Determination of electrochemical behavior of phenylalanine, leucine and valine as corrosion inhibitors for mild steel in sweet brine

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ABSTRACT

This study evaluated the effect of concentration and immersion time of phenylalanine (Phe), leucine (Leu) and valine (Val) for AISI 1018 in sweet brine through electrochemical impedance spectroscopy (EIS), polarization resistance (Rp), Scanning Electronic Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) as an ecological and biodegradable alternative as corrosion inhibitors. Electrochemical results showed that amino acids are good corrosion inhibitors according to their charge transfer resistance improvement. The effect of immersion time on corrosion behavior was studied through 24 h with amino acids concentration variation of 0, 10, 100 and 250 ppm. The preliminary results demonstrated that the three amino acids adsorbed over metal surface following the Langmuir adsorption isotherm model, and tend to agglomerate in bulk within time.

Key words: Corrosion inhibitors, biodegradable, amino acids, sweet brine.
Abbreviations: Phe; Phenylalanine, Leu; Leucine, Val; Valine, EIS; Electrochemical Impedance Spectroscopy, Rp; Polarization Resistance, SEM; Scanning Electronic Microscope, EDX; Energy Dispersive X-ray, FTIR; Fourier Transform Infrared Spectroscopy.

INTRODUCTION

In spite of all developments in new technologies, the search for new oil sources is utmost importance due to the growing demand for energy (Kermani and Harrop, 2019). It comes with new challenges to inhibit corrosion in extraction and transportation systems (Popoola et al., 2013) without neglecting the ecological issue. Recently, some researchers such as Olajire (2017) mentioned that the use of synthetic organic inhibitors in oil and gas industry leads to stricter environmental regulations to their usage, which thus necessitated the research of new natural, inexpensive and environmentally friendly corrosion inhibitors. In this way the presence of functional groups, heteroatoms and multiple bonds make organic compounds a good option as corrosion inhibitors (Sastri, 2011), due to this, amino acids have been used as corrosion inhibitors for several metals and alloys in different electrolytes for multiple applications. However, their efficiency depends on many factors, such as inhibitor and oxygen concentration, metal and compound chemical nature, surface preparation of metal, immersion time, hydrodynamic conditions, temperature, pH and additives (El Ibrahimi et al., 2020).

In general, it has been defined that amino acids have higher antirrrosive efficiency in neutral and acidic solutions, due to the protonation of the amino group, adsorbing and blocking the active sites for the corrosion process (Hamadi, 2018). Amino acids adsorb over metal surface following different adsorption models. Abdel-Fatal et al. (2017) specified that tryptophan was a good corrosion inhibitor for mild steel in HSO\textsubscript{3}NH\textsubscript{2} and HCl acid solutions obeying Temkin adsorption isotherm model. On the other hand, Bobina et al. (2013) studied that the L-histidine as corrosion inhibitor obeys Langmuir adsorption isotherm model.

In addition, it was determined that the concentration is a
decisive factor for a corrosion inhibitor, many authors have used amino acids in a wide range of concentrations in order to achieve high corrosion inhibition efficiencies, from tens of ppm (0-99 ppm) (Singh et al., 2008; Zhang et al., 2009; Yadav et al., 2015), followed by hundreds of ppm (100-999 ppm) (Gupta et al., 2016; Ashassi-Sorkhabi and Asghari, 2008; Nady, 2017), to thousands of ppm (+1000 ppm) (Hamed et al., 2012; Zhang et al., 2012). Due to this, the amino acids: phenylalanine (Phe), leucine (Leu) and valine (Val) (Figure 1) are proposed as an eco-friendly alternative as corrosion inhibitors for AISI 1018 in a sweet brine for an application in oil industry.

EXPERIMENTAL PROCEDURE

Surface preparation and electrochemical cell

Before the electrochemical tests, the working electrode samples were prepared by abrasion with emery paper to a 2000-grade, a subsequent cleaning with deionized water and acetone and dried at room temperature (25ºC) (Espinoza-Vazquez and Rodriguez-Gómez, 2016). The electrolyte was a sweet brine composed of a brine solution NACE (NaCl 106.58 g/L, CaCl₂·2H₂O 4.48 g/L and MgCl₂·6H₂O 2.96 g/L) and CO₂(g) until saturation (pH=3.9). The amino acids (Phe, Leu, Val) were reagent grade (≥98%) from Sigma Aldrich. Inhibitor concentrations were 0, 10, 100 and 250 ppm.

Electrochemical characterization

The electrochemical characterization was carried out using a GillAcpotentiostat with a typical three-electrode electrochemical cell composed of an AISI 1018 alloy as working electrode, graphite rod as counter-electrode and a saturated Ag/AgCl reference electrode. Electrochemical impedance spectroscopy (EIS) was carried out employing a sinusoidal perturbation signal of ±10 mV vs Ecorr, within a frequency range of 10⁻² Hz to 10⁴ Hz after rest potential monitoring during 1800 s. After EIS evaluation, a rest potential monitoring was performed during 300 s, then a perturbation of ± 20 mV vs Ecorr was applied in order to evaluate linear polarization resistance. The experimental data was fitted by ZView 2 software.

Morphological characterization

Samples were immersed in the sweet brine with the optimum concentration of each amino acid, during 24 h at room temperature. After immersion, specimens were washed with distilled water and dried in open-air inside a desiccator. The surface was analyzed using a Carl-Zeiss microscope SUPRA 55 VP at 5 kV accelerating voltage, with a 500X secondary electron detector.

Spectroscopic characterization

For Fourier Transform Infrared spectroscopic characterization, electrolyte samples were taken at the beginning of the tests and after seven days and were analyzed on a Perkim Elmer Spectrum One in the range of 650 to 4000 cm⁻¹.

RESULTS AND DISCUSSION

Electrochemical characterization

Nyquist plots of AISI 1018 in the sweet brine in absence and presence of Phe during 24 h of immersion is shown in Figure 2, which seem to appear as depressed semicircles caused by the heterogeneity of the metal surface (Bentiss et al., 2005). At time t = 0 h (Figure 2a) Phe at 10 ppm presents the higher impedance value (2442 Ωcm²), this is attributed to the decrease of molecular mobility with the increase of Phe concentration (Kothari et al., 2015). This
tendency persists during the first 12 h (Figures 2b and c), and after 24 h of immersion (Figure 2d) the Phe at 10 ppm remains stable and the other systems achieves similar values, due to oxide formation and amino acid adsorption.

Bode angle plots of AISI 1018 in absence and presence of different concentrations of Phe are shown in Figure 3; after 6 h of immersion (Figures 3a and b) can be appreciated only one time constant due to the inhibitor film resistance ($R_i$), and after 12 and 24 h (figures 3c and d) there is an arc widening, associated to the presence of a second time constant of the charge transfer resistance ($R_{ct}$) (Dehghani et al., 2020), furthermore, the wide frequency range covered by the phase angle signal provides information on a strong adsorption process over the substrate (Zhang et al., 2016) and the increasing of the phase angle values with the addition of the amino acid means of a formation of a higher protection layer (Tildiz, 2014).

In order to simulate the response acquired by EIS of all systems, the equivalent circuits in Figure 4 were used by fitting to the lowest error. Figure 4a shows the circuit used for the first 6 h of immersion and for the 12 and 24 h of immersion the two elements circuit in Figure 4b was used. Due to surface heterogeneity (Vieira, 2016), a constant phase element (CPE) was used instead of capacitances ($C$) for a more accurate fitting to EIS results. The CPE is defined in impedance representation by the following equation:

$$ Z_{CPE} = Y_0^{-1}(j\omega)^{-n} $$

(1)

where $Y_0$ is a proportional factor, $n$ is the phase shift. The CPE may represent a resistance ($n = 0$), a capacitor ($n = 1$), or an inductance ($n = -1$). The double layer capacitance ($C_{dl}$) is represented by,

$$ C_{dl} = Y_0(\omega_m)^{-n-1} $$

(2)

Where $\omega_m$ is the angular frequency in which the imaginary component of the impedance has a maximum value. Further, $n$ can be used as a measurement of the heterogeneity or roughness of the surface (Tang et al., 2013).

The obtained data from the fitting of the impedance results from AISI 1018 in the sweet brine and the addition of Phe are given in Table 1. As can be seen, with the presence of Phe, the $R_{ct}$ increases, meaning that in the

![Figure 2: Nyquist plots for AISI 1018 in a brine solution NACE + CO2 in absence and presence of Phe after a) 0 h, b) 6 h, c) 12 h and d) 24 h of immersion.](image-url)
formation of a protective film over the surface, in addition, the double layer capacitance \( C_{dl} \) values decrease due to the adsorption of the amino acid on the surface which changes in the dielectric properties of water molecules on the double layer by changing the orientation of the dipole molecules (Wang et al., 2001). Besides this, the effect of the addition of Phe can also be seen by the decrease of the corrosion current density \( i_{corr} \) meaning in a lowering of the corrosion rate \( CR, \text{ in mm/y} \).

Figure 5 shows the Nyquist plots of Leu, at beginning of the test (Figure 5a) the amino acid provides low corrosion protection in comparison with blank, nearly 10% of impedance improvement, which enhances within time. After 6 and 12 h of immersion (Figures 5b, 5c) the
Table 1: Impedance parameters calculated from EIS diagrams of AISI 1018 in sweet brine as a function of Phe concentration and immersion time.

<table>
<thead>
<tr>
<th>C (ppm)</th>
<th>T (h)</th>
<th>Rf (Ωcm²)</th>
<th>Cf [x10⁻⁴] (F)</th>
<th>Rct (Ωcm²)</th>
<th>Cdl [x10⁻⁴] (F)</th>
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Figure 5: Nyquist plots for AISI 1018 in a brine solution NACE + CO2 in absence and presence of Leu after a) 0 h, b) 6 h, c) 12 h and d) 24 h of immersion.
impedance value of Leu at 250 ppm increases to 70% in comparison with AISI 1018 in absence of the Leu. However, after 24 h (Figure 5d) the oxide products formed over the surface provide similar protection than that provided by the amino acid.

Figure 6 shows Bode angle plots of the system with variation of concentration and time immersion, during the first 6 h of immersion (Figures 6a, 6b) can be appreciated only one time constant associated to the film resistance. After 12 and 24 h of immersion

in time (Figures 6c, 6d), the widening in frequency of the phase angle signal implies the apparition of a second time constant associated to the charge transfer resistance. Compared with Phe, the phase angle value in presence of Leu increases to a lesser extent, which is associated with a lower adsorption of the amino acid since it slightly increases the capacitive behavior, which is reflected in the lower impedance values reported in Nyquist diagrams.

The data obtained by fitting the EIS experimental results are shown in Table 2, as can be appreciated, the capacitance of the double layer slightly decreases with the addition of Leu to the system what agrees with the small amount of increment in the diameter of the Nyquist plots compared with the results of the addition of Phe.

The Nyquist plots for the addition of Val are shown in Figure 7, where it is shown that from time \( t = 0 \) h (Figure 7a) the corrosion inhibitor effect is evident and proportional to Val concentration, achieving the higher impedance value (1826 \( \Omega \text{cm}^2 \)) at concentration of 250 ppm. This behavior persists during all 24 h of test (Figures 7b, 7c and 7d) providing corrosion protection in the sweet brine. The increase of the phase angle value in the Bode plots (Figure 8) with the addition of the Val implies the formation of the protection layer (Nady, 2017), which matches with the impedance enhancing seen in the Nyquist diagrams. During the first 6 h of immersion in the sweet brine (Figures 8a and b) can only be appreciated one well defined time constant associated with the amino acid film resistance (\( R_f \) and after 12 and 24 h of immersion, the widening of the phase angle signal implies a second time constant associated to the charge transfer resistance (\( R_c \)). Table 3 shows the data obtained by the fitting of the impedance results, with presence of Val, the double layer capacitance decreases, which implies its adsorption by the
Table 2: Impedance parameters calculated from EIS diagrams of AISI 1018 in sweet brine as a function of Leucine concentration and immersion time.

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Figure 7: Nyquist plots for AISI 1018 in a brine solution NACE + CO₂ in absence and presence of Val after a) 0 h, b) 6 h, c) 12 h and d) 24 h of immersion.
The difference in the concentration when the higher inhibitory effect is achieved by each amino acid is associated with the different molecular structure (Guo et al., 2017; Martínez and Stagliar, 2003), since the three amino acids interacts with the metal surface by the interaction of the lone-pair electron of the heteroatoms (Yadav et al., 2015; Vinutha and Venkatesha, 2016), the presence of an aromatic ring in the Phe provides a higher electronic density, so that π-electrons of the benzene ring have donor-acceptor interactions with the vacant d-orbital of the metal surface (Eddy, 2010; Yadav et al., 2015; Fu et al., 2011).

### Polarization resistance (Rp)

The effect of immersion time on the AISI 1018 resistance in the sweet brine is shown in Figure 9, in case of Phe (Figure 9a), shows a superior corrosion inhibition at concentration of 10 ppm. In addition, the Rp values increases initially followed by a subsequent leveling after 12 h, indicating a gradual reaction of the molecule with the metal surface followed by a surface saturation of simultaneous adsorption-desorption phenomenon (Taheri et al., 2020).

With Leu addition (Figure 9b), the system resistance hardly increases compared with blank, meaning in a slightly protection, agreeing with what was observed in the impedance results. Finally, with Val (Figure 9c) can be seen a superior corrosion protection with a gradual enhancing within immersion time, due to the formation of the amino acid film over the substrate surface.

### Amino acids inhibition efficiency

Polarization resistance was taken for amino acids inhibition efficiency (I.E.) calculations as follows:

\[
I.E. = \left( \frac{R_{P inh} - R_{P0}}{R_{P inh}} \right) \times 100
\]

where \(R_{P0}\) and \(R_{P inh}\) are the polarization resistances in absence and presence of corrosion inhibitor, respectively (Öskir et al., 2013), and results are shown in Figure 10. As immersion time increases, the polarization resistance also changing of the electrical permittivity of the film (Hamed et al., 2012).

Figure 9: Bode plots of AISI 1018 in a brine solution NACE + CO2 in absence and presence of Val after a) 0 h, b) 6 h, c) 12 h and d) 24 h of immersion.
Table 3: Impedance parameters calculated from EIS diagrams of AISI 1018 in sweet brine as a function of Valine concentration and immersion time.

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Figure 9: Variation of linear polarization resistance with immersion time with different concentrations of a) Phe, b) Leu and c) Val.
Increases due to further amino acid adsorption, and consequently the inhibition efficiency increases up to 89.87 and 93% for Phe, Leu and Val, respectively. It should be noted that in case of Phe, the I.E. achieves 89% since the first 12 h of immersion, and remains constant for 12 more hours, in comparison with Leu and Val which reach their highest efficiency after 24 h.

**Adsorption isotherms and thermodynamics**

The usual mechanism in which organic corrosion inhibitors provide anticorrosive protection is by their adsorption over the metal surface, isolating it from the aggressive electrolyte and preventing the substrate dissolution (Goyal et al., 2018). For a further analysis of adsorption processes carried out in the system, the implementation of adsorption isotherms provides information about the nature of the interactions between the corrosion inhibitor molecule and the metal surface (Khulood et al., 2011). The adsorption process is influenced by many factors such as the metal charge, chemical nature of metal and organic compound or charge distribution on the molecule (Obot and Obi-Eghedi, 2009). When considering adsorption isotherms, it is conventional to adopt the term surface coverage ($\theta$), which defines the saturation of a particular adsorbate on a given surface (McQuarrie and Simon, 1997). It can be calculated by the following equation:

$$\theta = 0.01 \left( \frac{R_{P_{in,h}} - R_{P_{in,h}}^{0}}{R_{P_{in,h}}} \right)$$

where the value of $\theta$ must be in the interval of 0-1. When $\theta = 0$ implicates the lack of surface coverage of the corrosion inhibitor and at the case of $\theta = 1$ implies the total coverage of substrate surface (Ituen et al., 2017). There are several adsorption isotherms models used for thermodynamic analysis, some of them are: Langmuir, Temkin, Freundlich, Frumkin, Fory-Huggins or Bockris-Swinkels (Abd El Rehim et al., 2016). The three amino acids systems adjusted more accurately to Langmuir’s model, given by the following equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

where $C$ is the corrosion inhibitor concentration (mol/L) and $K_{ads}$ is the adsorption constant (Abdullah, 2008). In order to determine the adsorption model, it is important to calculate the Gibbs free energy of adsorption ($\Delta G_{ads}^{0}$) which is related with the adsorption constant ($K_{ads}$) by the
Figure 11: Adsorption model adopted from the experimental results according to the theoretical model of Langmuir.

Table 4. Thermodynamic data calculated from Langmuir’s adsorption model adjustments of AISI 1018 in a sweet brine with Phe, Leu and Val.

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</table>

following equation:

$$\Delta G_{ads}^0 = -RT\ln K_{ads}$$  \hspace{1cm} (6)

where $R$ is the ideal gas constant and $T$ is the absolute temperature (K).

If the Gibbs free energy gets negative values, a spontaneous process is happening (Cleveland and Morris, 2014). When there is a physical interaction (physisorption) between amino acids and metal surface then $\Delta G_{ads} < -20 \text{ kJ/mol}$, for a chemical interaction (chemisorption) $\Delta G_{ads} > -40 \text{ kJ/mol}$,
and for values of $-20 \text{kJ/mol} < \Delta G_{ads} < -40 \text{kJ/mol}$ there is a combined process of physisorption and chemisorption (Espinoza-Vazquez et al., 2020; Ali Fil et al., 2014).

Figure 11 shows the adsorption isotherms of the three amino acids (Phe, Leu and Val) and Table 4 shows the thermodynamic data calculated from them. It can be seen that for Phe, at all immersion times the $\Delta G_{ads}$ values are near -40 kJ/mol meaning a chemisorption in comparison with Leu and Val where $\Delta G_{ads}$ are in the range of -20 and -40 kJ/mol meaning in a combined process, which implies a Weaker interaction with the metal surface, agreeing with Results seen in the electrochemical characterization.

**Morphological characterization**

**Scanning electronic microscopy (SEM)**

The surface morphology images of the polished AISI 1018 steel sample is shown in Figure 12a, and the steel sample after 24 h of immersion in the aggressive electrolyte with 10 ppm of Phe is shown in Figure 12b, 100 ppm of Leu (fig. 12c) and 250 ppm of Val (fig. 12d). It can be observed that the polished line of the sample can still be seen after the 24 h immersion in the presence of the three amino acids, meaning that organic molecules adsorbed in those areas...
forming a protecting layer and inhibiting the metal dissolution; the agglomerations seen in images are associated to corrosion products and NaCl incrustations due to the presence of Na and Cl signals in EDX images (Singh, 2017; Vengatesh, 2019). The cluster presence in substrate surface validates electrochemical results, since the system with Phe present the less agglomeration areas, followed by the system with Leu and finally with Val (Fatima, 2019; Ech-Chinbi, 2020).

Spectroscopic characterization

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum of the sweet brine (SB) with the different amino acids is shown in Figure 13a. The width peak observed in the range of 3000-3500 cm\(^{-1}\) is attributed to the O-H stretching vibrations \((\nu_1)\), the sharp peak in 1640 cm\(^{-1}\) is attributed to the O-H bending vibrations \((\nu_2)\) and at 2100 cm\(^{-1}\) is the combination band \((\nu_1 + \nu_2)\) (Nakamoto, 2009). As can be seen, it is basically the water FTIR spectrum due to the fact that characteristic bond of amino acids was not detected due to their low concentration in the solution. Figure 13b shows the spectrum of the same solutions after seven days, where agglomerations could be distinguished. The most intense peak is attributed to the O-H stretching vibrations (Bulgariu et al., 2019), the peak in the range of 1700-1500 cm\(^{-1}\) is associated to the C=O and C-N stretching vibrations (Krimm and Bandekar, 1986), the last is related to the peptide bond which suggests that amino acid molecules tend to agglomerate within time, diminishing their efficiency as corrosion inhibitors.

CONCLUSIONS

In order to contribute the necessitated development of new natural, inexpensive and environmentally friendly corrosion inhibitors, this study determinate the following results:

(1) From the electrochemical results, it was determined that the proposed amino acids are a good ecological alternative as corrosion inhibitors for AISI 1018 in sweet brine due to the system corrosion resistance increasing.

(2) The study determined that the amino acids form a monolayer on metal surface due to the systems fit the Langmuir's adsorption isotherms. It was also concluded that Phe needs lower concentration to inhibit corrosion due to its molecular structure, which provides it of a higher electronic density by the aromatic ring, improving the interaction between amino acid and metal surface, inducing chemisorption. In comparison with Leu and Val where the absence of the benzene ring leads to weaker bonds with the iron in surface, having a combination of physical and chemical interactions.

(3) The presence of amino acids prevents the metal dissolution, as shown in the SEM images, the areas where the polished lines are still visible were also where the inhibitor was adsorbed and protected by the substrate.

(4) The inhibition efficiency of the amino acids would decrease within time due to desorption process and due to their agglomeration in solution bulk, which could be seen in FTIR by the appearance of the C-N vibrational band associated to the peptide bond between amino acids.

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