Experimental and theoretical study of 1-(2-ethylamino)-2-methylimidazoline as an inhibitor of carbon steel corrosion in acid media

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Abstract

The electrochemical behavior of 1-(2-ethylamino)-2-methylimidazoline (imidazoline), its precursor N-[3-(2-aminoethylaminoethyl)]-acetamide (amide) and its derivative 1-(2-ethylamino)-2-methylimidazolidine (imidazolidine), is evaluated by using potentiodynamic polarization curves and electrochemical impedance spectroscopy, EIS, techniques in deaerated acid media to compare their corrosion inhibition efficiency. The experimental results suggest that imidazoline is a good corrosion inhibitor at different concentrations whereas amide shows low efficiency values; however, the properties of a corrosion inhibitor were not found in imidazolidine. The reactivity of these compounds was analyzed through theoretical calculations based on density functional theory (DFT) to explain the different efficiencies of these compounds as corrosion inhibitors both in the neutral and protonated form. The theoretical results indicate that imidazoline is the more efficient corrosion inhibitor because of its two very active sites (two nitrogen atoms) and the plane geometry of the heterocyclic ring, thus promoting coordination with the metal surface.

Keywords: Amide; Corrosion inhibitors; Imidazoline; Imidazolidine; EIS; DFT calculations

1. Introduction

Nowadays the study of carbon steel corrosion phenomena has become an important industrial and academic topic [1]. The use of corrosion inhibitors is one of the most effective methods to protect metal surfaces against corrosion, especially in acid media [2,3].

The development of corrosion inhibitors is based on organic compounds containing nitrogen, oxygen, sulfur atoms, and multiple bonds in the molecules that facilitate adsorption on the metal surface [4]. The corrosion inhibition efficiency of organic compounds is related to their adsorption properties. Adsorption depends on the nature and the state of the metal surface, on the type of corrosive medium and on the chemical structure of the inhibitor [4]. Studies report that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule, related to its functional groups, to the possible steric effects and electronic density of donor atoms; adsorption is suppose also to depend on the possible interaction of \( \pi \)-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of carbon steel, leading to the formation of a corrosion protecting film [1,5].

Different derivatives from imidazoline are employed as steel corrosion inhibitors. Even though they have been specially employed in the oil industry, only recently have many studies been undertaken to understand how they work [6]. The availability of sophisticated computational tools and electrochemical techniques and a better understanding of corrosion inhibitors and their mechanisms can now be achieved [7–9]. Ramachandran et al. [10], Wang et al. [11], and Cruz et al. [12] have published important papers concerning the molecular
structure of imidazoline as a corrosion inhibitor. In these implies some key questions regarding the structure–performance relationships of imidazolines and corresponding amines are: (a) the role of the hydrocarbon chain relative to the imidazoline head group and pendant amine group in film formation; (b) the thickness of the imidazoline film; (c) the stability of the imidazoline film; (d) the solution composition and hydrolysis of imidazoline.

One of the most common methods used to prepare 2-alkyl-imidazoline consists of the set of reactions depicted in Scheme 1 below [13–17]. The thermal reaction between 1,2-diamines (1) and carboxylic acids (2) leads to an intermediary amide (3), which then cycles to (4) at high temperatures and low pressure. The imidazoline cycle can be reduced to a saturated imidazolidinic-like class (5), which can be obtained when 1 reacts with an aldehyde [17].

According to some reports, a high-rate conversion from imidazoline to amide (up to 80%) has been reported [18] within a period of 2–9 days under atmospheric conditions, because of the low stability of the imidazoline cycle, which can be hydrolyzed to (3) [18]. Other authors [19,20] have found that amide and imidazoline have the same efficiency as corrosion inhibitors.

The purpose of this paper is to evaluate the behavior of 1-(2-ethylamino)-2-methylimidazoline (imidazoline), N-[3(2-amino-ethylamino-ethyl)]-acetamide (amide) and 1-(2ethylamino)-2-methylimidazolidine (imidazolidine) as corrosion inhibitors using potentiodynamic polarization curves and electrochemical impedance spectroscopy, EIS, techniques. The effect of the presence of the iminic double bond N=C in the imidazoline ring and the cyclic structure of imidazoline on its inhibition efficiency is compared with those of amide and imidazolidine, in order to seek correlation between the electronic and structural properties of the above compounds and their experimental behavior as corrosion inhibitors. A theoretical study is carried out based on density functional theory (DFT), which can provide an interpretation of the experimental results obtained. The structural and electronic parameters can be obtained by means of first principles theoretical calculations using the computational methodologies of quantum chemistry.

2. Experimental procedure

Electrochemical tests were carried out with an electrochemical interface Solartron 1287 connected to a frequency response analyzer (FRA) Solartron 1255B, which was controlled by CorrWare and Zplot software. The cell assembly consisted of a carbon steel working electrode (WE), two-graphite counter electrodes (CE), and a saturated calomel electrode (SCE) as the reference electrode. The test material was carbon steel (composition, wt%: 0.18 C, 0.35 Mn, 0.17 Si, 0.025 S, 0.03 P, and bal. Fe). Prior to exposure, it was polished with 400-grit silicon carbide (SiC) paper wetted with deionized water, then polished with 600-grit SiC paper wetted with ethanol (C₂H₆O), and then rinsed with C₂H₆O. Twice distilled water and analytical reagent-grade hydrochloric acid, 0.5 M HCl, were used to prepare the test solutions, which were de-aerated by means of nitrogen during a period of 45 min. The samples were exposed at static conditions and room temperature.

Polarization curves were recorded potentiodynamically at a rate of 0.5 mV/s in the range −300 to +300 mV versus the open circuit potential. Impedance was measured over a frequency range of 100 kHz–10 mHz. All the impedance experiments were carried out after dipping the working electrode into 0.5 M HCl solution containing the inhibitor at the open-circuit potential, Ecorr, with respect to a SCE reference electrode, with a 10 mV peak-to-peak perturbation. Two independent experiments have been recorded for each inhibitor concentration value.

N-[3-(2-amino-ethylamino-ethyl)]-acetamide (amide) and 2-methyl-N-(2-ethylamino)-imidazoline (imidazoline) were synthesized as follows. A solution of 10 ml of xylene in glacial acetic acid solution (6.0 g, 0.1 mol) was slowly added to a diethylenetriamine solution previously heated at 50 °C (10.3 g, 0.1 mol) in a closed system under a nitrogen atmosphere and constant agitation. The addition having been completed, the reaction was progressively heated to 190 °C at reduced pressure (3 mm Hg) until all the water was distilled. The product obtained was purified in a chromatographic column of silica-gel using petroleum ether as an eluant, imidazoline (91%) was obtained.

[Scheme 1]
2-methyl-N-(2-ethylamino)-imidazolidine (imidazolidine): 10.3 g (0.1 mol) of diethylenetriamine, mixed with 11.0 g of acetaldehyde (solution at 40%) (0.1 ml) in 100 ml of tetrahydrofuran (THF), was agitated continuously for 8 h at room temperature. The solvent was evaporated and the remaining product (raw) was purified in a chromatographic column of silica-gel with hexane + ethyl acetate (9:1) as eluant, to give imidazolidine in 79% yield.

The purity of the compounds was verified by means of infrared spectroscopy, IR, 1H and 13C nuclear magnetic resonance (NMR), and mass spectroscopy (MS).

3. Computational details

Calculations were performed with the Gaussian 98 program [21]. Exchange and correlation calculations were carried out with the functional hybrid B3LYP [22,23] and the 6-311G** orbital basis sets for all atoms. In all cases, total structure optimization together with the vibrational analysis of the optimized structures was carried out in order to determine whether they corresponded to a maximum or a minimum in the potential energy curve. The frontier molecular orbitals, namely, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and chemical reactivity were evaluated by taking into account the Fukui indexes [24], which were obtained by addition or subtraction of one electron, \( N+1 \) and \( N-1 \).

4. Experimental results and discussion

The effect of the exposure time on the corrosion rate was studied. The results obtained provided information about the determination of the WE exposure time. The corrosion current density, \( j_{\text{corr}} \) was recorded after an exposure to 1, 2, 3, 4, 5, 6, 7, 8 and 9 h. The results are presented in Fig. 1. It is seen that the corrosion rate depends on the immersion time of carbon steel in the solution. Fig. 1 illustrates the variation of \( j_{\text{corr}} \) with immersion time. The corrosion rate increase initially and then starts to decrease slowly. Thus it was found experimentally that a 9 h exposure seems necessary to minimize of the effects of the electrode’s preliminary treatment and of the possible corrosion products formed.

Fig. 1(a)–(c) shows the estimated corrosion rate during a 9 h period by means of the Tafel extrapolation technique for the three organic compounds under study. Fig. 1(a) corresponds to the corrosion rates obtained at different amide concentrations showing some discrepancies in the behavior of the corrosion rate. From all the inhibitor concentrations studied, 50 ppm show the higher corrosion rate, which is, however, less than the corrosion rate corresponding to the blank solution, but higher than the corresponding rate at 25 and 10 ppm. One can conclude a non-monotonic dependence of the corrosion rate on the concentration of amide.

Fig. 1(b) clearly shows a monotonic dependence of the corrosion rate on the concentration of imidazoline. In this case, the higher the imidazoline concentration, the lower is the associated corrosion rate.
Finally, Fig. 1(c), which corresponds to the corrosion rate determined for the different imidazolidine concentrations, shows an erratic behavior. Again a non-monotonic dependence of the corrosion rate on the concentration of imidazolidine can be observed.

The Nyquist representation of EIS data obtained before and after the addition of the three chemical compounds at the different concentrations studied and used as corrosion inhibitors after 9 h of being exposed in the corrosive medium are provided in Fig. 2(a)–(c). The impedance spectra were similar, exhibiting in all cases a single (capacitive like) semicircle and then only one time constant, which can be modeled as an electric equivalent circuit with a parallel combination of double-layer capacitance $C_{dl}$ and polarization resistance $R_p$ in series with the solution resistance, $R_s$ (Fig. 3), as has been reported previously for carbon steel studies in acid media [25–27]. With the addition of the water soluble chemicals, it is clearly seen that the diameter of the semicircle increases with increasing inhibitor concentration. However, the shape of the impedance spectra remained unchanged showing a single time constant, which is the result of the charge-transfer corrosion process.

It is important to point out that the three compounds under study exhibited the same behavior during all test times and for all concentrations. It can be observed that as the inhibitor is adsorbed onto the metal surface, the polarization resistance, $R_p$ increases. As the inhibitor adsorbs onto carbon steel, the capacitance of the interface starts decreasing. The change in the imaginary component of the impedance and consequently of capacitance can thus be used to follow the adsorption process. The double-layer capacitance $C_{dl}$ reduces after adsorption of the inhibitor since the adsorbed film reduces the dielectric constant between the metal and electrolyte. The large semicircles observed from high to low frequencies, Fig. 2, indicates that the polarization resistance, $R_p$ becomes dominant due to adsorption of the inhibitor.

In some cases impedance data obtained at the corrosion potential, $E_{corr}$ have the shape of depressed semicircles with the center of the circle below the real axis. Then the complex impedance $Z(j\omega)$ could be expressed as

$$Z = R_s + \frac{R_p}{1 + (j\omega C_{dl} R_p)^z}.$$

The $z$ exponent is a unitless parameter that equals one for an ideal capacitor. In most real systems, ideal capacitive behavior is not observed due to surface roughness, or other effects that causes uneven current distributions on the electrode surface. In the case when $z = 1$, the term $(j\omega C_{dl} R_p)^z$ reduces to $j\omega C_{dl} R_p$, where $C_{dl}$ is the interfacial double-layer capacitance. As can be appreciated in Table 1, in all the cases studied, $z$ reaches approximately the same value of 0.9. This can be interpreted as an indication of the degree of inhomogeneity of the metal surface, corresponding to a small depression of the double-layer capacitance semicircle, and $z$ has almost a constant value (0.9).

The impedance spectra of carbon steel in 0.5 M HCl in the presence of the different inhibitors studied are
shown in Fig. 2(a)–(c) in a Nyquist impedance plot. It is found that all the inhibitors decrease the double-layer capacitance and increase the polarization resistance of the metal-electrolyte interface to different extents, depending on the nature of the adsorption. As $R_p$ value increases, the inhibit power is higher.

A comparison of the inhibitor properties of amide, imidazoline and imidazolidine indicates that imidazoline is a much better inhibitor than amide and imidazolidine. From Fig. 2 we can clearly observe that the larger value of $R_p$ corresponds to imidazoline, followed by amide and imidazolidine, the $R_p$ values for this last inhibitor being very similar to those of the blank solution. These observations suggest that imidazoline forms a much better homogeneous film compared to amide. It seems necessary to obtain more information to understand how the imidazoline adsorption proceeds. The latter would be determined by the disposition of the molecule on the metal surface in the adsorption step, depending on its configuration and the number and disposition of its active centers.

Fig. 4(a)–(c) shows the behavior of $R_p$, as measured from EIS. The plots correspond to inhibitor concentrations of 0, 10, 25, 50 and 100 ppm. The results show clearly that the presence of imidazoline increases the $R_p$ values, Fig. 4(b), whereas for amide, Fig. 4(a), and especially imidazolidine, Fig. 4(c), a non-monotonic dependence of the $R_p$ values on the inhibitor concentration can be observed. These results confirm those previously obtained by means of the Tafel extrapolation technique, Fig. 1; thus, both techniques are consistent with the observed behavior.

The corrosion rates and $R_p$ values obtained from potentiodynamic polarization curves and impedance measurements as well as the calculated inhibition efficiencies (IE) for different concentrations of these compounds are given in Table 1. It can be observed that the values of corrosion inhibition efficiency obtained are similar, thus both techniques are consistent with the observed behavior and seem adequate for these calculations. It is interesting to note that because the Tafel extrapolation technique implies a larger perturbation of the system under study than the impedance technique, it seems more appropriate that the values are derived from the faradic impedance technique.

The equations used to determine the inhibition efficiency were:

$$\% E(\text{j corr}) = \frac{\text{j corr} - \text{j corr (inh)}}{\text{j corr}} \times 100,$$

where $\% E(\text{j corr})$ is the percentage efficiency determined by means of the Tafel extrapolation technique, $\text{j corr}$ is the corrosion current density without inhibitor, and $\text{j corr (inh)}$ is the same current density with inhibitor, and

$$\% E(R_p) = \frac{R_p (\text{inh}) - R_p}{R_p (\text{inh})} \times 100,$$

Table 1

<table>
<thead>
<tr>
<th>Inhibition efficiency for amide, imidazoline and imidazolidine</th>
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<tr>
<td>$10^4 \text{j corr}/A \text{ cm}^{-2}$</td>
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<tr>
<td>---------------------------------------------</td>
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<tr>
<td><strong>Amide /ppm</strong></td>
</tr>
<tr>
<td>0</td>
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<tr>
<td>10</td>
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<td>25</td>
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<tr>
<td>50</td>
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<tr>
<td><strong>Imidazoline /ppm</strong></td>
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<td>0</td>
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<tr>
<td>100</td>
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<tr>
<td><strong>Imidazolidine /ppm</strong></td>
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<td>10</td>
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<tr>
<td>50</td>
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<td>100</td>
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where \( R_p \) is the polarization resistance without inhibitor, and \( R_p(\text{inh}) \) is the polarization resistance with inhibitor.

The \( R_p \) values obtained from impedance measurements allow us to follow the corrosion inhibition properties of the three compounds studied as a function of time, as was previously done with the Tafel extrapolation technique (Fig. 1). From the Stern–Geary equation, \( R_p \) has a value inversely proportional to the corrosion current density, \( j_{\text{corr}} \). It can be observed from Fig. 4 that the \( R_p \) values are highest for imidazoline, followed by amide and finally by imidazolidine, which has \( R_p \) values of the same order of magnitude as those of the acid solution without inhibitor.

From the impedance data, it is possible to obtain the double-layer capacitance values, \( C_{\text{dl}} \) and its time constant, \( \sigma \), which are very important parameters for the understanding of the mechanism of corrosion inhibition for these substances. The frequency at the top of the semicircle (when \( -Z'' \) is at maximum) is given by

\[
\omega_{\text{max}} = 2\pi f_{\text{max}} = \frac{1}{R_p C_{\text{dl}}}. 
\]

The term on the right of the above equation dictates the time scale of current response of the Randles circuit of Fig. 3 to applied voltage. This time constant, in seconds, is defined for applied current as

\[
\sigma = R_p C_{\text{dl}} 
\]

being then inversely proportional to the maximum value of the imaginary term of the impedance:

\[
\sigma = \left[2\pi f(Z''_{\text{max}})\right]^{-1}. 
\]

The frequency at the top of the semicircle is not easy to estimate from the phase angle Bode plot commonly used, but can be obtained directly from the \( Z'' \) vs. frequency Bode plot. Another method [28] involves an estimation of capacitance from the Bode plot of \( \log |Z| \) vs. log frequency. If the solution resistance is small, as in this case, the impedance modulus, at high frequency, when \( \omega RC \) is large, is given by

\[
\log |Z| = -\log \omega - \log C
\]

At high frequencies the plot is a straight line, of slope \(-1\), and if extrapolated to \( \omega = 1 \) then \( \log |Z| = -\log C \) [28]. Fig. 5(a)–(c) displays the capacitance values \( C_{\text{dl}} \) obtained as a function of time for the three organic compounds studied at different concentrations. The results indicate that the amide and imidazoline inhibitors affect the values of the \( C_{\text{dl}} \) capacitance significantly and in all cases, show a clear tendency to increase as a function of time. Fig. 5(a) showing the amide values, indicates that the inhibitor concentration is inversely proportional to the capacitance; however, for concentrations of 50 ppm, the capacitance value increases notably. Fig. 5(b) shows a monotonic dependence between the imidazoline concentration and capacitance value, where the imidazoline concentration is inversely proportional to the capacitance value. Finally, in Fig. 5(c) the associated capacitance values of the imidazolidine are very similar to those of the blank solution; this again allows us to make conclusions about the small interaction between imidazolidine and the metal surface.

Fig. 6(a)–(c) shows the variation of the time constant \( \sigma \) associated with the capacitor at different times as a function of inhibitor concentration. While the capaci-
The time constant $r$ is a measure of the rate at which this charge can be stored. In Fig. 6(a) can be observed the effect of amide concentration on $r$ values as a function of time. Again the $r$ values corresponding to 50 ppm show erratic behavior. In Fig. 6(b), which corresponds to $r$ values of imidazoline at different concentrations, typical behavior is observed, the highest values of $r$ corresponding to a concentration of 100 ppm of imidazoline and the lower to 10 ppm. The physical meaning of this behavior takes into account that the required time for the associated capacitor to be charged or discharged is higher if the inhibitor concentration is higher too. Fig. 6(c) shows the $r$ values of imidazolidine. In this case the values are similar, independently of the inhibitor concentration, and of the same order of magnitude as for the solution without inhibitor, which confirms what was indicated previously in the sense that this substance does not affect the metal surface significantly.

Fig. 5. The double-layer capacitance against time for carbon steel in 0.5 M HCl containing different concentrations of: (a) amide; (b) imidazoline; (c) imidazolidine.

Fig. 6. The time constant against time for carbon steel in 0.5 M HCl containing different concentrations of: (a) amide; (b) imidazoline; (c) imidazolidine.
In general, significant differences can be appreciated referring to the inhibitory efficiency of imidazoline, amide and imidazolidine. The understanding that the corrosion inhibition efficiency of organic compounds is related to their adsorption properties allows us to propose a possible mechanism. The inhibition efficiency depends strongly on the structures and chemical properties of the species formed under the experimental conditions studied. The extent of adsorption is dependent upon the electronic structure of the metal and the inhibitor. The impedance spectrum of carbon steel in 0.5 M HCl in the presence of 100 ppm imidazoline gives a polarization resistance of $10^3 \times \Omega \text{ cm}^2$ compared to the blank value of $23 \times \Omega \text{ cm}^2$, which can be explained by the formation of a homogeneous film. The presence of this film leads to a reduction in the double-layer capacitance $C_{dl}$ of the interface from the bare electrode value of 274 to $116 \mu \text{F cm}^{-2}$. Imidazoline is a heterocyclic compound with three carbon and two nitrogen atoms in the ring.

Theoretical calculations were performed for both the neutral and protonated forms, in order to give further insight into the experimental results. In the 0.5 M HCl solution that was used in this work, all molecules would be protonated or even diprotonated [29]. The optimized geometry of the molecules using the B3LYP hybrid functional and the 6-311+G** basis set are presented in Fig. 7 for amide, imidazoline and imidazolidine, and its more stable protonated forms respectively. These results are of predictive character with respect to the geometry and reactivity of these compounds.

The bond distance, bond angles and dihedral angles are shown in Table 2. It can be seen that the distance $N5-C1$ is smaller for imidazoline with respect to imidazolidine because of the presence of the double iminic

Fig. 7. Optimized B3LYP/6-311+G** structures of amide, imidazoline and imidazolidine and its more stable protonated forms. The N–H hydrogen bridge is also indicated. (For colours see online version of this article.)
bond \( \text{N}=\text{C} \) in the former. The bond and dihedral angles show that the structure of the imidazolidine ring has an enveloped conformation, and thus it is susceptible to undergoing ring inversion. This suggests that the free electron pair of nitrogen changes place and for this reason, it is statistically more difficult for a reactant complex to be obtained by means of a collision, thus fixing the molecule on the metal surface. In contrast, the imidazoline ring, being plane, cannot present a conformational equilibrium because the position of the non-bonding electrons is less likely to change, thus helping the interaction of imidazoline with the metal surface.

The ground state geometry of the inhibitor as well as the nature of its frontier molecular orbitals, namely, the HOMO and LUMO is involved in the activity properties of the inhibitors. The natural analysis of charges is shown in Table 3. These values indicate that heteroatoms have a nucleophilic character. The most favorable sites for the interaction with the metal surface are the following nitrogen atoms: N5 and N8 for amide, N2, N5 and N8 for imidazoline and N2 and N8 for imidazolidine, because they have a larger charge density. However, when the frontier molecular orbitals are analyzed, Fig. 8, it is observed that for amide, the highest occupied molecular orbital (HOMO) is in the nitrogen N5, this being the favorite site for a nucleophilic attack. For the imidazoline, on the other hand, the HOMO is localized over the nitrogen atoms N2 and N5 of the plane ring; consequently this is the preferred zone of the molecule for interaction with the metal surface. Both the nitrogen atoms can coordinate with carbon steel. Finally, the amide presents a linear structure in which the hydrogen atoms block the interaction of the most reactive sites with the metal surface. This can explain the weak interaction with the metal. These results agree with reports of the coordination compounds of metals with imidazolines [30,31]. The HOMO for imidazolidine is over nitrogen N5, which is the most reactive site of this molecule but presenting a higher steric effect; this could explain its almost null interaction with the metal surface.

To obtain more information about the local chemical reactivity of these molecules, a study of Fukui indices was carried out. These indices were calculated from the optimized geometry of the neutral molecules by means of the subtraction of one electron, \( N - 1 \). The results are shown in Table 4. Here, it is observed that for amide the Fukui indices of the nitrogen N5 is more reactive than N8, in agreement with its HOMO obtained value. The Fukui indices for nitrogen N2 and N5 of imidazoline are very similar. This seems to indicate that both atoms are

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge distribution</th>
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<tr>
<td></td>
<td>Amide</td>
</tr>
<tr>
<td>N2</td>
<td>-0.640</td>
</tr>
<tr>
<td>N5</td>
<td>-0.684</td>
</tr>
<tr>
<td>N8</td>
<td>-0.845</td>
</tr>
<tr>
<td>O</td>
<td>-0.644</td>
</tr>
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Table 3
Charge distribution for amide, imidazoline and imidazolidine
involved in the chemical reactivity of this molecule with the metal surface, while the N8 atom seems not to participate in the reactivity, because its Fukui index was only of +0.09. These results also agree with the HOMO of this molecule (Fig. 8). Finally, imidazolidine showed only one reaction site, localized on the nitrogen atom N5, with a Fukui index of +0.477, but this atom presents a higher steric effect, as is observed in the optimized molecule (Fig. 7).

All possible protonated forms from the three organic compounds studied, amide, imidazoline and imidazolidine, have been calculated, the more stable being the molecules shown in Fig. 7. It can be noted from this figure that the molecular structure of the protonated form of imidazoline is very similar to the neutral form. For instance, the bond-length C1–N2 takes values of 1.28 Å for the neutral form against 1.32 Å for protonated imidazoline. With respect to the bond-length C1–N5, its value changes from 1.47 for the neutral to 1.32 Å for the protonated form. These values seem to indicate that a delocalization of \( p \)-electrons can take place in the N2–C1–N5 bond. This means that the N2–C1–N5 bond is of \( p-\pi \) conjugation action between the \( p \)-orbital of the N2 atom and \( \pi \)-MO of the C1–N5 bond. The theoretical calculations show that the molecular orbital HOMO of the protonated form of imidazoline can be localized on the N2–C1–N5 system. Owing to delocalization, the \( \pi \)-electron is easily translated to an Fe atom and is more favorable for chemical adsorption of the N atom on the metal surface.

Moreover, the imidazoline ring lies parallel to the electrode, in a planar form, which means that the other bond lengths, as well as angles, remain unchanged.

DFT analysis of protonated imidazoline shows that nitrogen atoms have charge density values between \(-0.45\) and \(-0.58\), showing that these atoms can play an important role in the adsorption process of the molecule with the metal surface, due to the fact that the molecules exhibit a high electronic density and thus form organic cations in acid environments.

The molecular structure of imidazoline remains unchanged, whereas for the case of amide, the formation of an intramolecular hydrogen bridge N5–H–O confers to the structure a greater degree of stability.

The molecular orbital for the amide is demonstrated to be very important, because it is mainly localized over the N–C=O system. Thus this site is more favorable for the interaction between the molecule and the metal surface. However, the reactivity of amide should be chemically lower than that for the imidazoline, due to steric factors. The linear structure of amide, Fig. 7, make it possible that hydrogen atoms can block the interaction of the active sites of the molecule with the metal surface.

The molecular structure of protonated imidazolidine remains unchanged with respect to its neutral form, the two N atoms on the ring remaining strongly blocked.

The only site for interaction could be the tertiary N atom, but as has been demonstrated previously with the Fukui analysis of the neutral compound, this atom does not participate in the chemical reactivity.

From the theoretical calculations carried out with both neutral and protonated forms of amide, imidazoline and imidazolidine, it can be concluded that the structural and electronic properties of these molecules are very similar. Consequently, theoretical calculations with only the neutral form of these molecules could be a good approach for the study of their potential inhibition capability for metal corrosion in acidic environments.

### 5. Conclusions

The relative inhibition efficiencies of the three compounds studied, including their protonated forms, in a deaerated 0.5 M HCl solution is found to be in the following order: imidazoline \( \gg \) amide \( \gg \) imidazolidine. With respect to imidazolidine, this compound showed a very low corrosion inhibition efficiency at high concentrations, being able to promote the corrosion even at low concentrations.

The electrochemical techniques of EIS and Tafel extrapolation provided consistent results during the evaluation.

The EIS data provided additional information with regard to the protective nature of the inhibitor film.

The reasons for which imidazoline was the better corrosion inhibitor are, among others, the plane geometry of the heterocyclic ring, thus favoring adsorption through the double iminic bond N=\( \rightarrow \)C. The iminic nitrogen seems to be directly involved in the coordination of the cycle with the metal surface.

The experimental results could be corroborated with that obtained by means of the first principles theoretical calculations using the computational methodologies of quantum chemistry, showing an electronic density more important on the iminic nitrogen N2 in the imidazoline, with respect to the analogous nitrogen in amide and imidazolidine. The inhibitor efficiencies of these compounds seem to be determined by the conjugation of electronic factors and molecular geometry.
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