

Revolutionizing Corrosion Defense: Unlocking the Power of Expired BCAA

M. Taha Mohamed¹, S.A. Naw¹, A.M. Mustafa², F.F. Sayyid², M.M. Hanoon², A.A. Al-Amieri^{*3,4}, A.A.H. Kadhum⁵, W.K. Al-Azzawi⁶

¹ Department of Material Engineering, College of Engineering, University of Diyala, P.O. Box: 34013, Diyala, Iraq

² Department of Production Engineering and Metallurgy, University of Technology, P.O. Box: 10001, Baghdad, Iraq

³ Energy and Renewable Energies Technology Center, University of Technology, P.O. Box: 10001, Baghdad, Iraq

⁴ Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Bangi, Selangor 43600, Malaysia

⁵ Al-Ameed University College, P.O. Box: 56001, Karbala, Iraq

⁶ Al-Farahidi University, P.O. Box: 10001, Baghdad, Iraq

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ABSTRACT

Corrosion of mild steel in acidic environments presents a significant challenge across diverse industries. This pioneering research explores the novel potential of expired BCAA (Leucine, Isoleucine, and Valine) as a dynamic corrosion inhibitor for mild steel immersed in HCl solution. Through meticulous weight loss techniques, we quantified the corrosion rates of mild steel, both with and without the intervention of BCAA. Complementing our experimental approach, Density Functional Theory (DFT) calculations illuminated the intricate molecular interactions between BCAA and the metal surface. Furthermore, a comprehensive study of the adsorption isotherm unraveled the adsorption behavior of BCAA molecules on the mild steel surface. Remarkably, the inhibition efficiency of BCAA soared to an impressive 92.2 % at a concentration of 500 mM, a temperature of 303 K, and an immersion time of 5 hours. However, with the temperature increase to 333 K, a notable reduction in inhibition efficiency was observed. Intriguingly, the adsorption isotherm analysis showcased BCAA's adherence to the Langmuir adsorption isotherm, revealing additional insights into its inhibitory prowess. These groundbreaking findings highlight the untapped potential of expired BCAA as a corrosion inhibitor, offering valuable insights into its inhibition efficiency, temperature dependence, and adsorption behavior. Prog. Color Colorants Coat. 17 (2024), 97-111© Institute for Color Science and Technology.

1. Introduction

Corrosion of metals, especially mild steel, in acidic environments, poses persistent challenges in diverse industries, such as oil and gas, chemical processing, and infrastructure [1-3]. Addressing these issues necessitates the development of effective corrosion inhibitors to mitigate financial losses, safety hazards, and environmental concerns [4, 5]. Corrosion

inhibitors, substances that reduce the corrosion rate of metals, form protective layers on metal surfaces, acting as barriers against corrosive agents [10]. Recently, there has been a growing interest in environmentally friendly corrosion inhibitors derived from natural sources [12]. This study explores the potential use of expired BCAA (Leucine, Isoleucine, and Valine) as a corrosion inhibitor for mild steel in HCl solution.

*Corresponding author: * dr.ahmed1975@ukm.edu.my
dr.ahmed1975@gmail.com

BCAA, a mixture of essential amino acids, is widely known for its role in muscle protein synthesis and recovery, making it a common nutritional supplement in the fitness industry.

The novelty of this approach lies in the investigation of BCAA as a corrosion inhibitor, offering several advantages. Firstly, BCAA is readily available, cost-effective, and environmentally friendly, aligning with the demand for sustainable alternatives in industries. Secondly, the functional groups present in BCAA molecules, such as amino and carboxyl groups, suggest potential interactions with the metal surface, leading to the formation of protective films. Our main research objective is to evaluate the corrosion inhibition performance of BCAA (Figure 1) and its potential as an alternative to synthetic inhibitors. The study adopts a multidisciplinary approach, combining weight loss techniques, Density Functional Theory (DFT) calculations, and adsorption isotherm analysis to comprehensively analyze the corrosion inhibition mechanism. By bridging experimental observations and theoretical understanding, this research aims to provide valuable insights into BCAA's effectiveness.

The findings of this study hold practical implications for industries dealing with mild steel corrosion in acidic environments. If proven effective, expired BCAA can offer an eco-friendly and cost-efficient solution for corrosion prevention. Additionally, this study sets the stage for further investigations into the optimization of BCAA formulations and the development of tailored inhibitors for specific applications.

In conclusion, exploring the use of expired BCAA as a corrosion inhibitor for mild steel in HCl solution shows great promise. Our comprehensive analysis of BCAA's corrosion inhibition capabilities through various techniques will provide a scientific basis for its potential practical application. Ultimately, the outcomes of this study will contribute to the development of sustainable corrosion mitigation strategies, benefiting industries and the environment alike.

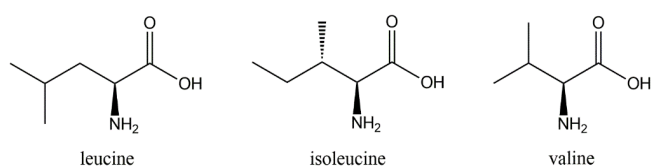


Figure 1: BCAA chemical structures.

Corrosion of mild steel in acidic environments is a well-known phenomenon that occurs due to the chemical reactions between the metal and the corrosive medium [13, 14]. Acidic solutions, such as hydrochloric acid (HCl), play a significant role in industrial processes and can cause severe damage to mild steel components. The corrosion process involves the dissolution of iron ions from the metal surface, leading to the formation of metal oxide and metal hydroxide compounds [15]. This results in the degradation of the metal, loss of material, and compromised structural integrity [16]. Understanding the mechanisms and factors influencing the corrosion of mild steel in acidic environments is crucial for the development of effective corrosion mitigation strategies [17]. Corrosion inhibitors are substances that can be added to corrosive environments to reduce the corrosion rate of metals [18]. They function by adsorbing onto the metal surface and forming a protective layer that acts as a barrier against corrosive agents [19]. Corrosion inhibitors can be classified into various categories, including organic and inorganic inhibitors [20]. Organic inhibitors, especially those derived from natural sources, have gained attention due to their environmentally friendly nature [21-25]. The efficiency of a corrosion inhibitor is influenced by factors such as concentration, temperature, immersion time, and the nature of the corrosive medium [26-28]. Expired BCAA, a mixture of essential amino acids including leucine, isoleucine, and valine, has gained popularity as a nutritional supplement in the fitness industry. BCAAs are known for their role in muscle protein synthesis, recovery, and energy production. These amino acids possess unique properties, including the presence of functional groups such as amino and carboxyl groups. BCAA supplements are readily available and are often consumed by athletes and fitness enthusiasts to enhance exercise performance and muscle recovery. Previous Research on BCAA as a Corrosion Inhibitor

Although the use of BCAA as a corrosion inhibitor is relatively unexplored, there have been studies investigating the corrosion inhibition properties of amino acids and related compounds. Amino acids, due to their functional groups, have the potential to interact with metal surfaces and form protective films. Previous research has shown promising results for the corrosion inhibition efficiency of amino acids, including leucine, isoleucine, and valine, on various metals. These studies have highlighted the importance of factors such as concentration, immersion time, and temperature in

determining the inhibitory performance of amino acids. However, further investigations are required to fully understand the corrosion inhibition mechanisms and potential applications of BCAA as a corrosion inhibitor for mild steel in acidic environments.

In summary, the corrosion of mild steel in acidic environments is a well-documented problem in various industries. Corrosion inhibitors play a vital role in mitigating the damaging effects of corrosion by forming protective layers on metal surfaces [29, 30]. BCAA, a mixture of essential amino acids, has gained popularity as a nutritional supplement but remains relatively unexplored as a corrosion inhibitor. Previous research on amino acids has shown promising results, indicating the potential of BCAA as a corrosion inhibitor. However, further investigations are necessary to evaluate its inhibitory efficiency, understand the corrosion inhibition mechanisms, and determine the optimal conditions for its application in acidic environments.

2. Experimental

2.1. Materials and reagents

All materials and reagents used in this study were purchased from Sigma-Aldrich/Malaysia. To create a corrosive media for the experiments, a 1 M HCl solution was prepared by diluting analytical grade 37 % HCl solution with double-distilled water. Inhibitor concentrations ranging from 0.1 to 1.0 mM were achieved by diluting the inhibitor in 1 M HCl solution [31].

2.2. Sample preparation

The mild steel samples used in this study were analyzed for their chemical composition using X-ray fluorescence spectrometry. The samples were prepared according to the ASTM G1-03 protocol and polished with silicon carbide series plates. Prior to immersion, the mild steel coupons were cleaned with double-distilled water and acetone, and then dried in an oven [32, 33].

2.3. Weight loss measurements

The weight loss measurements were conducted by immersing the mild steel samples in 500 ml glass beakers containing 400 mL of 1 M HCl solution with varying concentrations of the inhibitor. The experiments were conducted at 303 K using a water

bath, following the NACE TM0169/G31 protocol. The samples were exposed for different periods (1, 5, 10, 24, and 48 hours), and the products of corrosion were wiped off the surface before the coupons were dried and weighed. The weight difference was recorded, and the mass variation at the estimated time and original mass of the metallic sample represented the weight loss attained. The mild steel coupons were immersed in corrosive media (1 M HCl) containing different inhibitor concentrations (0.1, 0.2, 0.3, 0.4, 0.5, and 1 mM) at temperatures of 303, 313, 323, and 333 K using a water bath to determine the effect of temperature [32, 33]. The average rate of corrosion was calculated after being exposed in triplicate, and the rate of corrosion and inhibition efficiency were determined using the following equations 1 and 2.

$$C_R = \frac{W}{adt} \quad (1)$$

$$IE \% = \left[1 - \frac{C_{R(i)}}{C_{R_0}}\right] \times 100 \quad (2)$$

where W is the weight loss (mg) of the sample, a is the surface area of mild steel (cm^2), d is the density of the mild steel coupon (g/cm^3), and t is the exposure time (h). The corrosion rates in the absence and presence of the inhibitor were denoted as C_{R_0} and $C_{R(i)}$ respectively. The coverage area (θ) for both uninhibited and inhibited solutions was determined using the following equation 3.

$$\theta = 1 - \frac{C_{R(i)}}{C_{R_0}} \quad (3)$$

2.4. DFT calculations

Density Functional Theory (DFT) calculations were performed using the Gaussian 09 software to investigate the molecular interactions between the inhibitor and the metal surface. The optimization of the inhibitor structure in the gaseous state was achieved through the B3LYP method and the basis set "6-31G⁺⁺(d,p)". The ionization potential (I) and electron affinity (A) were determined based on Koopmans theory using the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LOMO}), respectively. The following equations 4 and 5 were employed for calculating I and A [34, 35].

$$I = -E_{HOMO} \quad (4)$$

$$A = -E_{LOMO} \quad (5)$$

The electronegativity (χ), hardness (η), and softness (σ) values were calculated using the following equations 6-8.

$$\chi = \frac{I+A}{2} \quad (6)$$

$$\eta = \frac{I-A}{2} \quad (7)$$

$$\sigma = 1/\eta \quad (8)$$

The number of electrons transferred (ΔN) was calculated using equation 9 from reference [36]. The electronegativity value of iron was determined as 7 eV, and its hardness value was found to be zero eV. Based on these results, Equation 10 was developed.

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (9)$$

$$\Delta N = \frac{7 - \chi_{inh}}{2(\eta_{inh})} \quad (10)$$

2.5. Adsorption isotherm studies

To gain a better understanding of the properties of the studied molecules, various types of adsorption isotherms, such as Frumkin, Temkin, and Langmuir, were employed. These isotherms assist in determining the amount of inhibitor coverage on the metal surface. Weight loss measurements were carried out to determine the extent of surface coverage of the inhibitor at various concentrations in corrosive media [37].

3. Results and Discussion

3.1. Weight loss measurements

Weight loss measurements were conducted to assess the corrosion behavior of mild steel samples in a corrosive environment. The experiments were carried out at 303 K, and the samples were immersed for 5 hours in a 1 M HCl solution with varying concentrations of BCAA. The results, depicted in Figure 2, illustrate the corrosion rate and inhibition effectiveness [38]. Figure 2 shows that the addition of BCAA to the corrosive solution results in a notable reduction in the corrosion rate of the mild steel samples. The inhibitory effect increases with increasing BCAA concentration up to 0.5 mM. This can be attributed to the higher concentration of BCAA molecules available for adsorption onto the mild steel surface, forming a protective layer that hinders the

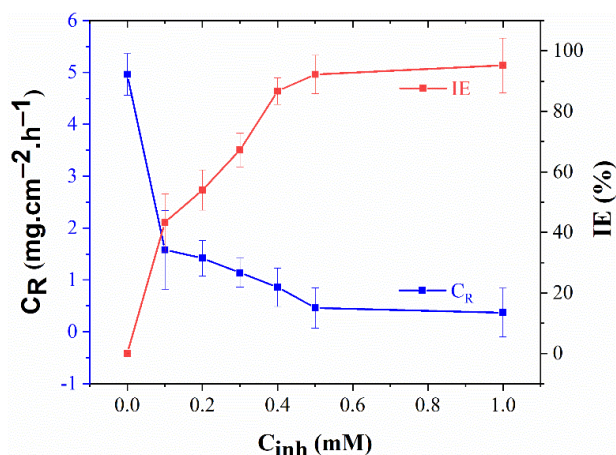


Figure 2: The corrosion rates and inhibition effectiveness of mild steel in hydrochloric acid solutions with and without the inhibitor after a 5-hour immersion period at 303 K.

corrosive attack, thus enhancing the inhibition effectiveness [39]. The formation of this protective layer acts as a barrier between the metal surface and the corrosive environment, thereby reducing the corrosion rate. However, it should be noted that at BCAA concentrations exceeding 0.5 mM, a decrease in the inhibition effectiveness is observed. This can be attributed to the desorption of BCAA molecules from the mild steel surface at higher concentrations. The desorption process weakens the protective layer, diminishing its ability to prevent corrosion effectively [40]. Overall, the weight loss measurements demonstrate the corrosion inhibition potential of BCAA for mild steel in a 1 M HCl solution. The results highlight the importance of optimizing the BCAA concentration to achieve the maximum inhibitory effect and provide insights into the adsorption behavior of BCAA molecules on the mild steel surface.

The effect of immersion duration on the corrosion inhibition efficiency of mild steel in a corrosive solution was investigated in this study. Mild steel samples were immersed in a hydrochloric acid solution containing different concentrations of the inhibitor for varying immersion periods (1, 5, 10, 24, and 48 hours) at a temperature of 303 K. The results obtained, as shown in Figure 3, indicate the corrosion inhibition efficiency as a function of immersion duration [41]. Figure 3 illustrates that the inhibition efficiency increases significantly as the immersion duration is extended up to 5 hours. Subsequently, it gradually increases up to 24 hours,

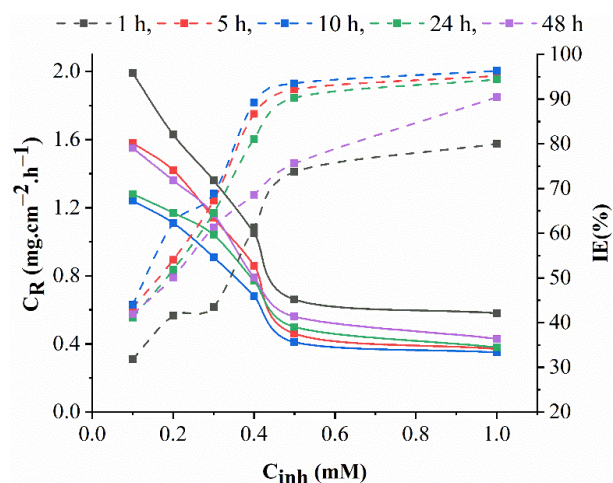


Figure 3: A corrosion rates and inhibition effectiveness of mild steel in hydrochloric acid solutions with and without the inhibitor for various immersion times at 303 K.

after which a decline in the protective performance is observed. Finally, after 48 hours, the inhibition efficiency stabilizes. The observed increase in inhibition efficiency can be attributed to the greater number of inhibitor molecules attaching to the surface of the mild steel, leading to the formation of a protective layer. This interaction allows the van der Waals forces to come into play, facilitating the adsorption of the inhibitor molecules onto the metal surface [42]. While it is possible for some inhibitor molecules to detach from the surface, reducing the coverage area and the overall effectiveness of the inhibitor, the sustained high inhibition efficiency observed during longer exposure durations demonstrates the stability of the adsorbed inhibitor layer in the corrosive solution. The protective layer formed by the inhibitor molecules acts as a barrier, preventing the corrosive agents from directly attacking the metal surface and, thus, reducing the corrosion rate [43]. These findings highlight the importance of immersion duration in the corrosion inhibition process. It is evident that longer exposure durations allow for a more substantial adsorption of inhibitor molecules and the formation of a stable protective layer. This understanding can aid in optimizing the immersion time and concentration of the inhibitor for practical applications, ensuring maximum corrosion protection for metallic substrates in corrosive environments [44].

The obtained results reveal interesting trends in the inhibition efficiency of BCAA as a function of immersion time. Initially, for a 1-hour immersion time, the inhibition efficiency was found to be 73.7 %. This

indicates that BCAA has a moderate inhibitory effect on the corrosion of the mild steel substrate during the initial stage of exposure [45]. However, as the immersion time increased, the inhibition efficiency of BCAA exhibited a notable improvement. After 1 hour of immersion, the inhibition efficiency increased to 92.2 %. This suggests that BCAA requires some time to establish a protective layer on the metal surface, which becomes more effective in preventing corrosion as the immersion time progresses. Furthermore, at a longer immersion time of 10 hours, the inhibition efficiency further increased to 93.5 %. This indicates that BCAA continues to build up and strengthen the protective layer over time, leading to enhanced corrosion inhibition [46]. However, as the immersion time extended to 24 hours, a slight reduction in the inhibition efficiency was observed, which decreased to 90.3 %. This could be attributed to various factors. Over an extended period, the corrosive environment may gradually weaken the protective layer formed by BCAA, leading to a reduction in its inhibitory effectiveness. Additionally, prolonged exposure to the corrosive media may cause the desorption of some BCAA molecules from the metal surface, further diminishing the overall inhibition efficiency. Notably, for a 48-hour immersion time, a more significant decrease in the inhibition efficiency was observed, with a value of 75.6 %. This suggests that the protective layer formed by BCAA becomes less stable and effective over an extended immersion duration. Factors such as chemical reactions, temperature effects, and the accumulation of corrosion products over time may contribute to the reduced inhibition efficiency [47].

Overall, the results highlight the time-dependent nature of BCAA's inhibitory effect. It is evident that BCAA requires an initial period to establish a protective layer, which subsequently enhances its corrosion inhibition properties. However, over longer immersion times, the effectiveness of the inhibitor diminishes, possibly due to degradation or depletion of the protective layer.

To optimize the use of BCAA as a corrosion inhibitor, it is essential to consider the immersion time and its impact on the inhibition efficiency. Further research is necessary to investigate the underlying mechanisms governing the time-dependent behavior of BCAA and to explore strategies for improving the stability and durability of the inhibitor's protective layer over extended immersion periods. In conclusion,

the results demonstrate that BCAA exhibits an increasing inhibition efficiency with increasing immersion time up to 10 hours, reaching a maximum of 93.5 % at 1-hour immersion and subsequently decreasing slightly at 24 hours to 90.3 % and significantly at 48 hours to 75.6 %. These findings emphasize the importance of considering immersion time when evaluating the performance of BCAA as a corrosion inhibitor and provide insights for optimizing its use in practical applications. The effectiveness of BCAA in reducing weight loss and activation variables was evaluated through weight loss experiments conducted at different temperatures (303, 313, 323, and 333 K) [48]. The results presented in Figure 4 demonstrate that as the temperature increases, there is a slight elevation in the corrosion rate of the metallic substrate in both inhibited and uninhibited solutions. This can be attributed to the increased thermal agitation of BCAA particles in the corrosive environment at higher temperatures, resulting in higher solution conductivity and acidity. Consequently, the inhibition efficiency decreases with rising temperature, leading to an increase in the corrosion rate [49]. At a temperature of 303 K in a 1 M HCl medium, an inhibitor concentration of 0.5 mM exhibited an impressive inhibition efficiency of 92.2 %. This finding indicates the efficacy of the novel inhibitor for hydrochloric acid solutions, which has not been previously reported.

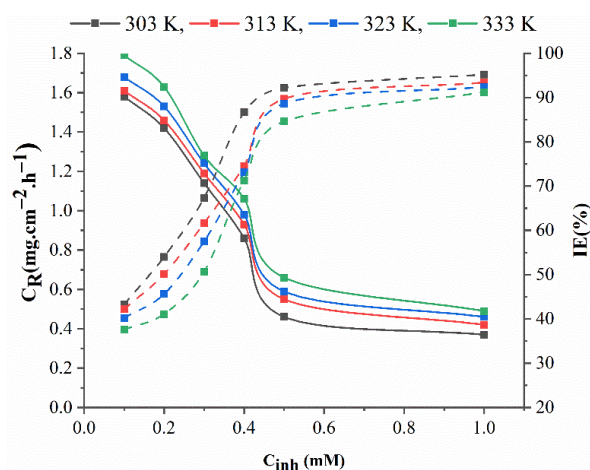


Figure 4: A comparison of corrosion rates and inhibition effectiveness in hydrochloric acid solutions with and without the inhibitor for a 5-hour immersion time at different temperatures.

The performance of this inhibitor surpasses that of previously studied inhibitors, underscoring the importance of maintaining protective performance, especially at high temperatures, as encountered in downhole conditions in the petroleum sector [50].

These results highlight the potential of BCAA as a corrosion inhibitor and its suitability for use in hydrochloric acid solutions. The inhibition efficiency achieved at 303 K demonstrates its effectiveness in protecting the metallic substrate from corrosion. The findings also emphasize the need for careful consideration of temperature effects in corrosion inhibition studies, particularly in industries where high temperatures are prevalent, such as the petroleum sector.

The obtained results indicate a significant decrease in the inhibition efficiency of BCAA as the temperature increases from 303 to 333 K. At 303 K, the inhibitor concentration of 0.5 mM exhibited a remarkable inhibition efficiency of 92.2 %, which demonstrates its effectiveness in protecting the metallic substrate from corrosion. However, at 333K, the inhibition efficiency decreased to 84.6 %, indicating a reduction in the inhibitory performance of BCAA at higher temperatures. Several factors can contribute to this observed reduction in inhibition efficiency with increasing temperature. Firstly, as the temperature rises, the thermal agitation of the BCAA molecules and the corrosive solution intensifies. This increased thermal agitation can disrupt the adsorption process of the inhibitor onto the metal surface, reducing the formation of a protective layer. Additionally, higher temperatures can enhance the reactivity of the corrosive environment, leading to increased corrosion rates even in the presence of the inhibitor [51].

Furthermore, the desorption of inhibitor molecules from the metal surface may also occur at higher temperatures. The higher thermal energy can weaken the interaction between the BCAA molecules and the metal surface, causing some of the adsorbed molecules to detach and reducing the coverage area of the protective layer. This desorption process can compromise the overall effectiveness of the inhibition and contribute to the observed decrease in inhibition efficiency. It is worth noting that the reduction in inhibition efficiency at higher temperatures does not negate the protective capabilities of BCAA. Despite the decrease in inhibition efficiency, BCAA still provides significant corrosion protection even at elevated temperatures. However, it is crucial to consider the

limitations of the inhibitor's performance under different temperature conditions. To optimize the use of BCAA as a corrosion inhibitor, it is important to conduct further investigations to understand the underlying mechanisms behind the temperature-dependent reduction in inhibition efficiency. This knowledge can guide the development of strategies to enhance the stability and effectiveness of BCAA as a corrosion inhibitor, particularly at higher temperatures. Additionally, exploring other factors such as inhibitor concentration, immersion time, and synergistic effects with other additives may offer potential avenues for improving the inhibition performance of BCAA at elevated temperatures.

In conclusion, the reduction in inhibition efficiency from 92.2 % at 303 K to 84.6 % at 333 K for the same BCAA concentration of 0.5 mM highlights the temperature sensitivity of the inhibitor's performance. This finding underscores the importance of considering temperature effects when designing corrosion inhibition strategies and emphasizes the need for further research to optimize the protective capabilities of BCAA under different temperature conditions.

3.2. DFT calculations and molecular interactions

Quantum chemical techniques offer valuable insights

into the structural properties of BCAA molecules and various thermodynamic parameters. Analyzing Gaussian records at B3LYP/6-311G (d,p) allows for the determination of these parameters based on the structural characteristics of BCAA. Figure 5a, b, and c provide an example of the information that can be obtained from such analysis.

Mulliken charges are commonly utilized to identify favorable adsorption sites for inhibitors. In the case of BCAA, oxygen and nitrogen atoms with negative charges are found to be preferred adsorption locations due to their donor-acceptor interactions with metal surfaces, as depicted in Figure 6a, b, and c. The functional groups within BCAA molecules facilitate complexation between the adsorbate and surface coordination bonds. Furthermore, examining the highest occupied molecular orbital (HOMO) of the BCAA components reveals the sites for electron donation within the molecules. The HOMO indicates that the oxygen and nitrogen atoms have the ability to transfer electrons to the metallic substrate. On the other hand, the lowest unoccupied molecular orbital (LUMO) represents the molecule's capacity to accept electrons [52]. Figure 6a, b, and c demonstrate that the most reactive LUMO locations in BCAA are the nitrogen, oxygen, and carbon atoms.

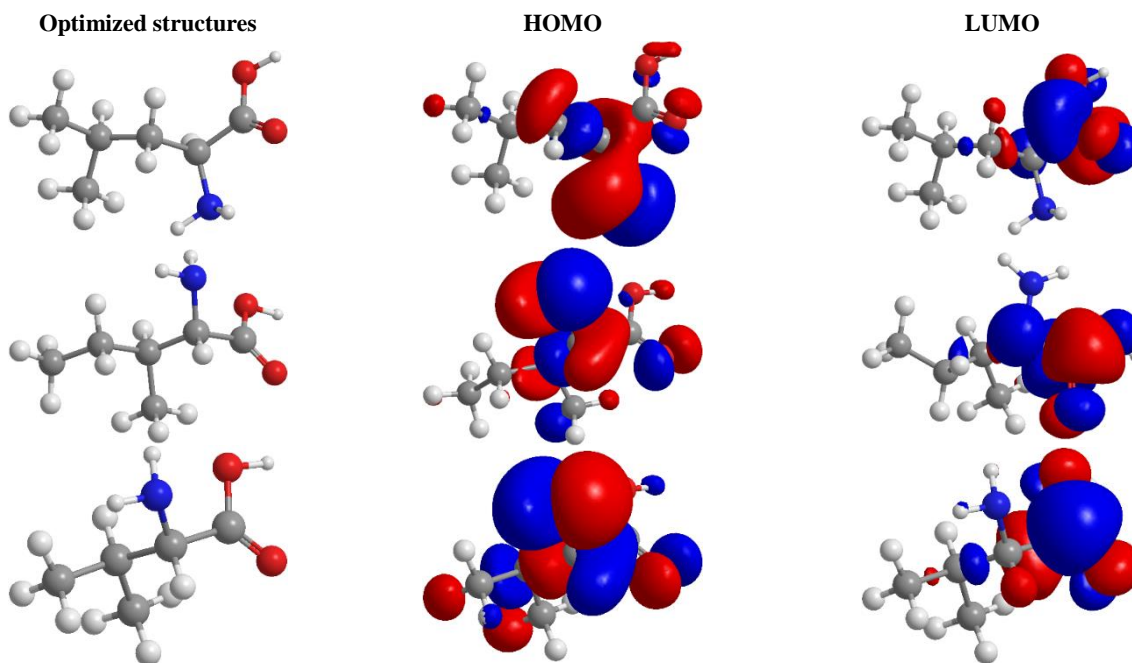


Figure 5: Optimized structures of BCAA (a, Leucine; b, Isoleucine; c, Valine).

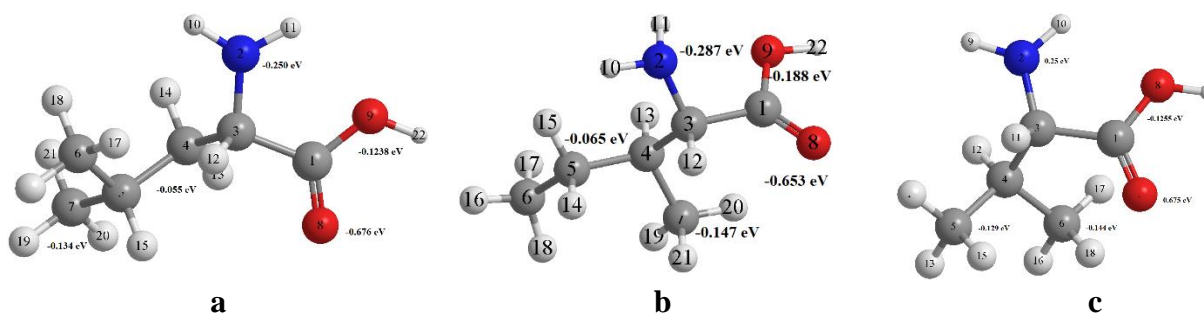


Figure 6: Mulliken charges of BCAA (a, Leucine; b, Isoleucine; c, Valine).

Table 1: DFT variables for BCAA molecules in gas phase.

BCAA	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	χ (eV)	η (eV)	σ (eV ⁻¹)	ΔN (eV)
a	-11.720	0.154	-11.566	5.937	5.783	0.1729	0.0919
b	-11.399	0.65	-10.749	6.024	5.3745	0.186	0.0907
c	-11.490	0.033	-11.457	5.7615	5.7285	0.1745	0.1080

Quantum chemical techniques provide valuable structural information about BCAA molecules, including various thermodynamic parameters. By employing Gaussian records at B3LYP/6-311G (d,p), these parameters can be calculated based on the structural characteristics of BCAA, as exemplified in Figure 5a, b, and c. Table 1 summarizes the computed quantum chemical parameters, such as E_{HOMO} , E_{LUMO} , ΔE , electronegativity (χ), softness (σ), hardness (η), and the number of transferred electrons (ΔN). A higher E_{HOMO} value indicates greater electron-donating ability, while a smaller E_{LUMO} value suggests a molecule's propensity to accept electrons. An effective corrosion inhibitor should exhibit low ΔE values and high σ values [53]. BCAA molecules, represented by the three compounds, possess low E_{HOMO} values, indicating their electron-donating capabilities, and high ΔN values, indicating favorable electron exchange abilities. The calculated values in Table 1 affirm the effectiveness of BCAA molecules as corrosion inhibitors, showing good agreement between the test results and the quantum chemical parameters. Additionally, when a metal shares electrons with the inhibitor (back donation), it establishes a connection between the metal surfaces and the inhibitor.

The quantum chemical analysis conducted in this study offers valuable information about the structural characteristics and thermodynamic parameters of BCAA molecules, shedding light on their effectiveness

as corrosion inhibitors. The findings presented in Figure 5a, b, and c provide a glimpse into the detailed properties of BCAA and how they interact with the metal surface. The Mulliken charges are widely used to identify the preferred adsorption sites of inhibitors. In the case of BCAA, it is observed that oxygen and nitrogen atoms exhibit negative charges, making them favorable locations for adsorption. This can be attributed to the donor-acceptor interactions between these atoms and the metal surface, as depicted in Figure 6a, b, and c. The functional groups present in BCAA molecules further facilitate the formation of complexation bonds with the metal surface, enhancing the adsorption process.

Moreover, the analysis of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) provides insights into the electron-donating and electron-accepting capabilities of BCAA molecules. The HOMO indicates the sites within the molecule that can readily donate electrons, while the LUMO represents the ability to accept electrons. In the case of BCAA, the HOMO reveals that the oxygen and nitrogen atoms have a higher propensity to transfer electrons to the metallic substrate, indicating their potential role in forming a protective layer on the metal surface. Conversely, the LUMO analysis suggests that the nitrogen, oxygen, and carbon atoms in BCAA are more reactive and likely to accept electrons, further contributing to the inhibition

process. The calculated quantum chemical parameters presented in Table 1, including E_{HOMO} , E_{LUMO} , ΔE , electronegativity (χ), softness (σ), hardness (η), and the number of transferred electrons (ΔN), provide additional insights into the inhibitory behavior of BCAA. A higher E_{HOMO} value signifies a greater ability to donate electrons, which is desirable for an effective corrosion inhibitor. On the other hand, a lower E_{LUMO} value indicates a higher electron-accepting capability. The small ΔE values and high σ values indicate that BCAA exhibits good corrosion inhibition characteristics, suggesting that it can effectively prevent the corrosion of mild steel. The ΔN values, representing the number of electrons transferred, further support the electron exchange abilities of BCAA, which contribute to its inhibitory action.

Overall, the quantum chemical analysis conducted in this study provides a deeper understanding of the structural properties and thermodynamic parameters of BCAA molecules. These insights help explain the inhibitory behavior of BCAA as a corrosion inhibitor, corroborating the experimental observations. By elucidating the interactions between BCAA and the metal surface, as well as the electron transfer capabilities, this analysis confirms the potential of BCAA as an effective inhibitor in mitigating corrosion processes.

3.3. Adsorption isotherm analysis

To gain a deeper understanding of the adsorption process of amino acids as corrosion inhibitors in HCl solutions for mild steel, various adsorption isotherms, including Frumkin, Temkin, and Langmuir, were investigated. These isotherms provide insights into the adsorption behavior and help assess the effectiveness of the inhibitors. Among the three isotherms examined, the Langmuir isotherm was found to be the most suitable for describing the adsorption process of amino acids on the mild steel surface. The Langmuir isotherm assumes a monolayer adsorption and a homogeneous surface, and it is commonly used for studying the adsorption of inhibitors on metal surfaces. Figure 7 illustrates the adsorption isotherm of the tested amino acid inhibitor, showing a good fit to the Langmuir model. The Langmuir adsorption isotherm is typically represented by equation 11, which describes the relationship between the surface coverage and the concentration of the inhibitor. The Langmuir adsorption isotherm provides important parameters to

characterize the adsorption process. One such parameter is the equilibrium constant of adsorption (K_{ads}), which represents the extent of inhibitor adsorption on the mild steel surface. Table 2 summarizes the calculated K_{ads} values for the amino acid inhibitors studied. A higher K_{ads} value indicates stronger adsorption and better corrosion inhibition performance. Based on the results, it can be observed that the amino acids exhibit significant adsorption on the mild steel surface, as evidenced by their relatively high K_{ads} values. Furthermore, the standard free energy of adsorption ($\Delta G_{\text{ads}}^{\circ}$) can be determined using equation 12 by utilizing the K_{ads} values. The negative values of $\Delta G_{\text{ads}}^{\circ}$ indicate a spontaneous and favorable adsorption process, suggesting the formation of a stable inhibitor layer on the mild steel surface. The magnitude of $\Delta G_{\text{ads}}^{\circ}$ can provide insights into the strength of the adsorption and the nature of the bonding between the inhibitor molecules and the metal surface.

In addition to the Langmuir isotherm, the Frumkin and Temkin isotherms were also considered to investigate the adsorption behavior of amino acids. However, the Langmuir isotherm was found to be the most suitable for describing the adsorption process, as indicated by its higher regression coefficient (R^2) value and better fit to the experimental data. Understanding the adsorption mechanism of amino acids in HCl solutions for mild steel involves considering several factors, including electrostatic interactions, unshared electron pairs interactions, and p-electron interactions. The presence of nitrogen and oxygen atoms, heterocyclic and benzene rings in amino acids contributes to their high inhibitory effectiveness, with the unpaired electron pairs of these atoms acting as potential coordinating centers. The adsorption mechanism may involve interactions between donor and acceptor π -bonds, unoccupied iron d-orbitals, electrostatic interactions, and interactions between unoccupied iron d-orbitals and unpaired electrons of nitrogen and oxygen atoms. The combination of these mechanisms facilitates the adsorption of amino acid inhibitors onto the metallic surface. In summary, the adsorption behavior of amino acids as corrosion inhibitors in HCl solutions for mild steel can be effectively described using the Langmuir adsorption isotherm. The Langmuir model provides valuable information about the extent of adsorption (K_{ads}) and the stability of the adsorbed layer ($\Delta G_{\text{ads}}^{\circ}$). The adsorption mechanism involves a combination of

electrostatic interactions, unshared electron pairs interactions, and p-electron interactions, which contribute to the adsorption of amino acids on the mild steel surface and their corrosion inhibition effectiveness. Chemical inhibitors function by adsorbing onto the metal surface, and various adsorption isotherms were studied to understand this process. Among the isotherms examined (Frumkin, Temkin, and Langmuir), the Langmuir isotherm was found to be the most suitable, exhibiting a high regression coefficient (R^2) close to unity and a linear relationship, as shown in Figure 7. The Langmuir adsorption isotherm is commonly represented by equation 11 [49].

$$C_{inh}/\theta = (K_{ads})^{-1} + C \quad (11)$$

Where K_{ads} is the constant of adsorption and θ is the surface coverage.

The Langmuir adsorption isotherm for the tested inhibitor is depicted in Figure 7, with the Langmuir model deemed the most appropriate. The Langmuir equation 11 is commonly used to describe this adsorption isotherm [50]. Table 2 summarizes the K_{ads} values, which indicate the extent of inhibitor adsorption on the mild steel surface. A higher K_{ads} value corresponds to stronger adsorption and better corrosion inhibition performance. The BCAA inhibitor exhibited the highest K_{ads} value, indicating its superior adsorption on the mild steel surface. The standard free energy of adsorption (ΔG_{ads}^0) can be calculated using equation 12 based on the K_{ads} values [51].

$$\Delta G_{ads}^0 = -RT \ln(55.5K_{ads}) \quad (12)$$

Table 2 presents the calculated thermodynamic parameters obtained from weight loss measurements at different temperatures. The negative values of ΔG_{ads}^0

suggest a spontaneous adsorption process, leading to the formation of a stable layer of inhibitor molecules on the mild steel surface.

The strength of the adsorption process is often evaluated by the ΔG_{ads}^0 value, where values less than -20 kJ.mole^{-1} typically indicate Van der Waals forces, while more negative values exceeding -40 kJ.mole^{-1} suggest chemisorption. In chemisorption, the unpaired electrons from the heteroatoms of the inhibitor molecule transfer to the d-orbitals of iron atoms on the metal surface, forming coordination bonds. Our findings demonstrate the occurrence of both physisorption and chemisorption mechanisms, as indicated by the ΔG_{ads}^0 values ranging from -34.7 to $-38.9 \text{ kJ.mole}^{-1}$. Chemisorbed molecules are expected to provide enhanced protection by reducing reactivity at the bonded sites on the metal surface. It is important to note that distinguishing between chemisorption and physisorption based solely on ΔG_{ads}^0 values is challenging, as there is some overlap between the two mechanisms, and physical adsorption is believed to precede chemical adsorption [52].

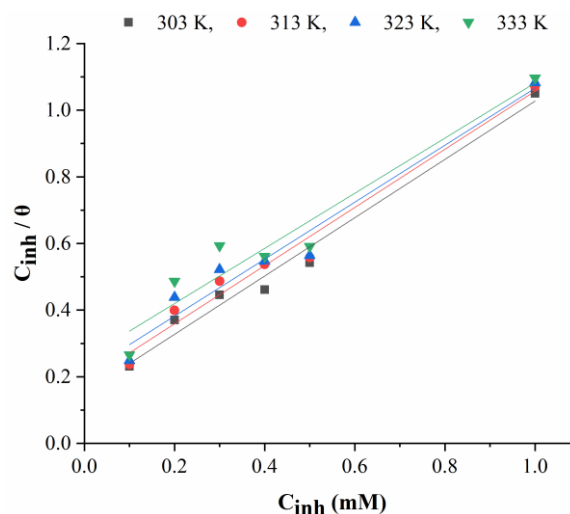


Figure 7: BCAA Langmuir model plot.

Table 2: The thermodynamic parameters computed based on weight loss measurements at different temperatures.

Parameters	303 K	313 K	K 323	333 K
Intercept	0.152 ± 0.030	0.184 ± 0.033	0.210 ± 0.042	0.254 ± 0.055
Slope	0.875 ± 0.060	0.872 ± 0.065	0.854 ± 0.083	0.827 ± 0.109
R-Square	0.990	0.988	0.98139	0.966

3.4. Corrosion inhibition mechanism

The corrosion inhibition mechanism of amino acids in HCl solutions for mild steel involves a combination of factors and interactions that contribute to the formation of a protective layer on the metal surface. Amino acids, such as BCAA, possess functional groups and chemical properties that make them effective inhibitors against corrosion. One of the key mechanisms of corrosion inhibition by amino acids is through adsorption. In an acidic environment, amino acids exist in their protonated form, with positively charged amino and carboxyl groups. These positively charged species can interact with the negatively charged metal surface through electrostatic interactions. The adsorption of amino acids on the metal surface creates a barrier that inhibits the corrosive attack. The functional groups present in amino acids, such as amino ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) groups, can also form coordination complexes with metal ions. The lone pair of electrons on the nitrogen atom and the oxygen atom in these functional groups can coordinate with metal cations present in the corrosive solution. This coordination interaction helps in the formation of a protective film on the metal surface, preventing the corrosive species from coming into direct contact with the metal.

Additionally, amino acids contain aromatic and heterocyclic rings that possess π -electrons. These π -electrons can interact with the d-orbitals of the metal surface through π -electron interactions. This interaction strengthens the adsorption of amino acids on the metal surface, further enhancing the corrosion inhibition properties. Furthermore, the presence of amino acids can alter the pH of the corrosive solution near the metal surface. The protonation of amino acids generates H^+ ions, which can decrease the acidity in the vicinity of the metal surface. This change in pH can slow down the corrosion reaction, reducing the rate of metal dissolution. The inhibitory effectiveness of amino acids can also be influenced by their molecular structure, size, and concentration. Different amino acids may exhibit varying levels of inhibition efficiency due to differences in their functional groups and molecular configurations. Additionally, the concentration of amino acids in the corrosive solution can impact the extent of inhibition, with higher concentrations generally leading to improved corrosion protection [53]. Overall, the corrosion inhibition mechanism of amino acids in HCl solutions for mild steel involves a combination of adsorption, coordination complex

formation, π -electron interactions, pH alteration, and concentration-dependent effects. Understanding these mechanisms and their specific contributions is crucial for the development of effective corrosion inhibitors based on amino acids and can guide further research in this area [54].

The adsorption mechanism of organic inhibitors on metallic substrates is influenced by several factors, including the chemical composition of the inhibitor, the type of metal, the surface charge, and the distribution of charges within the inhibitor molecule. In the case of BCAA, its nitrogen and oxygen atoms, contribute to its high inhibitory effectiveness. The unpaired electron pairs of these atoms serve as potential coordinating centers for adsorption [55]. In acidic environments, BCAA exists as protonated molecules on uncharged particles. The adsorption mechanism of inhibitor particles onto metallic surfaces can involve various mechanisms, such as interactions between donors and acceptors of π -bonds and unoccupied iron d-orbitals, electrostatic interactions, and interactions between unoccupied iron d-orbitals and unpaired electrons of nitrogen and oxygen atoms. While it may be challenging for positively charged ion particles in corrosive solutions to reach positively charged mild steel surfaces, protonated inhibitor molecules can be adsorbed through electrostatic interactions [56]. The inhibitor ions (protonated inhibitor molecules) interact with negatively charged chloride ions on the steel surfaces, leading to the hydration of chlorides and facilitating the formation of positively charged inhibitor ions. However, it is important to note that a single adsorption mechanism cannot fully explain the adsorption process of inhibitor molecules onto metallic substrates in corrosive environments. The adsorption process is complex and may involve a combination of different mechanisms, as depicted in Figure 8. This illustrates the diverse interactions that occur between BCAA and the metal surface, highlighting the multifaceted nature of the adsorption process [57].

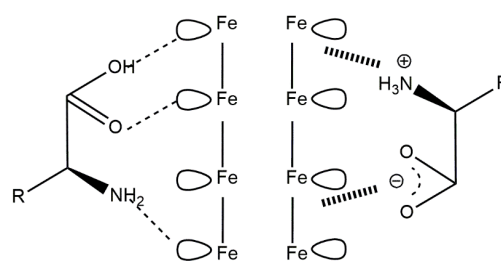


Figure 8: The suggested inhibition mechanism.

The understanding of the inhibition mechanism of BCAA is crucial in comprehending its effectiveness as a corrosion inhibitor. The interactions between BCAA and the metal surface play a vital role in the formation of a protective layer, which prevents the corrosive attack on the mild steel substrate. Further investigations and studies can provide more insights into the specific details of the adsorption mechanisms involved and help develop a comprehensive understanding of the inhibition process.

4. Conclusion

In this study, we conducted a comprehensive investigation into the corrosion inhibition properties of amino acids in HCl solutions for mild steel. Through a combination of experimental measurements, quantum chemical calculations, and adsorption isotherm analysis, we gained valuable insights into the inhibitory effectiveness and adsorption behavior of amino acids on the metal surface. Our findings revealed that amino acids, particularly BCAA, exhibited remarkable inhibition efficiency against mild steel corrosion in HCl solutions. The inhibition efficiency was influenced by key factors, including inhibitor concentration, exposure duration, and temperature. Notably, at a concentration of 0.5 mM, BCAA demonstrated inhibition efficiencies ranging from 73.7 % to 93.5 % for different immersion times. The Langmuir adsorption isotherm successfully described the adsorption behavior of amino acids on the mild steel surface, with high regression coefficients (R^2) confirming its suitability for modeling the adsorption process. Furthermore, the calculated equilibrium constant of adsorption (K_{ads}) indicated strong adsorption of amino acids on the metal surface, and the negative values of the standard free energy of adsorption (ΔG_{ads}^o) validated the spontaneous and favorable nature of the adsorption process. The inhibition mechanism of amino acids involved a combination of electrostatic interactions, unshared electron pairs interactions, and p-electron interactions, with nitrogen and oxygen atoms, heterocyclic, and benzene rings playing a vital role in

their inhibitory effectiveness as potential coordinating centers.

The findings of this study have important implications for the development of corrosion inhibitors for mild steel in HCl solutions. Amino acids, such as BCAA, have shown promising inhibitory properties and can be considered as potential candidates for corrosion protection in various industrial applications, including the petroleum sector. Future research in this field should focus on several aspects. Firstly, further investigation is needed to understand the molecular interactions between amino acid inhibitors and metal surfaces at a more detailed level. Advanced characterization techniques, such as surface analysis and spectroscopic methods, can provide valuable information about the adsorption mechanism and the formation of the protective layer. Additionally, the performance of amino acid inhibitors should be evaluated under more realistic conditions, such as in the presence of other corrosive species or in simulated industrial environments. This would provide a better understanding of the inhibitors' effectiveness and their stability over extended periods. Furthermore, exploring the potential synergistic effects of amino acids in combination with other corrosion inhibitors or additives could lead to enhanced inhibition efficiency and improved protection against corrosion. Lastly, the development of novel amino acid-based inhibitors with optimized chemical structures and tailored functionalities could further advance corrosion inhibition strategies and offer more sustainable and environmentally friendly alternatives.

In conclusion, this study demonstrated the inhibitory effectiveness of amino acids, such as BCAA, in HCl solutions for mild steel corrosion. The adsorption behavior was well-described by the Langmuir adsorption isotherm, and the inhibition mechanism involved various molecular interactions. The findings pave the way for future research and the development of effective corrosion inhibitors for industrial applications.

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