Assessment of Corrosion Inhibition Efficiency of Some Amino Acids on Stainless Steel in Ethaline

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Abstract—**This study evaluates simple amino acids as green corrosion inhibitors for AISI 302 stainless steel in Ethaline, a chloride-rich deep eutectic solvent (DES). General and localized corrosion behaviors were assessed using Tafel analysis and cyclic potentiodynamic polarization (CPP) in blank Ethaline and with 0.05 M, 0.075 M, and 0.1 M glycine, alanine, and leucine. Results show complex interactions between amino acid structure, concentration, and inhibition. The high viscosity of Ethaline shifts anodic control from charge transfer to mass transfer at higher potentials. All amino acids shift corrosion potential (E_{corr}) nobly, with 0.05 M glycine giving the largest increase (~0.26 V) for general corrosion resistance, though it yields the narrowest passivation range (0.52 V), increasing pitting susceptibility. Alanine and leucine, with bulkier side chains, enhance localized corrosion resistance via steric hindrance to Cl^- ions. Low concentrations (0.05 M) optimize protection by lowering passivation current (i_{pass}) and forming stable films, but higher levels (>0.05 M for glycine/leucine) reverse this, accelerating corrosion via acidity or complexation. A 0.05 M glycine/leucine binary mixture produces negative CPP hysteresis, indicating strong repassivation and self-healing. These findings reveal trade-offs between general and localized protection, emphasizing precise concentration control. The study advances tailored, synergistic amino acid inhibitors as sustainable, self-healing systems for DES environments.**

Index Terms—**AISI 302, Amino acid inhibition, Choline chloride, Electrochemical polarization, Self-healing film, Steric hindrance.**

I. Introduction

A versatile austenitic chromium-nickel stainless steel (SS) AISI 302 (FeCr18Ni8) is widely used across numerous industries due to its strength and corrosion resistance, particularly in mild-to-moderate environments. Its extensive use is largely attributed to its ability to form a stable oxide layer that protects the metal surface from further corrosion. However, this protective layer is susceptible to breakdown in corrosive environments, particularly those containing chloride ions (Cl^-), leading to severe localized corrosion such as pitting corrosion (Saha Podder and Bhanja, 2013, Galleguillos Madrid, et al., 2024). Therefore, the use of corrosion inhibitors is critical in environments where SS are exposed to aggressive agents such as Cl^-, which compromise the integrity of passive protective films.

The emergence of the green chemistry approach has restricted the use of traditional, toxic corrosion inhibitors, aiming to reduce environmental pollution by developing eco-friendly alternatives. As part of this shift, environmentally sustainable corrosion inhibitors such as bio-based extracts and pharmaceutical compounds are increasingly being considered. These corrosion inhibitors are organic substances that work by adsorbing onto metal surfaces through specific polar functional groups to form a protective layer. These functional groups, which are rich in electrons, help molecules bind more effectively to a metal surface, either by forming a direct bond with metal surfaces or by making other parts of the molecule more electron-rich, which in turn strengthens their attraction to the surface (Verma, et al., 2021). Amino acids are particularly promising candidates as green corrosion inhibitors because they are non-toxic, biodegradable, and readily available. Their molecular structure, containing both amine ($-NH_2$) and carboxyl (-COOH) functional groups, allows them to effectively adsorb onto metal surfaces, blocking active sites and reducing the corrosion process (Hamadi, et al., 2018, Verma, et al., 2021).

While the development of green inhibitors for traditional aqueous systems is advancing, the increasing adoption of novel green solvents such as deep eutectic solvents (DESs) presents new and poorly understood corrosion challenges. Among the many available DESs, Ethaline, a mixture of choline chloride (ChCl) and ethylene glycol (EG), was specifically selected for this study. Ethaline characteristically possesses a high concentration of Cl^-, a moderately acidic pH, and due to its low viscosity, it has highly mobile Cl^- (Abbott, et al., 2014, Ahmed, Ryder, and Abbott, 2021). This combination forms a uniquely aggressive and corrosive medium. While Ethaline's components are environmentally benign, its inherent corrosivity toward common engineering materials presents a significant barrier to its widespread industrial adoption. Therefore, developing effective corrosion inhibition

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strategies is crucial to unlocking the full potential of these green solvents. A recent review (Bučko, Bajat and Engineering., 2022) effectively summarizes the current state of research on metallic corrosion in DESs, highlighting a significant knowledge gap. However, the vast majority of studies focus on pure metals rather than industrially vital alloys such as SS, and there is a scarcity of research on effective, eco-friendly inhibitors in these media.

This study addresses this gap by investigating simple amino acids, specifically, glycine, alanine, and leucine, as green corrosion inhibitors for AISI 302 in Ethaline. These amino acids were systematically chosen to evaluate the influence of alkyl side-chain size and hydrophobicity on inhibition efficiency, with glycine having the smallest side-chain and leucine the largest and most hydrophobic. The primary objective is to clarify the effectiveness of these amino acids in preventing both general and pitting corrosion. By employing electrochemical techniques, such as potentiodynamic polarization (PDP), we analyze the resulting Tafel plots and polarization curves to understand the underlying inhibition mechanisms. This research provides critical insights into the interplay between amino acid structure, inhibitor concentration, and the unique electrochemical environment of the DES. Ultimately, the findings will contribute to the development of tailored, sustainable corrosion protection strategies, enabling the broader industrial use of DESs.

II. Materials and Methods

Chemicals were used as received, without any additional treatment. Ethaline was prepared following a procedure from the literature (Abbott, et al., 2014). EG >99% from Biochem-France and ChCl >98% from Biochem-France in a 2:1 mole ratio were mixed and gently heated to about 60°C in an oven (Lab Teach/model LDO-030E) until a clear liquid formed. All electrochemical tests were conducted in blank Ethaline and Ethaline containing 0.05 M, 0.075M, and 0.1M alanine (99+% from Honeywell Riedel-de Haën, Thermo Scientific Chemicals – Germany), glycine (99% from R-B-India-UK), and leucine (>99.5% from DC Fine Chemicals – London) at 35°C, using a Corretest CS310M potentiostat/galvanostat. The experiments were performed with a standard three-electrode cell setup.

The AISI 302 working electrode (disc diameter = 1 mm) from Goodfellow Cambridge Ltd. – UK used in the present work has the following chemical composition;

With potentials referenced to a saturated Ag/AgCl reference electrode (CS901), and a platinum disc as the counter electrode, both from Corretest instruments. Tafel plots were obtained by sweeping the potential from −300 mV vs. Ag/AgCl(sat.) to 350 mV at a scan rate of 5 mV/s. For pitting corrosion analysis, polarization curves were measured at potentials 1.5 V more positive than the $E_{corr.}$ To examine the effect of forward and reverse scans on corrosion, the potential was scanned forward from $\mathbf{E_{corr}}$ to 1.5 V, and then reversed over the same range.

Elements	S	P	N	Si	C	Mn	Ni	Cr	Fe
Wt.%	0.01	0.041	0.07	0.95	0.096	1.66	8	18	Balance

S: Sulfur, P: Phosphorus, N: Nitrogen, Si: Silicon, C: Carbon, Mn: Manganese, Ni: Nickel, Cr: Chromium, Fe: Iron

III. Results and Discussion

A. Tafel Plots

Tafel slopes have been determined using linear sweep voltammetry measurements over small potential ranges of 5 mV for AISI 302 in blank Ethaline and in Ethaline containing amino acid. Fig. 1a shows the polarization plot of the alloy in blank Ethaline and in Ethaline containing alanine at ambient temperature. The Butler–Volmer equation is experimentally used to describe the polarization resistance between the applied potential and resulting current density at the electrode, provided that no other redox reaction happens at the electrode surface.

$$i_{app} = i_{corr}\left[\left(e\frac{+2.3\left(E-E_{corr}\right)}{\beta_{ox,M}} - e\frac{-2.3\left(E-E_{corr}\right)}{\beta_{red,X}}\right)\right]$$

Where β_{red} and β_{ox} are cathodic and anodic Tafel slopes,
i_{app} is applied current density = i_{ox}–i_{red}

$$\Delta E = E–E_{corr}$$

The equation offers a phenomenological explanation of the rate of an interfacial redox reaction, in which the reaction rate rises exponentially with the applied potential. In this context, the electron transfer process is a function of potential, as described by the equation. There is a maximum rate at which electroactive species can reach the metal or alloy surface, regardless of the mass transport conditions in the cell. This is because the rate of electron transfer is finally limited by the rate at which the electroactive species can diffuse to the electrode surface and interact with it (Pletcher and Walsh, 2012, Li, et al., 2018).

In this study, Ethaline exhibits significantly higher viscosity than conventional aqueous solutions, a characteristic feature of DESs and ionic liquids. Consequently, mass transfer-controlled currents are expected to be a dominant feature of AISI 302 anodic currents in this medium, consistent with observations in other highly viscous electrochemical systems (Ma, et al., 2018, Labík, et al., 2017). Thus, kinetically in blank Ethaline, as anticipated, when the potential is shifted toward more positive values from the E_{corr}, the nature of the anodic current gradually changed from being a charge transfer current to a mixed charge/mass transfer current after 30 mV from E_{corr}. This transition is typical for electrochemical reactions where the concentration of redox species near the electrode surface becomes depleted as the reaction rate increases, moving away from purely kinetic control (Bard, Faulkner and White, 2004). This is because, at the beginning, the concentration of redox species near to electrode surface is almost the same as in the bulk liquid, therefore, the current will have a linear shape. Moving away from the charge

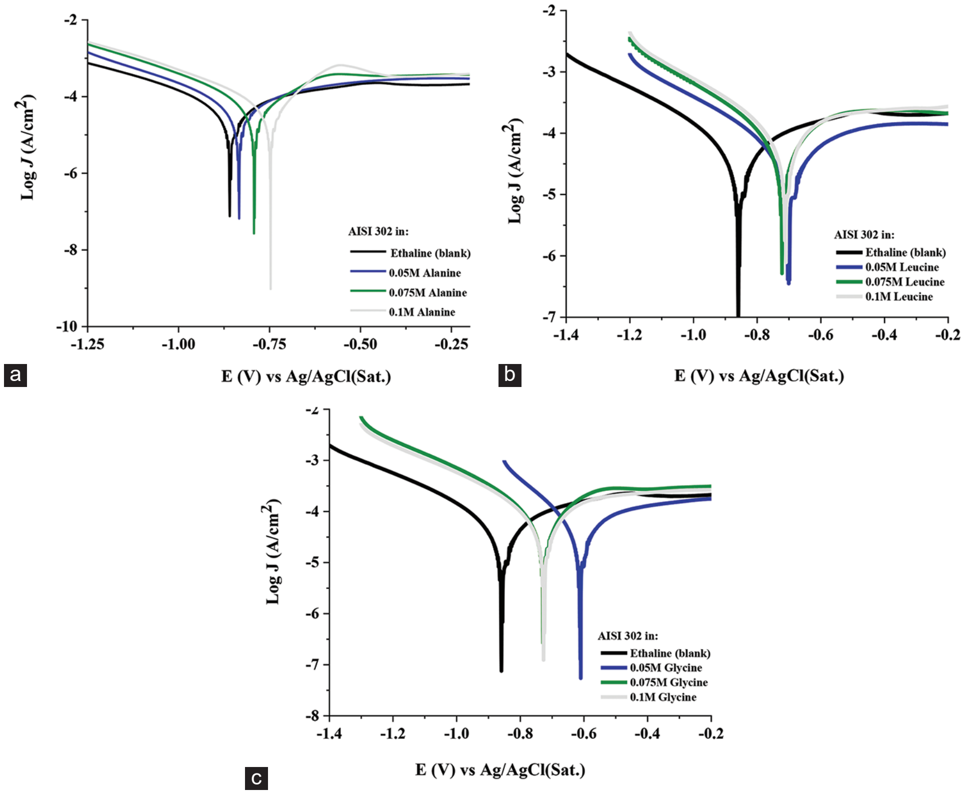

Fig. 1. Potentiodynamic polarization plots of AISI 302 in blank Ethaline and in Ethaline containing different amino acid concentrations. (a) Alanine, (b) leucine, and (c) glycine.

transfer range toward more positive potentials, the currents have been transformed to a mixed current as a consequence of the concentration gradient at this range (Pletcher and Walsh, 2012, Bard, Faulkner and White, 2004). Later, after ~300 mV from E_{corr} the anodic currents have taken a mass transfer-based shape, because the current after this value depends on the mobility of redox species toward the electrode surface. The rate of movement of these species is clearly affected by a layer adjacent to the electrode surface, which is expected to be enriched with species involved in the reaction, and later, with adsorbed amino acid molecules when inhibitors are present.

As shown in Fig. 1a, for alanine-containing Ethaline, depending on the concentration, the range at which the currents exhibit a mixed nature, their shapes differ significantly from the current in blank Ethaline. The anodic currents become steeper as a function of alanine concentration, suggesting that the carboxylic acid group of the amino acid may be directly involved in the corrosion process or in facilitating adsorption. This behaviour is consistent with previous findings where amino acids, particularly through their carboxylate groups, have been shown to interact strongly with metal surfaces, influencing the anodic dissolution kinetics (Ghanyl, El-Shenawy and Hussien, 2011).

At potentials more positive than −0.6V, for both alanine-containing Ethaline and blank Ethaline, the shape of all anodic currents becomes mass transfer-based, indicating that the supply of reactive species to the electrode surface is the rate-limiting step in this region. Compared with cathodic currents, all anodic currents are less steep, which indicates that the anodic currents are controlling the overall reaction rate and becoming the rate-determining step in the corrosion process.

This anodic control aligns with observations in other corrosion inhibition studies where inhibitor adsorption primarily impacts the metal dissolution pathways (Zhao, Yu and Niu, 2022). Figs. 1b and 1c show that leucine- and glycine-containing Ethaline behave similarly to alaninecontaining Ethaline, with the notable exception that their concentration has a less pronounced effect on the mixed charge/mass transfer range. This difference implies a sizedependent mechanism: glycine's small side chain minimizes steric interactions, while leucine's bulky isobutyl group likely prevents efficient packing on the SS surface. In contrast, alanine appears to possess an intermediate size that allows for a more concentration-dependent adsorption equilibrium (Vander Zee, et al., 2023).

Amino acids can inhibit the corrosion of SS by forming a protective layer on the metal's surface. This process, known as adsorption-based inhibition, occurs as the inhibitor molecules attach to the alloy. They do this through the lone pair electrons on their nitrogen and oxygen atoms and the π-electrons in their carboxyl groups, which effectively block the active sites where corrosion would normally occur. This adsorbed layer creates a physical barrier, separating the metal from the corrosive environment (Ashassi-Sorkhabi, Majidi and Seyyedi, 2004, Hamadi, et al., 2018).

The plots in Fig. 2 shows passivation currents and pitting corrosion behave of SS in Ethaline and its amino

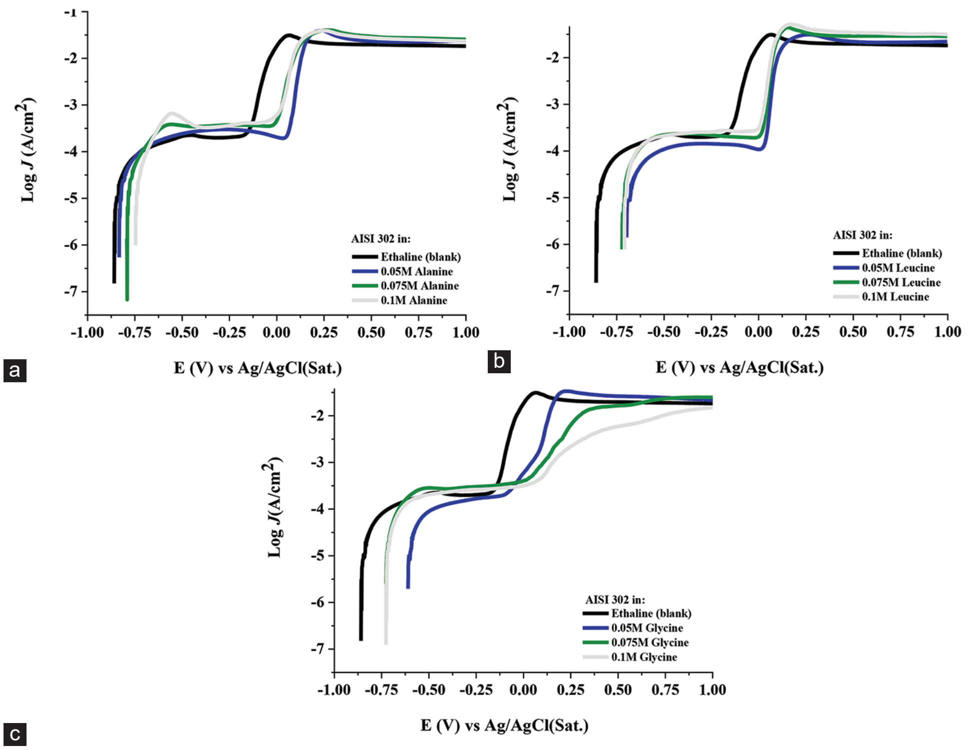

Fig. 2. Measured pitting potentials of AISI 302 in blank Ethaline and in Ethaline containing various amino acids. (a) Alanine, (b) leucine, and (c) glycine.

acid solutions. Near Epit, a number of electrochemical and physical processes can happen, leading to the formation and growth of pits. As shown in Fig. 2, when the potential has been scanned in the noble direction from Ecorr, a passive region (the region in which the current density remains independent of the applied potential) has been detected for the alloy in all samples. This region is characterized by a specific current density, known as passivation current (ipass).

The addition of amino acids to Ethaline makes the SS thermodynamically less likely to corrode. This is seen as a shift in the E_{corr} to more positive, or "noble," values. At optimal concentrations, the amino acids significantly increased the nobility of AISI 302. For example, 0.1M alanine, 0.05M leucine, and 0.05M glycine increased the E_{corr} by approximately 0.11V, 0.16V, and 0.26V, respectively. However, a critical concentration effect was observed. When the concentration of leucine and glycine was increased beyond 0.05M, the protective effect diminished, and the corrosion potential shifted back toward more active values. This suggests a dual role for these amino acids. They act as inhibitors at low concentrations but can accelerate corrosion at higher concentrations. This reversal may occur due to two reasons. At high concentrations, the acidic nature of the carboxylic acid group (-COOH) can increase local acidity at the metal surface, promoting dissolution (Singh Raman, et al., 2022).

B. Passivation Currents (i_{pass}) and Pitting Potential (E_{pit})

Excess inhibitors can form soluble complexes with the metal, which can carry the material away from the surface and accelerate corrosion. While E_{corr} reflects the tendency to corrode, the i_{pass} measures the rate of corrosion of the protective passive film. A lower i_{pass} indicates a more stable and protective film (Aslam, Zehra and Aslam, 2022). The results showed that 0.05M leucine and 0.05M glycine successfully reduced the i_{pass}, indicating they formed a more compact and effective barrier. In contrast, alanine and higher concentrations of leucine and glycine resulted in a higher i_{pass}. This suggests that while these conditions made the steel thermodynamically more stable (higher E_{corr}), the protective film they formed was kinetically less stable and more defective. This could be due to the organic molecules being incorporated into the film, creating a more porous structure (Veluchamy, et al., 2017).

Localized corrosion, or pitting, begins when the protective film breaks down at the E_{pit}. The difference between the E_{pit} and the E_{corr} is defined as the passivation potential (E_{pass}) range;

$$E_{pass} = E_{pit} - E_{corr}$$

This range is a window where the material is protected from localized attack (Frankel, 1998, Frankel and Sridhar, 2008).

A key finding supposes a complex relationship between general corrosion protection and pitting resistance. The 0.05M glycine-containing Ethaline, which provided the best general protection (most noble E_{corr}), unexpectedly had the smallest E_{pass} and the least resistance to pitting. This highlights that an effective inhibitor must not only adsorb to the surface but also resist being displaced by aggressive ions such as chloride, which initiate pitting (Aslam, Zehra and Aslam, 2022). The results suggest that while glycine provides excellent surface coverage, it is less effective at competing with Cl¯ under anodic polarization. In contrast, other amino acids such as alanine and leucine provided superior resistance to pitting, likely because their larger size offers better steric hindrance, preventing Cl¯ from reaching the surface.

A noteworthy feature was observed in the glycine solutions, where the pitting corrosion rate appeared to be limited by mass transfer. This is likely a result of the fact that glycine is the smallest and most polar amino acid studied, and interacts strongly with Ethaline, hindering its movement. It is reasonable that once a pit forms, the rapid metal dissolution becomes limited by either the slow diffusion of aggressive Cl¯ into the pit or the slow diffusion of dissolved metal-glycine complexes out of it, causing the corrosion current to plateau.

C. PDP

Cyclic potentiodynamic polarization was used to assess the alloy's capacity to repassivate following the beginning of pitting (Fig. 3). In most amino acid-containing Ethaline tests, a positive hysteresis loop was detected, which was characterized by higher current densities during the reverse scan compared to the forward scan. This behavior indicates that once pits are initiated, they tend to propagate at potentials below the E_{pit}. The potential at which the reverse and forward scans intersect is known as the repassivation potential (E_{rp}), representing the threshold below which active pits can repassivate. The difference between E_{pit} and E_{rp} ($\Delta E = E_{pit} – E_{rp}$) serves as a key indicator of the material's vulnerability to sustained localized corrosion. A larger ΔE, or wider hysteresis loop, suggests a greater tendency for pit growth once initiated (Trethewey and Chamberlain, 1995). The values presented in Table I can be used to comparatively assess the effectiveness of different inhibitors in promoting passive film healing.

Notably, the binary glycine/leucine inhibitor mixture exhibited a negative hysteresis loop, wherein the reverse scan current was lower than that of the forward scan. This is a particularly favorable result, as it suggests a strong tendency for the alloy to repassivate, effectively overcoming stable pit growth (Lekatou and Tsouli, 2022). In this case, the protection potential exceeds the E_{corr}, indicating that any initiated pits are rapidly passivated. This beneficial behavior may be attributed to a synergistic interaction. Leucine contributes a bulky, hydrophobic barrier, whereas glycine, being smaller, may effectively plug emerging pits, hindering their propagation.

Furthermore, across all tests, a shift in the corrosion potential to more positive values during the reverse scan was consistently detected. This suggests that areas initially affected by pitting or corrosion transition into cathodic sites relative to the surrounding passive matrix.

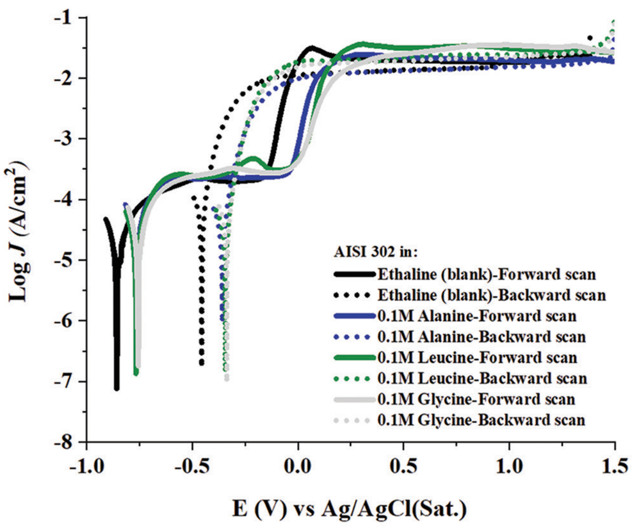

Fig. 3. Potentiodynamic polarization curves (potential vs. log current density) for AISI 302 in blank Ethaline and in Ethaline containing 0.1 M of alanine, leucine, or glycine.

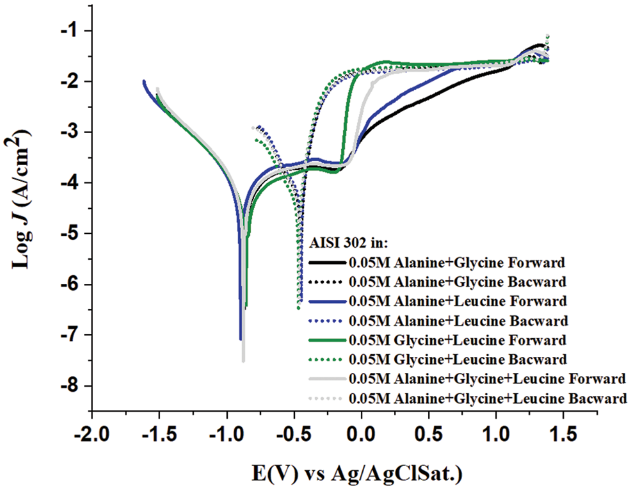

Fig. 4. Potentiodynamic polarization curves for AISI 302 in Ethaline containing 0.05 M of various binary and tertiary amino acid mixtures.

TABLE I
Corrosion Potential, Pitting Potential, and Passivation Potential Range

Liquids	E_{corr}/V	E_{pit}/V	E_{pass}/V	E_{rp}/V
Ethaline (blank)	−0.8989	−0.1680	0.7309	−0.4250
0.05M Alanine	−0.8328	+0.0481	0.8809	
0.075M Alanine	−0.7910	−0.0118	0.7792	
0.1M Alanine	−0.7464	−0.0169	0.7295	−0.3000
0.05M Leucine	−0.6980	+0.0231	0.7211	
0.075M Leucine	−0.7220	−0.0041	0.7180	
0.1M Leucine	−0.7090	−0.0029	0.7061	−0.2977
0.05M Glycine	−0.6100	−0.0904	0.5196	
0.075M Glycine	−0.7260	+0.0270	0.7530	
0.1M Glycine	−0.7270	+0.0704	0.7974	−0.2977

As a result, the corrosion mode becomes more uniform and generalized, rather than sharply localized (a hallmark of a self-healing or damage-arresting mechanism) (Zheludkevich, et al., 2007). This transformation, coupled with a high E_{rp}, highlights the alloy's remarkable ability to maintain structural integrity even after localized damage, a critical trait for long-term durability in aggressive environments.

Binary and tertiary amino acid inhibitors

The corrosion behavior of AISI 302 in binary and ternary 0.05M amino acid-containing Ethaline was evaluated using PDP. The resulting polarization curves are presented in Fig. 4. A notable feature of these curves (except for the glycine/leucine system) is the appearance of a negative hysteresis loop, where the current density on the reverse scan is lower than on the forward scan. This behavior is a strong indicator of the material's ability to repassivate or to form a more protective surface layer after undergoing anodic polarization. In contrast, a positive hysteresis loop, often associated with pitting corrosion, reflects a breakdown of the passive film and ongoing pit propagation. The occurrence of negative hysteresis, therefore, suggests that the passive layer remains largely intact or is rapidly repaired, enhancing the alloy's resistance to localized attack (Lekatou and Tsouli, 2022).

The underlying mechanism for this improved protection can be attributed to the adsorption ability of amino acid molecules onto the steel surface. Amino acids are widely recognized as green corrosion inhibitors due to their dual functionality (the amine [-NH_2] and carboxyl [-COOH] groups) that readily interact with metal surfaces, effectively blocking active corrosion sites (Ghanyl, El-Shenawy, and Hussien, 2011). The specific protective effect appears to depend on the nature of the amino acid involved. For example, glycine, the most polar amino acid in the tested mixtures, exhibits behavior indicative of mass transfer-controlled corrosion. This suggests that while glycine adsorbs onto the surface, its layer may be relatively permeable, allowing corrosive species to diffuse through to the metal or enabling metal cations to escape. In contrast, solutions containing leucine, a non-polar and bulkier amino acid with an alkyl side chain, shift toward a charge transfer-controlled mechanism. This implies the formation of a denser, more hydrophobic protective film that inhibits electrochemical reactions by acting as a physical barrier to charge exchange at the metal-solution interface (Aouniti, et al., 2017). Further confirmation of surface protection is seen in the consistent positive shift in E_{corr} during the reverse scan across all tested systems. This magnification of E_{corr} indicates that the surface becomes more passive after polarization. In particular, an E_{rp} that is more noble than the original E_{corr} is a well-established marker of strong resistance to localized corrosion. This suggests that if pits initiate at high anodic potentials, they will likely repassivate quickly as the potential returns toward open-circuit conditions, preventing further propagation. Such behavior suggests that corroded or damaged areas may become cathodic relative to the surrounding passive surface, redirecting corrosion activity laterally instead of allowing deep penetration. This transition promotes uniform, less aggressive corrosion, a characteristic of self-healing systems (Szklarska-Smialowska, 1999).

IV. Conclusions

This study demonstrates that amino acids function as effective yet complex corrosion inhibitors for AISI 302 in an Ethaline. The baseline corrosion behavior in blank Ethaline is dominated by its high viscosity, which causes a transition from charge transfer control to mass transfer control at elevated anodic potentials. The addition of amino acids fundamentally alters this mechanism through surface adsorption, leading to distinct electrochemical responses. A central finding of this work is the trade-off between different modes of corrosion protection. All amino acids tested contributed to a noble shift in the E_{corr}, reflecting improved thermodynamic stability. However, this shift did not uniformly translate to enhanced kinetic resistance or protection against localized corrosion. For instance, 0.05 M glycine yielded the greatest noble shift in E_{corr}, yet also exhibited the highest pitting susceptibility, as indicated by the narrowest passivation range. In contrast, bulkier amino acids such as alanine and leucine offered better resistance to pit initiation, likely due to steric hindrance against aggressive Cl^-, but had a more modest impact on the general corrosion potential. These findings underscore a key insight: Optimizing for one form of corrosion resistance may compromise another, highlighting the need for a balanced formulation strategy. An additional layer of complexity arises from the dual role of inhibitor concentration. At optimal concentrations, amino acids function effectively as inhibitors; however, exceeding this threshold can reverse their role, turning them into corrosion accelerators. This emphasizes the importance of precise concentration control in practical applications. The most noteworthy outcome of this investigation was the synergistic performance of the binary glycine/leucine mixture. This combination exceptionally produced a negative hysteresis loop during cyclic polarization, a hallmark of exceptional repassivation capacity and self-healing behavior. The mechanism appears to be complementary: glycine, with its small, polar structure, may effectively plug incipient pits, whereas leucine contributes a bulky, hydrophobic barrier that blocks aggressive species. This synergy effectively mitigates the individual limitations of each amino acid, resulting in superior localized corrosion protection. Ultimately, while individual amino acids offer targeted benefits, this work highlights that tailored amino acid mixtures – specifically those exhibiting synergistic interactions – represent the most promising route for developing advanced, environmentally friendly corrosion inhibition systems for SS in DES environments. The ability of such systems to induce self-healing responses, as demonstrated by the glycine/leucine blend, marks a significant step forward in creating durable materials for long-term industrial use in these novel solvent systems. This study establishes a solid foundation for understanding the complex and sometimes contradictory roles of amino acids as corrosion inhibitors for AISI 302 in Ethaline. Among the findings, the synergistic and self-healing behavior observed in the glycine/leucine mixture stands out as particularly promising. Building on these insights, future research should prioritize explaining the underlying mechanisms of inhibition and synergistic interactions, optimizing and broadening the scope of amino acid-based inhibitor systems, and assessing long-term performance under more realistic and application-specific conditions.

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