trends

Recent trends in the use of amino acids as corrosion inhibitors are the cases of Self-Assembly Monolayer (SAM) and Smart Coatings [22]. The Self-Assembled Monolayer (SAM) is prepared by utilizing the strong interaction between the heads of the amphiphiles molecules and the surface of the solid support on one hand, and intermolecular forces (involving van der Waals and hydrophobic forces) between backbone hydrocarbon chains in amphiphiles molecules on the other. The method of formulation involves the submergence of the support into a solution containing the corresponding amphiphiles induces (spontaneous) self-assembly of the amphiphiles components as a monolayer on the support surface. Washing the support removes

excess adsorbent, resulting in a strongly immobilized monolayer. The application of the SAM of some amino acids and their related compounds as inhibitors of corrosion has been reported [93 - 95].

The smart coating technology involves the formation of corrosion inhibitors into microcapsules prior to their integration into a protective film. This permits the gradual release of the inhibitor in case the coating got damaged [96 -98]. This technology provides long-term active protection against corrosion of metal surfaces after the coating fails. In addition to corrosion protection and repair, the smart coatings also perform the functions of sensing and warning. A trial application of this on an amino acid as an inhibitor for galvanized steel has been reported [85, 86].

Table 1. Amino acids and their derivatives used as corrosion inhibitors for iron and its alloys

Tabela 1. Aminokiseline i njihovi derivati koji se koriste kao inhibitori korozije za gvožđe i njegove legure.

Inhibitor	Parameter/s studied	Other Details	Results / Findings	Reference
Cysteine cystine, methionine	Concentration	<i>Alloy</i> Mild steel <i>Medium</i> 1N H ₂ SO ₄ <i>Methods</i> WL, PDP	Methionine was the best inhibitor. More than 60% IE was achieved with concentrations of amino acid as low as 10 ⁻³ M Mixed type inhibitors.	[99]
22 amino acids and four related compounds	Concentration/type of amino acid	<i>Metal</i> Iron <i>Medium</i> Deaerated <i>Method</i> 1M HCl PDP	Amino acid with highest IE (80%) was tryptophan while related compound with highest IE (87%) was 3,5-diiodotyrosine. Both IEs were obtained at 10mM concentration. Longer-chain amino acids showed better inhibition.	[100]
Cystine Parameter studied:	Concentration (0.1, 0.5, 1, 5mM)	<i>Alloy</i> Mild steel <i>Medium</i> 0.5M H ₂ SO ₄ <i>Methods</i> EIS, SEM, AFM	86% maximum IE obtained. IE increased with concentration. Combined physical and chemical adsorption mechanism observed.	[101]
L-methionine	Rotation speed (300, 600, 900, 1500, 2000, 2200rpm)	<i>Alloy</i> Mild steel rotating disk electrode <i>Medium</i> 1M H ₂ SO ₄ <i>Methods</i> EIS, PDP	IE increased with speed of rotation of electrodes. Maximum IE obtained was 66.5% at the highest speed with the EIS method.	[91]
Glycine, leucine, D-L aspartic, arginine and methionine	Concentration (5 x 10 ⁻⁵ , 10 ⁻⁴ , 5 x 10 ⁻⁴ , 10 ⁻³ , 5 x 10 ⁻³ , 10 ⁻² , 2 x 10 ⁻² M), temperature (30, 40, 50, 60°C) and pH (2.7, 3, 4, 5).	<i>Metal</i> Iron <i>Medium</i> Citric acid <i>Methods</i> WL, EIS, PDP	Methionine gave maximum IE of 90% at 2 x 10 ⁻² M concentration, pH 5 and temperature 30°C. IE reduced with temperature increase and pH decrease. All tested amino acids exhibited cathodic inhibition	[83]
Alanine, glycine, and leucine.	Concentration of inhibitor (0.1, 0.01, 0.001, 0.0001M) and conc. of acid	<i>Alloy</i> Steel <i>Medium</i> Different HCl concentrations (0.1M, 0.01M, 0.001M, 0.0001M) <i>Methods</i> WL, PDP	Highest IE of 91.64% obtained with 0.1M leucine in 0.1M HCl	[102]
Methionine methyl ester (MME), methionine ethyl ester (MEE), methionine	Concentration (10 ⁻⁵ , 10 ⁻⁴ , 10 ⁻³ , 5 x 10 ⁻³ , 10 ⁻² M) of MEE, temperature (22, 37, 50, 60°C)	<i>Metal</i> Iron <i>Medium</i> 9g/L NaCl <i>Method</i> PDP	Maximum IE of 80% at 10 ⁻² M concentration and 37°C. was obtained with MEE. Adsorption was enhanced by sulphur and nitrogen whose electronegativity was enhanced by the ethyl group. Frumkin adsorption isotherm was proposed	[103]

Methionine, cysteine, cystine, glycine, leucine, arginine, serine, glutamic acid, ornithine, lysine, aspartic acid, alanine, valine, asparagine	Concentration	Metal Iron Medium 1M HCl Methods WL, PDP, EIS, DFT/B3LYP, DNP, QSAR (with Genetic Function Algorithm)	Best inhibition efficiencies were obtained with Methionine, cysteine and cystine.	[104]
Methionine ethyl ester	Temperature (30 – 60°C)	Metal Iron Medium Citric chloride Methods PDP, EIS	IE slightly increased with increasing temperature (range 30 – 60°C). Temkin adsorption isotherm.	[105]
Glycine	Concentration (1, 2, 5, 10, 20, 50mM), temperature (20, 30, 40, 50, 60°C).	Alloy Low alloy steel ASTM A213 grade T22 boiler steel Medium 0.5M HCl Methods SEM, PDP, EIS, LP, EFM, EDX ICP-AES	Efficient mixed-type inhibitor with cathodic predominance, Maximum IE of 79.88% obtained with the Tafel polarization. IE increased with concentration of inhibitor but decreased with temperature.	[84]
Tyrosine	Concentration (1, 2, 5, 10, 20, 50mM), temperature (20, 30, 40, 50, 60°C).	Metal Low chromium alloy steel Medium 0.5M HCl Methods SEM, PDP, EIS, EFM, energy dispersive X-rays, WL	Efficient mixed-type inhibitor with cathodic predominance. Maximum IE obtained was 85.23% with the PDP measurement. IE increased with concentration of inhibitor but decreased with temperature	[106]
Methionine methyl ester, glycine methyl ester, leucine methyl ester, phenylalanine methyl ester and cysteine methyl ester	Concentration and temperature (20 – 50°C)	Metal Iron Medium 1M HCl Methods PDP, WL	Methionine methyl ester was best inhibitor, (IE – 95% at 10 ⁻² M). It was also cathodic. IE increased with temperature. Frumkin adsorption isotherm.	[107]
L-Histidine	Concentration (1 x 10 ⁻⁴ , 5 x 10 ⁻⁴ , 1 x 10 ⁻³ , 5 x 10 ⁻³ , 10 ⁻² M).	Alloy Carbon steel Media 0.5M acetic acid and 0.25 M acetate Methods LP, EIS, WL, EDX, SEM, cyclic voltammetry	Maximum IE of 81.6% obtained with 10 ⁻² M inhibitor concentration for the WL method	[108]
Tryptophan	Concentration	Alloy Carbon steel Media 0.5M acetic acid and 0.25M acetate Methods LP, WL, SEM, cyclic voltammetry	IE increased with an increase in concentration in the range of 10 ⁻⁴ - 10 ⁻² mol L ⁻¹	[109]
Cysteine	Concentration (10 ⁻⁶ , 10 ⁻⁵ , 10 ⁻⁴ , 10 ⁻³ , 10 ⁻² M)	Alloy 304L stainless steel Medium Deaerated Molar H ₂ SO ₄ Methods SEM, EIS, PDP	Cysteine at high concentration (10 ⁻⁴ – 10 ⁻² mol/L) turned alloy electrochemically active	[110]
Cysteine	Concentration (0.1mM, 0.5mM, 1.0mM and 5.0mM)	Alloy Low carbon steel Medium 0.5M H ₂ SO ₄ Methods EIS, PDP, SEM	Addition of low conc. (0.1–0.5 mmol L ⁻¹) of cysteine, enhanced corrosion while higher concentration ((1.0–5.0 mmol L ⁻¹) inhibited corrosion which was enhanced on deaeration of the test solution	[111]

L-Leucine	Concentration (10^{-1} , 10^{-3} , 10^{-5} M) and temperature ((25, 35, 45, 55°C).	Alloy Mild steel Medium $1\text{NH}_2\text{SO}_4$ Methods OCP, PDP, SEM, IR	Maximum IE - 78% at 0.1M. Mixed-type and passivating inhibitor. IE increased with an increase in concentration but decreased with temperature. Freundlich adsorption isotherm proposed	[112]
cysteine, methionine, cystine, and N-acetylcysteine acids + F^- , Cl^- and Fe^{3+}	Type of ion added	Alloy Mild steel Medium Phosphoric acid (40%) Methods PDP, EIS	The binary mixtures of Cl^- or F^- with cysteine or methionine showed a good anti-corrosion ability (IE > 90%), in contrast to those containing Fe^{3+} ions or ternary mixture ions and an amino acid	[113]
Glutamic acid (Glu-A) ($\pm\text{Zn}^{2+}$)		Alloy Carbon steel Medium Natural sea water. Methods WL, AFM	IE increased from 35% at 200ppm of Glu-A to 87% with addition of small amounts of Zn^{2+} (25ppm).	[114]
L-Cysteine (+ triton X-100 (TX), sodium dodecyl sulphate (SDS) and cetyl pyridinium choride (CPC))	Concentration of L-Cysteine (100, 200, 300, 400 and 500ppm) and additives, and temperature (30, 40, 50, 60°C).	Alloy Mild steel Medium 1M HCl Methods WL, PDP, EIS, SEM, FTIR	IE decreased in the order: Cys + TX (97.76%) > Cys + CPC (91.99%) > Cys + SDS (95.09%) > Cys (85.62%) for the WL method. All occurred at 500ppm of Cys and temperature of 30°C. IE increased with concentration but decreased with temperature.	[115]
Derivatives of glycine: 2-(4(dimethylamino) benzylamino) acetic acid hydrochloride (GlyD1), GlyD2 and Glycine (Gly)	Concentration (0.5mM, 1mM, 5mM, 10mM, 50mM) and temperature (5, 15, 25, 35, 45, 55, 65°C).	Alloy Mild steel Medium $4\text{M H}_2\text{SO}_4$ Methods PDP, LPR, EIS, ICP-AES,	IE decreased in the order, GlyD1(98%) > GlyD2 (76%) > Gly (64%) at 50mM for the LPR method. IE increased with increase in inhibitor concentration and decreased with temperature. Physisorption of all three inhibitors proposed	[116]
Derivative of Cystine (RSSR), Cysteine (RSH), methionine (CH_3SR), N-Acetylcysteine (ACC) and S-benzylcysteine (BzC)	Concentration	Alloy Mild steel Medium 5% of sulfamic acid at 40°C Methods PR, EIS, PDP	IE followed the order: ACC (97.3%) > RSH (94.3%) > RSSR (92.7%) > BzC (91.7%) > CH_3SR (86.5%) at 1000 μM and with the PR method. Chemisorption proposed.	[117]
Derivative of Glycine: 2-(bis (2-aminoethyl) amino) acetic acid (GlyD) and glycine	Concentration	Alloy Cold-rolled steel Medium 1M HCl Methods PDP, EIS, LPR, ICP-AES, EFM, DFT	IE of derivative (96.02%) was higher than that of glycine alone (75% at 5mM) for the PDP and LPR methods. Higher IE attributed to the presence of extra NH link in derivative through computational study.	[118]
L-Lysine derivatives, SB-1, SB-2, and SB-3	Concentration and temperature (35, 45, 55 and 65°C)	Alloy Mild steel Medium 1M HCl Methods WL, PDP, EIS, SEM, AFM, EDX, quantum chemical calculations	Maximum IE decreased in the order, SB-3 (95.6%) > SB-2 (94.7%) > SB-1 (93.9%) from the WL method all at maximum concentration of 400mg/L. IE decreased with increasing temperature. Strong electron releasing - $\text{N}(\text{CH}_3)_2$ group responsible for high IE of SB-3. Chemical and physical adsorption proposed	[119]
L-tryptophan derivatives designated as S1 and S2		Alloy Mild steel Medium 1M HCl Methods PDP, EIS, SEM-EDX, FTIR, UV-VIS, X-Ray diffraction (XRD), DFT, computational technique	IE of S2 greater than that of S1 due to strong electron-donating ability and presence of additional phenyl rings in the molecule	[120]

Cysteine		Alloy Mild steel Medium 0.5M H ₂ SO ₄ PDP, EIS, DFT/B3LYP 6-311++G (d.p)	IE = 96% at 10 mM. Langmuir adsorption isotherm. Chemisorption mechanism. Electrophilic site is the sulphur atom	[121]
Cysteine (Cys) and its derivatives: N-acetyl- L-cysteine (NACYS), N-acetyl-S-benzyl-L- Cysteine (NASBCYS), and N-acetyl-S-hexyl- L-cysteine (NASHCYS)	Concentration	Alloy Mild steel Medium 1M HCl Methods WL, PDP, DFT, B3LYP 6-31G (d.p), molecular dynamics Fe(1,1,0)	IE: NASBCYS (95.7%) > NACYS (92.5%) > NASHCYS (92.4%) > Cys (90.4%) at 10 ⁻² M with the PDP method. Mixed-type inhibitors. E _{HOMO} , ΔE, and molecular volume were good and correlated with experimental results.	[122]
Cysteine (Cys), serine (Ser), amino butyric acid (Abu), threonine (Thr), alanine (Ala), valine (Val), phenylalanine (Phe), tryptophan (Trp), and tyrosine (Tyr)		Alloy Mild steel Medium 0.1M H ₂ SO ₄ Methods WL. Computational schemes with statistical analysis	IE ranking: Cys > Ser > Abu, Thr > Ala > Val and Trp > Tyr > Phe.	[123]
Cysteine		Alloy Mild steel Medium 1M HCl and 0.5M H ₂ SO ₄ Methods EIS, PM3, molecular dynamics Fe (0 0 1)	Higher IE (90.4%) obtained in 1M HCl at 0.1M conc. of the inhibitor because of adsorption of Cl ⁻ . Inhibitor molecules adsorbed on iron surface in a vertical way	[124]
Cysteine	Concentration	Alloy Mild steel Medium 1M HCl and 0.5M H ₂ SO ₄ Method PDP	IE increased with increasing concentration of L-cysteine in both acids though the higher one was obtained with 1 M HCl.	[125]
Triazolyl bis-amino acid of threonine and phenylalanine	Concentration	Alloy Mild steel Medium 1M HCl Methods WL, PDP, EIS, SEM, DFT/B3LYP 6-31*G	The 1,4-disubstituted triazolyl performed better than the natural amino acids as a result of the triazole ring. IE of one of the tested compounds generally increased with concentration.	[126]
Alanine	Concentration	Alloy Mild steel Medium 1M HCl Methods PDP, EIS, Molecular dynamics Fe (1 1 1)	Maximum IE of 80% obtained at 50mM of inhibitor. Adsorption occurred through the N/O atoms	[127]
Polyaspartic acid (± I ⁻)	Concentration and temperature (10, 20, 30, 40°C)	Alloy Mild steel Medium 0.5M H ₂ SO ₄ Methods WL, PDP, EIS, SEM, XPS, FTIR	IE = 88% at 2 g/L of acid alone and 98.8% in the presence of 1mM of I ⁻ with the PDP method. IE increased with increase in temperature and concentration Inhibitor was cathodic. XPS analysis revealed a co-adsorption of I ⁻ and polyaspartic acid molecules on alloy surface.	[128]
Poly (vinyl alcohol-histidine)	Inhibitor concentration, exposure time, and temperature	Alloy Mild steel Medium 1M HCl Methods WL, PDP, LPR, EIS, SEM, FTIR, UV-VIS, AC conductance measurement using LCZ analyzer, Thermogravimetric analysis (TG/DTG)	IE = 95% at 0.6%wt. Mixed type inhibitor. Temkin adsorption isotherm. Physisorption	[129]

Methionine (\pm sodium dodecyl sulfate: SDS and cetyltrimethyl ammonium bromide (CTAB))	Concentration (10, 25, 50, 100, 200, 300, 500ppm), temperature (30, 40, 50, 60°C)	Alloy Mild steel Medium 0.1M H ₂ SO ₄ Methods WL, PDP, SEM, AFM	The synergism between methionine and CTAB is better than that of methionine and SDS. For the WL method, the best IEs were obtained at 300ppm of inhibitors used. IE decreased with temperature increase in all cases. Methionine acted as a mixed-type inhibitor. Physisorption proposed.	[130]
Poly (vinyl alcohol-leucine). (\pm Br ⁻ and I ⁻)	Concentration (0.06, 0.12, 0.15, 0.18, 0.24, 0.30, 0.36, 0.42, 0.45, 0.48, 0.54 and 0.60%), temperature (30, 40, 50, 60, and 70°C) and immersion time (1, 3, 5, 12, 24hrs)	Alloy Mild steel Medium 1M HCl Methods WL, PDP, EIS, SEM, UV-VIS	Maximum IE = 98.18% at 0.6 wt% in the presence of I ⁻ . Synergism effect of inhibitor with Br ⁻ and I ⁻ ions. IE did not change significantly with rise in temperature. Also, IE decreased with prolonged immersion (12 -24hrs).	[131]
Glutamine	Concentration (25, 50, 75 and 100ppm), temperature (35, 45, 55 and 65°C) and immersion time (2, 3, 4 and 6hrs)	Alloy Mild steel Medium 1M HCl Methods DFT/B3LYP 6-31 G* (d.p)	Maximum IE of 96% obtained at an optimum conc. of 100ppm. IE increased with immersion time and concentration but decreased with temperature. Chemisorption proposed. Langmuir adsorption isotherm.	[88]
Decylamides of tyrosine, glycine, alanine and valine.	Concentration (10, 25, 50 and 100ppm), temperature (25, 35, 45, and 60°C).	Alloy Mild steel Medium 1M HCl Methods WL, PDP, XPS, IR	Order of IE of derivatives: tyrosine > glycine > alanine > valine. Flory-Huggins adsorption isotherm obtained. The XPS analyses confirmed the presence of a chemisorbed film of decylamides derivatives on the alloy. IE increased with concentration but decreased with temperature.	[132]
Glutaraldehyde + glycine = (CPI), and glutaraldehyde + methionine = (CP2)	Concentration (0.1, 0.3, 0.5, 0.6, 0.7%, temperature (25, 35, 45 and 65°C) and immersion time (1, 2, 3, 4 and 6hrs)	Alloy Mild steel Medium 2M HCl Methods PDP, WL, IR	CP2 performed better than CP1 for 1 and 2 hrs. of immersion, but the opposite was the case for 3, 4, and 6hrs of immersion. Optimum concentration for IE was 0.6%. IE increased up to 45°C for CP2 and then decreased slowly after 55°C.	[133]
Poly(vinyl alcohol cysteine)	Concentration (0.12, 0.24, 0.36, 0.48 and 0.60wt%, temperature (30, 40, 50, 60 and 70°C) and immersion time (1, 2, 4, 6, 12 and 14hrs).	Alloy Mild steel Medium 1M HCl Methods UV-VIS, PDP, EIS, FTIR, SEM-EDX and WL.	Maximum IE of 94% obtained with inhibitor concentration of 0.6wt% for the WL method. IE increased with immersion time up till 6hrs and then began to reduce. IE also increased with temperature up till 50°C and then reduced on further temperature increase. Inhibitor was mixed type. IE depended on rate of doping of PVA by cysteine. Physisorption proposed.	[134]
1,4-disubstituted 1,2,3-triazolyl bis-amino acid derivatives constituted by L-serine, L-threonine, L-phenylalanine and L-tyrosine	Concentration (1.0 x 10 ⁻⁵ , 3.2 x 10 ⁻⁵ , 5.6 x 10 ⁻⁵ , 1.0 x 10 ⁻⁴ , 3.2 x 10 ⁻⁴ , 5.6 x 10 ⁻⁴ , 1.0 x 10 ⁻³ M)	Alloy Mild steel Medium 1M HCl Methods WL, PDP, EIS, SEM, AM1	IEs of these derivatives were better than those of their original natural amino acids counterparts. IE generally increased with concentration.	[135]
Thermal polyaspartate (TPASP)		Alloy Mild steel Medium Synthetic salt solution 35ppt (Ph 8) Methods SEM-EDX, EIS, LP, OCP	TPASP is a mild corrosion inhibitor of the mixed type	[136]

Polyaspartic acid (PASP)		Alloy Carbon steel Medium 0.5M H ₂ SO ₄ Methods WL, PDP, EIS, SEM, FTIR	Performed as a good anodic-type inhibitor with maximum IE obtained at 80.33% at 10°C. Freundlich adsorption isotherm was proposed	[137]
N,N-Bis (phosphono methyl) glycine + Zn ²⁺ ions. (± Tungstate)	Concentration	Alloy Carbon steel Medium 200ppm NaCl (pH 5 – 9) Methods WL, SEM, PDP, EIS, XPS, FTIR	Tungstate exhibited a synergistic effect. Ternary inhibitor formulation performed well in neutral, slightly acidic and slightly alkaline media. Higher IEs were obtained at higher concentrations of the ternary compound. Inhibitor is mixed type. The protective film consisted of iron oxides/hydroxides, zinc hydroxide, heteropolynuclear complex and WO ₃	[138]
N,N-Bis(phosphonomethyl) glycine + Zn ²⁺ ions. (± Ascorbate ions)	Concentration and pH	Alloy Carbon steel Medium Low chloride environment Methods WL, PDP, EIS, XPS (X-ray photoelectron spectra), SEM, FTIR.	The binary system consisting of 20 ppm of BPMG and 30ppm of Zn ²⁺ accelerated corrosion of carbon steel. But the addition of 25ppm of ascorbate to the system gave an IE of 94%. The inhibitor is mixed type and effective between pH of 5 and 11	[139]
Two derivatives: 2-(2-oxo-2-phenothiazin-10-yl) ethylamino)-3-mercaptopropanoic acid (OPEM) and 2-(2-oxo-2-phenothiazin-10-yl) ethylamino) acetic acid (OPEA)	Concentration (20, 50, 100, 150, 200, 250ppm) and temperature (30, 40, 50, 60°C).	Alloy Mild steel Medium 15% HCl Methods WL, PDP, EIS, AM1, SEM.	Maximum IE obtained in the order: OPEM (97.5%) > OPEA (95.8%) at 200ppm and 60°C. IE of both inhibitors increased with increase in concentration and temperature. Both inhibitors are mixed-type. Langmuir adsorption isotherm confirmed.	[140]
N,N-Bis(phosphonomethyl) glycine ± Zn ²⁺	Concentration of both substances and pH (5 – 8)	Alloy Carbon steel Medium 200ppm NaCl in different pH environment. Methods WL, PDP, EIS, XPS, FTIR, SEM	Inhibitor effective in the pH range 5 – 8. Glycine derivative and Zn ²⁺ showed strong synergistic effect. The inhibitor is mixed-type. Formed film contained oxides/hydroxides of iron (III), Zn(OH) ₂ and [Zn (II) inhibitor] complex.	[141]
Phenylalanine (PA) + Zn ²⁺ ions	Concentration of both substances.	Alloy Carbon steel Medium Well water with pH 8 Methods WL, PDP, EIS, SEM-EDAX	Maximum IE of 90% obtained with 5 ppm of Zn ²⁺ and 150ppm of PA. Inhibitor is anodic.	[142]
Four alkylamides derived from tyrosine and glycine	Concentration (10, 25, 50 and 100ppm) and temperature (25, 35, 45, and 60°C)	Alloy Carbon steel Medium 1M HCl Methods WL, PDP	80% < IE < 90% at ≥50 ppm. Inhibitor is mixed type. Dodecyl amine of tyrosine exhibited the higher IE because of its large steric body of the last against glycine. The IE correlated with the length of alkyl chain. IE reduced with temperature increase in all cases.	[143]
Cysteine derivative: methyl ester hydrochloride	Concentration (10 ⁻² , 10 ⁻³ , 10 ⁻⁴ and 10 ⁻⁵) and temperature (30, 35, 45 and 55°C)	Alloy Carbon steel Medium 2M H ₃ PO ₄ Methods WL, PDP, EIS	Maximum IE=93% at 10 ⁻² M from WL method. IE increased with increasing inhibitor concentration but decreased with increasing temperature, Inhibitor is mixed type. Physisorption proposed.	[144]
Methionine ((± I ⁻))	Concentration of both substances.	Alloy Low carbon steel (SNCLCS) and bulk steel (BLCS) Medium 0.5M H ₂ SO ₄	Synergism effect of I ⁻ ions with methionine. For BLCS, IE = 53% at 5 mM of methionine and 97.7% in the presence of 5mM of KI, and for SNCLCS, the IE = 53% at 5 mM of	[145]

		Methods PDP, EIS, AFM, OCP.	methionine and 71% in the presence of 5 mM of KI Inhibitor behaved as mixed type for both alloys	
Serine, cysteine, phenylalanine, aspartate, asparagine, and 70 other organic substances.		Alloy Carbon steel rebar Medium Saturated CaOH solution +NaOH 0.01M (Ph 12.6 +NaCl (0.1, 0.3 and 1M) Method CP	Tested amino acids showed some inhibition effect, but not sufficient for an industrial application.	[146]
Leucine, alanine, methionine, and glutamic acid (Glu-A)	Concentration of inhibitors	Alloy NST-44 mild steel Medium Lime fluid Methods WL, OM	Order of IE of tested amino acids in lime fluid: Alanine > Methionine > Leucine > Glu-A, IE in this medium also increased with concentration.	[147]
Leucine, alanine, methionine, and glutamic acid (Glu-A)	Concentration of inhibitors	Alloy NST-44 mild steel Medium Cassava fluid Methods WL, OM	Order of IE of tested amino acids in cassava fluid: Alanine (50%) > Leucine (46%) > Methionine (45%) > Glu-A (30%).	[148]
Tryptophan		Alloy Low carbon steel Medium 1M HCl Methods WL, PDP, Molecular dynamic Fe (1 1 0). DFT/B3LYP 6-311*G (d.p)	Maximum IE = 91% at 10 ⁻² M. Cathodic inhibitor. Physisorption and chemisorption mechanism. Tryptophan molecules assumed a nearly flat orientation with Fe (1 1 0) surface.	[89]
Tryptophan, tyrosine and serine	Concentration (0.01, 0.02, 0.04 and 0.06M), temperature (30, 40, 50, and 60 ± 1 °C), stirring velocities (400, 800, 1,200, and 1,600 rpm)	Alloy Low alloy steel Medium 0.2M ammoniated citric acid Methods PDP, EIS, EFM, OM	Order of maximum IE = Tryptophan (86%) > Tyrosine (83%) > serine (82%) at 0.06M. Physisorption proposed. IE decreased with increase in solution stirring speed due to removal of layers of inhibitor on alloy surface. IE also increased with increase in concentration but decreased with increase in temperature.	[90]
Serine	Concentration (1, 2, 5, 10, 20, 50mM) and temperature (10, 20, 30, 40, 50, 60°C).	Alloy Low alloy ASTM A213 Medium 0.5M HCl Methods PDP, EFM, XPS	Inhibitor is cathodic. XPS confirmed film formation of inhibitor. Physical adsorption proposed. Temkin adsorption isotherm confirmed. IE increased with increase in Serine concentration, while it decreased with temperature increase.	[149]
Methionine, alanine and glycine, Citrulline and hydroxyproline		Alloy 16/14 austenitic stainless steel Medium HCl Methods PDP, PR	There is more passivation at wide potential range in the presence of the amino acids	[150]
Aspartic acid	pH of corrosive media	Alloy Steel (UNS G10180) Media Solutions with different pH values (8 -12) Methods WL, EIS with RDE	At a pH less than ~9.5 to 10, aspartic acid appeared to speed up corrosion, while at pH above those, it inhibited corrosion	[151]
Tryptophan	Concentration (0.005, 0.01, 0.02, 0.04M), temperature (25, 40, 50, 60°C) and immersion time	Alloy Low alloy steel Medium 0.6 M HSO ₃ NH ₂ Methods WL, EIS and EFM	Inhibitor performed very well. IE increased with concentration increase but decreased with temperature increase.	[152]

Tryptophan	Concentration (0.005, 0.01, 0.02, 0.04M), temperature (25, 40, 50, 60°C) and immersion time	Alloy Low alloy steel (ASTM A213 grade T22) Media 0.6 M HSO ₃ NH ₂ and 0.6 M HCl Methods WL, EIS and EFM	Inhibitor performed better in 0.6 M HCl (IE =94.46%) than in 0.6M HSO ₃ NH ₂ (IE=91.58%) from the EFM method. The adsorption can occur via adsorbed SO ₃ NH ₂ ⁻ and Cl ⁻ anions at the surface of the alloy. IE increased with increase in concentration but decreased with increase in temperature and immersion time.	[153]
Methionine	Concentration of inhibitor (0.25, 0.50, 0.75 and 1.0g/L)	Alloy Low alloy steel (39 and 44) Medium 1M H ₂ SO ₄ + 1mM NaCl Method PDP	IE = 74% for Steel 39 and 81% for steel 44 at 1 g/L of methionine. Inhibitor is mixed type. IE increased with increase in concentration	[154]
Polyaspartic acid (PASP)	pH	Alloy Steel Medium CaSO ₄ + MgCl ₂ + NaHCO ₃ + Na SO ₄ solutions and deionized water (pH 3.5 -12) Methods WL, EIS, RCE	At low to neutral pH values, PASP increased the corrosion rate and at high pH values, it functioned as an inhibitor. At lower pH values, Fe-PASP complexes were stable, while at higher pH values, no such complexes were predicted.	[155]
Cysteine	Concentration (0.1, 0.5, 1.0, 2.0 and 5.0g/L)	Alloy Steel 08-kp Medium 0.5M H ₂ SO ₄ Methods WL, PDP, SEM	Maximum IE of 66% obtained at 5g/L concentration of inhibitor. Inhibition functioned as mixed type	[156]
L-arginine	Concentration (100, 300, 700, 900mg/L)	Alloy Steel Medium 1M HCl Methods WL, PDP, EIS, EFM	Maximum IE of 70.53% obtained with 900mg/L of inhibitor (from EIS measurements)	[157]
L-arginine	Concentration (100, 300, 700, 900mg/L)	Alloy Steel Medium 3.5% NaCl Methods PDP, EIS, EFM, DFT	Maximum IE of 88.20% obtained with 900mg/L of inhibitor (from EIS measurements). MD simulations revealed shape of adsorption on Fe (1 1 1).	[158]
Serine, threonine, glutamine		Alloy Cold-rolled steel Medium 1M HCl Methods WL, PDP, EFM, AFM, SEM, computational schemes	IE of Glu was better than those of serine and threonine. Temkin adsorption isotherm was confirmed. IE increased with an increase in total negative charge values of the molecules. R ² = 0.96 with 3LYP/6-311 G(d,p) was found as the best model among models generated by the Genetic Function Algorithm	[159, 160]
Tyrosine, polyacrylic acid and yeast	Concentration (5ppm) and temperature (25, 35, 45, 55°C)	Alloy Stainless steel (S41000) Medium Synthetic seawater Methods PDP, EIS	Yeast performed better as an inhibitor than others	[161]
4,6-diamino-2-pyrimidinethiol (4D2P)	Concentration (0.5, 1.0, 5.0, 10mM) and immersion time (1, 24, 72, 120hrs)	Alloy Mild steel Medium 0.1M HCl Methods LPR, PDP, EIS, SEM, DFT with 6-311++G (d, p)	Maximum IE of 97.2% obtained with the 10mM concentration at 72hrs of immersion.	[6]
Polyaspartic acid-glycine derivative	Concentration (50, 100, 150, 200 250ppm)	Alloy Carbon steel Medium Sea water Methods PDP, EIS, SEM, EDX, H NMR	Maximum IE (83.8%) obtained at 250ppm of inhibitor	[162]

Methionine, cysteine, serine, arginine, glutamine and asparagine		Alloy Carbon steel Medium 0.5M H ₂ SO ₄ Methods PDP, EIS, DFT/BLYP 3.5 DNP, molecular dynamics on Fe (1 0 0)	Order of IE; = Methionine > Cysteine > Serine > Arginine > Glutamine > asparagine at 10 ⁻² M.	[163]
Cysteine (± imidazoline derivative (IM))		Alloy Carbon steel Medium CO ₂ -saturated brine solution Methods PDP, OCP, EIS, WL, XPS, contact angle	Order of IE (at 50ppm cysteine): cysteine (91.8%) < cysteine + IM (96.7%). Inhibitor exhibited mixed type inhibition.	[164]
Tetra-n-butyl Ammonium methioninate	Concentration (1.33 x 10 ⁻⁵ M, 1.33 x 10 ⁻⁴ M, 2.66 x 10 ⁻⁴ M, 7.97 x 10 ⁻⁴ M, 1.59 x 10 ⁻³ M)	Alloy Mild steel Medium 1M HCl Methods PDP, SEM-EDX, OCP, DFT/B3LYP 6-311++G**	Maximum IE of 95.1% obtained with 1.59 x 10 ⁻³ M. Mixed type inhibitor with prevalent anodic inhibition. Freundlich adsorption isotherm confirmed.	[165]
Leucine, phenylalanine and methionine derivatives		Alloy Carbon steel Medium 1M HCl Methods PDP, EIS, MINDO, FTIR, H, C NMR and elemental analysis	Phenylalanine-based derivative exhibited highest IE of 94.14% with 10 ⁻³ M concentration Inhibitor is mixed type. Langmuir adsorption isotherm proposed.	[166]
L- Lysine (Lys) and L- Arginine (Arg)		Alloy 316L Stainless Steel Medium 0.5 M NaCl, pH 6.0 Methods FTIR, SERS, SEM	Lysine and Arginine showed excellent inhibition properties and effectively restrained the corrosion of 316 stainless steel. Addition of Iodide ion increased their inhibition efficiency. In all, Arginine performed as a better inhibitor than lysine	[167]
Glutamic acid, (Glu), Glutamine (Gln), Cerium Glutamate (Ce-Glu), Cerium Glutamine (Ce-Gln)	Concentration (25-200ppm) and temperature (25 and 55°C)	Alloy Mild Steel Medium 0.5 M HCl Methods PDP, EIS, SEM, UV-VIS, FTIR	The efficiency of inhibition was found to be Ce-Gln > Gln and Ce-Glu > Glu	[168]
L-Amino Acids		Alloy Mild Steel Medium Gas phase Methods Monte Carlo Simulations	Inhibitors were studied based on different side chain lengths. The efficiency of inhibitions was in the following order: Glu (acidic) < Gln (polar) < Trp (nonpolar) < Arg (basic)	[169]
Cysteamine-modified Polyaspartic acid (PASP-S) and Polyaspartic acid (PASP)	Concentration (10, 20, 50, 100mg/L) and temperature (25, 35, 45°C)	Alloy Mild steel Medium 0.5 M H ₂ SO ₄ Methods WL, PDP, EIS, DFT, XPS	Maximum IE of 93.9% obtained with the WL method using 100mg/L PASP-S. IE reduced with temperature but increased with concentration	[170]
Phenylalanine (P1) Aspartic Acid (P2)	Concentration	Alloy Mild Steel Medium 1M HCl Methods UV-VIS SEM, EIS, PDP	Adsorption increased with increase in concentration of both P1 and P2. P2 gave highest adsorption of 89% as compared to P1 that gave maximum adsorption of 87%	[171]
Amino acids.	Concentration (1-1000 × 10 ⁻⁶ mol/l) and temperature (25–40°C)	Alloy Carbon steel Medium H ₃ PO ₄ Methods galvanostatic techniques	Increases in the amino acid concentrations inhibited the electroplating process by 83.33% in the case of L-methionine at 25°C.	[172]

Cysteine-doped Polyvinylpyrrolidone (PVPC)	Concentration (25, 100, 300, 500, and 700 ppm)	Alloy Mild steel Medium 1M HCl Methods WL, FTIR, XRD, SEM/EDX	Maximum IE of 97% obtained at 700 ppm	[173]
L-histidine (LHD), 1-phenylthiourea (PT), LHD+PT, phenylcarbamothioyl)histidine (PT-HD)	Concentration (0.05, 0.1, 0.2, 0.4Mm), temperature of 60°C	Alloy Carbon steel Medium CO ₂ -saturated formation water Methods WL, EIS, PDP, SEM, AFM, ATR-AFM, quantum chemical calculation, GFN-xTB calculations	Inhibition efficiency decreased in the order: PT-HD (99.3%) > LHD + PT (99.2%) > PT (97%) > LHD (70.9%) at concentration of 0.4mM with the EIS method	[174]
L-histidine + thiourea, L-cysteine + thiourea)		Alloy N80 carbon steel Medium CO ₂ -containing environment Methods EIS, PDP, OCP, SEM, AFM, XPS, theoretical calculations	Maximum IE of 99.4% obtained with L-histidine + thiourea and 99.3% obtained with L-cysteine + thiourea using the PDP method	[175]
Benzotriazole (BZT), 5- methyl-1H-benzotriazole (5MBZT), and 3-amino-5-methylthio-1H-1, 2,4, triazole (3AMT)	Type of metal, molecular structure, and immersion time	Alloy/Metal C1020 steel and copper Medium 2% HCl Methods EIS, PDP, LPR, theoretical simulations	For C1020 steel, order of IE using EIS data was 5MBZT (91.8%) > BZT (78.1%) > 3AMT (24.8%) after 24hrs of immersion	[176]
Tryptophan, histidine	Concentration (100,200, 300, 400, 500ppm), temperature (20, 30, 40, 50°C)	Metal SABIC iron Medium 0.5M HCl Methods PDP, EIS, mass loss, SEM, DFT, MC simulation	Maximum IE of 92.09% for tryptophan and 89.37% for histidine at a concentration of 500 ppm and 30°C using the PDP method. IE increased with concentration but reduced with temperature (using the mass loss method)	[177]
Thiazolidine-2,4-diones (TZD) and its amino derivative 2-aminothiazolidin-4-one (AT).	Concentration (1×10^{-6} , 5×10^{-6} , 1×10^{-5} , 5×10^{-5} , 1×10^{-4} , 5×10^{-4} , 1×10^{-3} , 5×10^{-3} and temperature (30, 40, 50, 60°C).	Alloy Mild steel Medium 5% HCl Methods WL, OCP, PDP, EIS, FTIR, UV-VIS, XPS, SEM-EDS, AFM	Maximum IEs of 98.0% and 99.7%, obtained with TZD and AT respectively at a concentration of 5×10^{-4} M at 60 °C. IE increased with temperature and concentration.	[178]
2 Indoline compounds designated as FTTI and FTMI	Concentration (5, 10, 15, 20, 25, 30, 35, 40, 45, 50 μ ML ⁻¹) and temperature (30, 40, 50, 60°C)	Alloy oil well/ tubing steel Medium 15% HCl Methods WL, OCP, PDP, EIS, SEM-EDX, AFM, XPS, DFT, MD Simulation	IEs of 99.08% and 97.75% obtained for the two compounds respectively at 30°C and concentration of 50 μ ML ⁻¹ . IE remained nearly constant at elevated temperatures due to predominant chemisorption of the inhibitors upon the metallic substrate	[179]
Protein and its amino acids, isolated from tofu pulp,	Concentration (40, 60, 80, 100, 120ppm)	Alloy Carbon steel Medium brackish water media Method EIS	IE % of isolated protein in fraction 3 was found to be 92% at 80 ppm.	[180]
Two new thiazoles designated as APNT and APT		Alloy Mild steel Medium 1M HCl WL, DFT	IE values of 98.1% and 94.74% were recorded as results of inhibition of the mild by the inhibiting compounds APNT and ATP respectively	[181]

Methionine (MTI)	Concentration (500, 1000, 1500, 2000ppm), temperature (40, 60, 80°C), and speed of rotation	Alloy carbon steel 1018 Medium 5.0 mol/L MEA Methods WL, EIS, PDP, OCP	IEs of up to 83.56% and 74.96% were obtained under static and dynamic conditions, respectively. IE increased with MTI concentration and solution temperature but decreased with rotational speed.	[182]
Ortho-, meta- and para-aminobenzoic acid (ABA)		Alloy Mild steel Medium HCl solution Methods Computational methods	IE occurred in the order (OABA > MABA > PABA).	[183]
L-valine + additives (salts, both inorganic (potassium iodide, KI) and organic (Sodium benzoate, SB), and non-ionic sugar based surfactant (N-decyl-N'-glucosylethylenediamine, SS)	Concentration (100, 200, 300, 350, 400ppm), temperature (30, 40, 50, and 60 °C) and immersion time extending from 1 to 7 days.	Alloy Mild steel Medium 5% HCl Methods EIS, PDP, FTIR, SEM-EDX	The inhibition effect of the additives in 5% HCl is in the following order: Val + SS > Val + SB > Val + KI > Val + KI. The IE of Val and Val + additives increased with temperature rise from 30 °C to 60 °C. However, increases in the exposure period within the first three days resulted in IE increases, but thereafter it decreased.	[184]
D-cysteine	Concentration (2.5mM, 5mM) and time of immersion (1, 3, 7days)	Alloy 304 stainless steel Medium Sterile and <i>Pseudomonas aeruginosa</i> -inoculated culture media Methods XPS, SEM	The biofilm inhibition effect of D-cysteine greatly reduced the destructive effect of the adhered <i>P. aeruginosa</i> cells on the passive film of the stainless steel, thus inhibiting the microbiologically influenced corrosion of the stainless steel.	[185]
L-histidine based ionic liquid (LHIL)		Alloy Mild steel Medium 1M HCl Methods FTIR, UV-VIS, XPS, H-NMR and high-resolution mass spectrometry, PDP, EIS, localized electrochemical strategies, Theoretical calculations	Maximum IE attained was 98.8%	[186]

4. CONCLUSIONS

From the literature scan, amino acids have shown high efficacy as corrosion inhibitors for metals in acidic solutions. Much of the research focused on the synthesis of the derivatives of the amino acid compounds. Some experimental results indicated that the inhibition efficiency of some amino acids increases with increasing pH values. Computational modeling employed in some of the studies provided useful insights into the interactions between the metal and the studied amino acids including the inhibition mechanisms of the compound.

The efficiency of those compounds has been found to be greatly influenced by many factors, such as temperature, concentration of inhibitor, immersion time, pH, hydrodynamic conditions, etc. Highest values of inhibition efficiency were obtained in the presence of I⁻ ions and Br⁻ ions. Mechanism of inhibition by amino acid is found to

be principally due to adsorption of the heteroatoms/groups and π -electrons (polar groups) to the metal/alloy surface.

Further research should consider experimental studies and computational modeling to evaluate the effect of amino acid and its derivative compounds on other metals/alloys such as stainless steel, bronze, zinc, etc. with a larger scale of application. In addition, when developing a predictive model for Corrosion Science and Engineering, such factors as concentration of inhibitor, temperature, solution flow, solution pH, inhibitor-metal surface bonding, solubility of inhibitor, etc. must be put into consideration. These factors should also be considered during experimental investigations.

ABBREVIATIONS

HPLC - high-performance liquid chromatography.
ATR-FTIR – Attenuated total reflection FTIR.
LP – Linear polarization

PR – Polarisation resistance
 OCP – Open circuit potential.
 IR – Infrared spectroscopy
 EDX – Energy Dispersive X-ray spectroscopy.
 SEM-EDS – Scanning electron microscopy – energy dispersive spectroscopy
 SEM-EDAX - Scanning electron microscopy – energy dispersive spectroscopy
 OM – Optical microscopy.
 RCE - Rotating cylinder electrode
 RDE – Rotating disk electrode
 SERS - Surface-enhanced Raman spectroscopy.
 GC – Gas Chromatography.
 MC – Mass spectroscopy.
 XRD - X-ray diffractometer.
 MC - Monte Carlo.
 QM - quantum mechanics
 GFN-xTB: Geometries; F: Frequencies; N: Noncovalent interactions) tight-binding based electronic structure.
 H, NMR - Hydrogen-nuclear Magnetic Resonance.
 C, NMR – Carbon Nuclear Magnetic Resonance
 MNDO - Modified Neglect of Diatomic Overlap.
 ICP-AES - inductively coupled plasma atomic emission spectroscopy
 DNP - double numerical with polarization
 PM3 - Parameterized Model number 3.
 AM1 - Austin Model 1

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IZVOD

PREGLED AMINOKISELINA KOJE SE KORISTE KAO INHIBITORI KOROZIJE NA METALU/LEGURAMA GVOŽĐA U AGRESIVNIM SREDINAMA

Istraživanje upotrebe bezbednih i ekološki prihvatljivih inhibitora korozije može utrti put za razumevanje njihovih mehanizama inhibicije za materijale od metalnih legura. Ovaj pregled ima za cilj da predstavi i prodiskutuje istraživački rad objavljen u literaturi o upotrebi aminokiselina i njihovih derivata kao inhibitora korozije gvožđa i njegovih legura u različitim agresivnim rastvorima. Ovaj netoksičan, biorazgradiv i relativno jeftin inhibitor korozije pokazao se efikasnim kao inhibitor metala/legura u kiselim, alkalnim i neutralnim rastvorima u zavisnosti od eksperimentalnih uslova. Elektrohemijske i površinske tehnike bile su među najčešće korišćenim tehnikama za procenu efikasnosti inhibicije korozije aminokiselina. Najveće vrednosti efikasnosti inhibicije mogu se dobiti u prisustvu jona kao I- i Br-. Ovaj pregled predstavlja i razmatra većinu doprinosa u literaturi o upotrebi aminokiselina i njihovih derivata kao inhibitora korozije gvožđa i njegovih legura.

Ključne reči: inhibitor korozije, gvožđe, metal, legura, amino kiselina, računске metode

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