DFT and Electrochemical Studies: N,N',N'',N'''-tetrakis(2methylpyridyl)-1,4,8,11-tetraazacyclotetradecane (TMPC) as an Efficient Corrosion Inhibitor for Carbon Steel Surfaces in an Acid medium

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The corrosion inhibition of N,N',N",N"'-tetrakis(2-methylpyridyl)-1,4,8,11-tetraazacyclotetradecane (TMPC) was analyzed by electrochemical and theoretical methods. Electrochemical data show that TMPC forms an adsorption layer over an iron surface that obeys the Langmuir isotherm (ΔG°_{ads} of - 32.96 kJ mol⁻¹). Furthermore, the value is higher than -20 kJ mol⁻¹ but less than -40 kJ mol⁻¹, thus it is classified as a conversion stage of physical adsorption to chemical adsorption or a comprehensive adsorption. Furthermore, the fractal dimension of the electrode surface, estimated by an impedance depression angle of a semicircle, shows that the surface is homogeneously covered by the formation of an inhibitor film. The DFT results show that TMPC possesses corrosion inhibition properties that give up its p orbital electron density through its HOMO orbital to the metal LUMO to form an adsorption layer.

Keywords: pyridine, corrosion inhibition, DFT, impedance, carbon steel.

1. INTRODUCTION

The study of corrosion inhibition based on organic compounds containing hetero atoms (N, O, S) is of growing interest in the field of corrosion and industrial chemistries since the molecules having these atoms show promising results for corrosion inhibition. To discover a corrosion inhibitor that exhibits a greater stability in forming a protect-film over an iron metal surface with its smaller quantity in the corrosive medium is a challenging problem in the steel industry because the corrosion on mild steel surfaces affects long-term industrial projects[1-11]. However, the stability of the inhibitor film formed over the metal surface depends on some physico-chemical properties of the molecule related to its functional groups, aromaticity, possible steric effects, the electronic density of donors, the type of the corrosive medium and the nature of the interaction between the π -orbital of inhibitors and the dorbital of iron [2-4, 12-14].



Figure 1. N, N', N'', N'''-tetrakis(2-methylpyridyl)-1,4,8,11- tetraazacyclotetra- decane (TMPC)

To analyze the characteristics of an inhibitor/surface mechanism and to describe the structural nature of the inhibitor on the corrosion process, Density Functional Theory (DFT) was used [15-26]. In addition, DFT is considered a very useful theoretical method to probe the inhibitor /surface interaction as well as to analyze experimental data. In previous studies[27-30], compounds containing benzimidazole / imidazole groups have been shown to be competent corrosion inhibitors in an acid

medium, accounting for their applicability in the petroleum industry, mostly in boiler cleaning and heat exchangers[1-3, 11, 31-33].

Several metal complexes of tetra-aza macrocycles with pendent arms on the nitrogen atoms have been studied as they often showed an efficient coordination ligand to form metal complexes [34-37]: furthermore, the macrocyclic compounds containing N-pyridyl group is believed to be a efficient coordinator for the metal surface because the pyridyl groups in addition to macrocyclic nitrogen donors [38-44] can potentially bind with metal surface. In the process of the searching for an inhibitor, we intend to study the corrosion inhibition behaviors of N,N',N"',N"'-tetrakis(2-methylpyridyl)-1,4,8,11-tetraazacyclotetradecane (TMPC) (Fig.1) by using experimental and theoretical methods; the ligand possesses four pyridyl groups connected to a tetraaza-macrocycle ring. Since the pyridyl group of the ligand is an efficient π acceptor and a good σ - donor, it is expected that TMPC could create a strong binding with metals^[45] in an acidic medium. Thus, the present study deals with the corrosion N,N',N"'.tetrakis-(2-methylpyridyl)-1,4,8,11-tetraazacyclotetradecane inhibition behavior of (TMPC) by employing electrochemical techniques. Electrochemical polarization curves were used to determine the intensity of the corrosion over a steel surface, specifically to see the effectiveness of the anodic and cathodic reactions in the corrosive medium having TMPC; besides, the performance of an electrochemical double layer was analyzed by electrochemical faradaic impedance spectroscopy to determine the double layer capacitance and the time constant; these parameters are essential in the modification of a fractal surface. DFT was also employed to analyze the structural and electronic properties of TMPC neutral and protonated structures in the gaseous state and in the aqueous medium with PCM method.

2. EXPERIMENTAL PROCEDURE

2.1 Chemicals

The reagents were used as received: Acetic anhydride (Fluka), ethylenediamine, benzene, magnesium powder, ethyl acetate, methyl iodide (Aldrich).

2.2 Physical Measurements

Elemental analyses were carried out on a Fisons (Model EA 1108 CHNSO), Faculty of Chemistry, UNAM, Mexico. The NMR spectra at room temperature on a Varian (300 MHz) spectrometer were measured, using tetramethylsilane (TMS) as an internal standard.

2.3 Synthesis of TMPC

This ligand was prepared by applying the procedure reported elsewhere [46, 47]. The spectral data and elemental analysis of the compound coincide with the reported values: Anal. Calcd. for

 $C_{34}H_{44}N_8$ (%): C, 72.3; H, 7.8; N, 19.8. Found: C, 72.4; H, 8.1; N, 20.0. ¹H (CDCl₃-TMS) NMR (in ppm): (s: singlet, d: doublet, t: triplet, q: quintet) 1.90 (4H, q), 2.61 (8H, t), 2.90 (8H, s), 3.90 (8H, t) 7.19 (4H, t), 7.54 (4H, d) 7.65 (4H, t), 8.52 (4H, d), and ¹³C (CDCl₃) NMR: 23.55, 50.60, 51.57, 59.21, 122.84, 124.36, 136.85, 149.11, 156.76.

2.4 Electrochemical Procedure

A standard electrochemical Princeton Applied Research cell (1.0 L) was assembled with a carbon steel working electrode (WE) and two graphite counter electrodes (CE); a saturated calomel electrode (SCE) was used as the reference electrode in the experiment. The carbon steel working electrode (WE) was a flat specimen with an exposure area of 1.0 cm², which was abraded with using different grades of emery paper (120-1200). The specimens had to be degreased with acetone and then washed with bi-distilled water to avoid carbon pollution. The composition of the carbon steel (AISI 1018 normalized) was: wt%: 0.18 C, 0.35 Mn, 0.17 Si, 0.025 S, 0.03 P and the remaining composition content was Fe. The cell was connected to a Solartron 1287 interface coupled Frequency Response Analyzer (FRA, Solartron 1260), which was controlled by CorrWare and Zplot software. The aggressive HCl medium (0.5M) was first purged with nitrogen gas for 45 min to eliminate any dissolved oxygen in the medium. The electrochemical tests were carried out at room temperature $(298^{\circ}\pm 2)$ K under static conditions. All the experiments were performed after dipping the working electrode into HCl (0.5 M) containing different concentration of the inhibitor (0.05, 0.1, 1.0, 2.0, 4.0 mmol) dissolved in ethanol at the open-circuit potential, E_{corr} , with respect to the SCE reference electrode. Three independent experiments having been carried out for each concentration, the data were collected. For our experimental concentrations, the corrosion data are reproduced.

The same arrangement was employed for both electrochemical polarization curves and impedance faradaic spectroscopy. In order to apply the electrochemical Tafel extrapolation, polarization curves were recorded by the potential-dynamical method at a rate of 1.0 mV/s from -300 mV to + 300 mV versus the open circuit potential; the scan rate was 1.0 mV/s. The published method[28, 48-52] that suited for our experiments was employed (carbon steel in HCl medium) for our corrosion inhibition studies. Electrochemical impedance spectroscopy (EIS) was recorded between 10 kHz and 10 mHz, with a 15 mV peak-to-peak perturbation. All the electrochemical experiments were carried out for three times for the consistency of the results and the standard deviation was less than 3.0% ; additionally, a time interval of one hour was given between each EIS experiment without any external perturbation. Furthermore, the working electrode was immersed in the acid medium and waited for 20 min. and then the impedance data were measured during 6 hours.

2.5 Computational Procedure

Theoretical calculations were carried out for TMPC (Fig. 1) by a Gaussian-09 program [53] and the exchange-correlation was treated using PBE hybrid functional [54-56] (PBE is also known as PBE0 or PBE1PBE). The 6-311G** orbital basis sets were employed for all atoms. A full optimization

was performed for the molecule and the total structure optimization, together with the vibrational analysis of the optimized structures, was derived in order to determine whether they corresponded to a maximum or a minimum in the potential energy curve. The structural and electronic parameters of TMPC were calculated by the same method. For the molecular structures, the nucleophilic or electrophilic sites where an electron transfer reaction occurs with metallic surfaces were localized by applying the Hirshfeld charge data and an electrostatic potential map. Furthermore, the molecular orbitals (HOMO-1 HOMO and LUMO) of the inhibitors were analyzed in order to predict the behavior of corrosion inhibition. All the geometries were optimized using PBE/6-311++G** in the aqueous medium (a dielectric constant $\varepsilon = 78.39$) by means of PCM method [57].

3. RESULTS AND DISCUSSION

3.1 Electrochemical analysis of corrosion inhibition



Figure 2. Potentiodynamic polarization curves of mild steel in 0.5 M HCl in absence and presence of different concentrations of inhibitor.

The electrochemical inhibition properties of TMPC were analyzed by the polarization Tafel extrapolation and Faradaic impedance spectroscopy [1-3, 31, 32]. The polarization experiments were carried at different concentrations of TMPC in order to estimate the corrosion rate on the electrode surface. The polarization curves were analyzed by using a CorrView program, the Tafel slopes were then obtained by applying the Tafel extrapolation analysis. The data show that in the presence of the inhibitor, the polarization current decreased considerably, i.e. the intensity of corrosion decreased. For instance, for the curve before the addition of TMPC to the corrosive medium (at 0.0 mmol), the current

density was 1.28×10^{-3} A/cm², while the current density was considerably reduced to 6.45×10^{-4} A/cm² after the addition of TMPC (0.05 mmol); it was observed that the current density decreased in both cathodic and anodic branches (Fig. 2); this shows that TMPC performed as a mixed inhibitor. Furthermore, it is also seen that there is a considerable difference in the behaviors of the cathodic and anodic branches. For example the cathodic branches obey to typical Tafel behavior, making an accurate evaluation of the cathodic Tafel slope (β_c) and also corrosion currents (i_{corr}) by the Tafel extrapolation method. However, in the case of the anodic polarization segment, the slope of curves was increased with the increasing concentration of inhibitor until -0.35 V vs. SCE, thus Tafel analysis sometimes was not considered for the whole anodic Tafel range. This is corroborated with the EIS interpretation. This anodic behavior is probably attributed to the deposition of the corrosion products or impurities in the metal surface (e.g., Fe₃C) to form a non-passive surface film[58, 59]. This is consistent with the Likhanova et al. [11] report that the adsorption of corrosion products (iron sulphates such as melanterite, rosenite, szomolnokite and oxyhydroxides as goethite) could influence the anodic polarization curve behavior.

 Table 1. Corrosion Inhibition data of TMPC at Different Concentration over Carbon Steel in HCl (0.5 M)

Concentrations	E_{corr} *	${eta_{\mathrm{a}}}^{*}$	${eta_{ m c}}^*$	Icorr	CR	θ	% <i>E</i>
(mmol)	(mV vs	(mV	(mV	$(A \text{ cm}^{-2})$	(mm/yea		
	SCE)	dec^{-1}	dec^{-1})		r)		
0.0	-535	194	-137	$1.28 \text{ x} 10^{-3}$	14.78	0.0	0.0
0.05	-558	235	-115	6.45 x10 ⁻⁴	7.49	0.49	49
0.1	-557	322	-191	4.36 x10 ⁻⁴	5.06	0.65	65
1.0	-554	233	-121	3.40 x10 ⁻⁴	3.95	0.73	73
2.0	-521	138	-96	1.97 x10 ⁻⁴	2.28	0.84	84
4.0	-534	148	-86	1.52 x10-4	1.76	0.88	88

Note: *All the electrode potential are relative to SCE; β_a = Tafel slope of anodic polarization curve; β_c = Tafel slope of cathodic polarization curve; $\& \varepsilon$ = efficiency of corrosion inhibition; E_{corr} = Corrosion potential; I_{corr} = Corrosion current densities. θ = the degree of inhibitor coating; CR = corrosion rate

The corrosion rates (Table 1) were measured after the metal surface was exposed to the corrosive medium for 6.0 hours in the presence of TMPC at different concentrations, verifying that with the increasing inhibitor concentration, the corrosion rate continuously decreased; particularly, the corrosion potential did not change significantly. This indicates that the mechanism of corrosion inhibition on the metal surface merely presented an adsorption phenomenon that hampered both anodic and cathodic reactions. The polarization curve perturbs the system substantially above 220 mV that is why the dc technique was applied after studying the performance of the inhibitor by the EIS experiments which are considered as a non-destructive method.

The degree of inhibitor coating over the metal surface at different concentrations, which is directly related to the efficiency of the inhibitor (ε) [50, 60] was determined as follows:

$$\theta = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \tag{1}$$

$$\%\varepsilon = \theta \times 100$$

 θ = the degree of inhibitor coating over the metalic surface; i_{corr} = the corrosion current densities without the inhibitor and $i_{corr(inh)}$ = the rate of corrosion current densities with the inhibitor. Since the corrosion rate (t) is directly proportional to the value of the corrosion current density, the inhibition efficiency, was evaluated from the measured i_{corr} values using the relationship from the Tafel analysis.

(2)



Figure 3. Adsorption isotherms of inhibitor on mild steel surface in 0.5 M HCl.; a) Langmuir adsorption isotherm plot; b) Temkin adsorption isotherm plot

b

Moreover, it was found that the adsorption process of TMPC on the metal surface followed the Langmuir isotherm model [60, 61], yielding a straight line for the plot of C_{inh}/θ vs. C_{inh} (Fig. 3).

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{3}$$

In the present work, the Langmuir adsorption isotherm model indicates that the TMPC molecule interacts significantly with the metallic surface to form an inhibitor film over the iron surface that corresponds to a single layer[62], where the interaction between adsorbed inhibitor molecules is insignificant. In addition, with this model (Langmuir isotherm adsorption is better than Temkin isotherm plot), the Gibbs free energy (ΔG°_{ads}) which can be used to describe the stability of the adsorption bond between TMPC and the metal, was determined by using K_{ads} in the following equation.

$$\Delta G_{ads}^0 = -RT \ln \left(55.5 \, K_{ads} \right) \tag{4}$$

The ΔG°_{ads} value obtained for the adsorption of inhibitor was -32.96 kJ mol⁻¹, indicating that a strong bond was formed between TMPC and the metal through a chemisorption. Generally, if the ΔG°_{ads} value turns out to be around -20.0 kJ mol⁻¹, the ligand-metal interaction is classified as physisorption, i.e., there is an electrostatic interaction of the inhibitor molecule with the metal surface; on the other hand, if the ΔG°_{ads} is around -40.0 kJ mol⁻¹ or above, there are present chemisorptions between the ligand and the metal, where a covalent bond is formed between the donor atom of the inhibitor and iron [63]. The ΔG°_{ads} value yields a negative parameter and it suggests the inhibitor molecule spontaneously adsorbs over the metal surface. Furthermore, the adsorption behavior of inhibitor generally depend on the value of ΔG°_{ads} ; if the value is up to -20 kJ mol⁻¹, it can be classified as an electrostatic interaction between electron donator (inhibitor) and electron acceptor (metal (physical adsorption). In case, the value is more negative than -40 kJ mol⁻¹, then it is characterized as a charge sharing or charge transfer from the inhibitor molecules to the metal surface, i.e., coordinate type of bond (chemical adsorption) [64, 65]. In the present work, the calculated ΔG°_{ads} value is higher than -20 kJ mol⁻¹ but less than -40 kJ mol⁻¹, from the published reports, it is classified as a conversion stage of physical adsorption to chemical adsorption or a comprehensive adsorption.

The impedance diagram (Fig. 4) describes the behavior of the inhibitor at different concentrations in the corrosive medium and it is seen that there is present a single capacitive semicircle corresponding to a one time constant (τ), equivalent to an electric circuit (Fig. 5) of the corrosion process, which is similar to the proposal of many researchers [66, 67]. Besides, the previously published papers[48-52] clearly establish the presence of one time constant for the inhibitor in the HCl as a corrosive medium; moreover, the phase angle (Fig. 4b) of the impedance diagrams clearly indicate the existence of one time constant despite the straight lines (Fig. 4c) were obtained in the zoom at high frequency zone of the Nyquist plots. In the electric circuit, the constant phase element (CPE)

represents the electrochemical metal interface corresponding to the solution resistance (R_s) while R_t represents the resistance transfer. The CPE is determined by the following equation[68, 69]:

$$\frac{1}{Z_{(cpe)}} = Q(j\omega)^n \tag{5}$$

Z(cpe) = the impedance of CPE; Q corresponds to a proportionality factor, j is $(-1)^{\frac{1}{2}}$; ω = the angular frequency, n = surface irregularity estimation [31, 32, 69].



Figure 4. Electrochemical studies of corrosion inhibition for mild steel in 0.5 M HCl in absence and presence of different concentrations of inhibitor ; a) Nyquist plots; b) Bode plots; c) Zoom at high frequency zone of Nyquist plot



Figure 5. Simple equivalent circuit of a rough electrode.

The CPE is considered to be a surface irregularity of the electrode[70] causing a depression in the Nyquist semicircle diagram for the presence of the inhibitor in the corrosive medium (Fig. 4) [71]; hence, we could not conclude that the metal solution interface performs as a capacitor, in which case, the metal surface should be flat and homogeneous. If the electrode surface is considered homogeneous and plane, the exponential value (n) becomes equal to 1.0 and the metal-solution interface acts as a capacitor with a regular surface. The time constant (τ) and the capacitance value (C) of the CPE can be calculated by the following equations [72, 73].

$$Q = \frac{\tau^n}{Rp}$$

$$C = (QRp^{1-n})^{\frac{1}{n}}$$
(6)
(7)

 τ = the time constant, C = the capacitance of double layer associated with one CPE.

The low frequency region is originated from the adsorption relaxation of intermediates[74]. The depressed nature of the semicircle which is a characteristic for electrode/solution interface is also related with the roughness of electrode surface[75]. Furthermore, with the increase of the inhibitor concentration, the size of the semicircle was increased, indicating the presence of the corrosion inhibition process. Additionally, in the presence of inhibitor TMPC, the characteristic of the impedance plots does not considerably different from those of the electrodes without inhibitor, it means that the inhibitor presence increases the impedance without changing other aspects of the behavior. This observation agrees with the polarization measurements where the inhibitor does not involve the electrochemical reactions responsible for corrosion, suggesting that the corrosion inhibition occurs primarily through its adsorption on the metal surface.

What is more, by using the depression angle of the impedance semicircle of the impedance diagram, the fractal dimension of the electrode surface can also be estimated [71, 76, 77] with the following equation:

$$n = \frac{1}{Ds - 1} \tag{8}$$

 D_s = a fractal dimension of metallic surface

The fractal dimension (D_s) parameter of the metallic surface is around 2.0 or smaller than 3.0. Generally, if the D_s value decreases to around 2.0, this indicates that the metal surface is plane and homogeneous; otherwise, if the value is lower than 3.0, it indicates that the metal surface is crumpled, rough or wrinkled. Since Gasparovic [78] described the surface of the electrode by using the fractal geometry, this technique was employed as a powerful tool to study the organic molecule adsorption over the metal surface.



Figure 6. Resistance variations (R_t) of charge transfer over 6 hours at different concentrations of TMPC inhibitor.

Fig 6 shows the behavior of resistance transfer (R_t) at different concentrations of inhibitor during a period of 6.0 hours. It was clearly observed that the resistance was a minimum value in the absence of TMPC in the corrosive medium, i.e., the speed of corrosion is high on the metal surface without the inhibitor in the solution. However, in the presence of the inhibitor in the solution, the R_t value increased steadily, suggesting that TMPC forms a protective layer over the metal surface immediately, becoming stabilized in a period time of two hours; this is in agreement with the results obtained from the polarization curves.

The behavior of resistance transfer (R_t) led to a study of the performance of the double layer caused by CPE. The electrochemical capacitance values of the double layer was therefore plotted

against time over a period of 6.0 hours (Fig. 7), showing that the capacitance was maximum in the absence of the inhibitor and it steeply decreased in the presence of the inhibitor until its concentration reached to 1.0 mmol with an inhibition efficiency of 80%, indicating that the electrode surface was in the main, completely covered by an inhibitor film. After this concentration, there was an increase in the capacitance value, thus indicating that at the higher concentration, i.e. after the inhibition efficiency of 80%, the electrode surface underwent a major change.



Figure 7. Variation of electrochemical double layer capacity (C) over 6.0 hours at different concentrations of TMPC inhibitor.



Figure 8. Variation of time constant value (τ) over 6 hours at at different concentrations of TMPC inhibitor.

The plot of the time constant (τ) against time, over a period of 6.0 hours (Fig. 8), shows that there was a continuous decrease in the speed of the loading and unloading of the capacitor when the inhibitor (TMPC) concentration was increased, indicating that since the τ value was high, the charge transfer of electrochemical corrosion reaction was continuously delayed. The time constant (τ) was observed in both the absence and the presence of the inhibitor; the value was 0.025 seconds when the concentration of TMPC was 1.0 mM in the solution; when the inhibitor concentration was increased to 2.0 and 4.0 mM, the time constant value substantially also increased to 0.08 s, illustrating that at high concentrations with the efficiency of inhibition (80%), the amount of charge increased in the electrochemical interfaces with the decrease of the speed of charge transformations; thus, the speed of the corrosion inhibition decreases at high inhibitor concentrations. In the surface fractal dimension (D_f) studies (Fig. 9), it is seen that in the absence of TMPC in the solution, the fractal dimension of electrode exhibits a low value, illustrating that the metallic surface is homogeneously plane.



Figure 9. Variation of fractal dimension of electrode surface (D_s) over 6.0 hours at different concentrations of TMPC inhibitor.

This is entirely logical because on a rough surface, the surface peaks are high-energy points which preferably dissolve into the solution to yield a more homogeneous surface. In the presence of TMPC in the solution, a high fractal dimension (D_f) value was obtained; however, with the increase of the concentration of inhibitor, the surface was expected to be homogeneously covered by the inhibitor film. At the inhibitor concentration between 2.0 and 4 mmol, there was a decrease in the values of D_f , clearly indicating that the inhibitor film uniformity decreases; however, the D_f value was always higher than those reported in the absence of the inhibitor. This can be explained by stating that at the high concentration, the interaction of the inhibitor molecule with the other molecules is large; in this case, the metal surface is not homogenously covered and a non-homogeneous surface film is obtained. All these observations are consistent with the results observed in the polarization curves and the impedance technique.



Figure 10. Optimization geometrical parameters of TMPC with PBE/6-31G**: a) the neutral and the protonated structures in the gaseous state; b) the neutral and the protonated structure in the aqueous medium (dielectric constant $\varepsilon = 78.39$) using PBE/6-311++G**, employed with the PCM method; c) the neutral and the second protonated structure in gaseous state.

DFT analysis of inhibitors: Structural and Electronic Properties:- The structural and electronic properties of TMPC and its protonated structures were analyzed. The results show that there is a strong effect on the chemical properties, specifically in the electron-donating capability to the metal. The calculated bond distances (N-C) in pyridyl and in tetraaza ring are in good agreement with the experimental values[44] (Fig. 10 a, b, c). For instance, the bond distance of N1-C2 (aza ring) is 1.47 Å in the neutral structure, indicating that there is single bond between those atoms, while for N17-C16, the equilibrium distance (1.35 Å) implies that there is formation of a localized double bond that has C16 in sp² hybridization. These structural parameters suggest that the pyridyl ring possesses a relatively high electron density, which is available for donation to another species. This observation is in good agreement with previously reported papers [27]. In the structures (Fig. 10a,b,c), both N1-C2 and N1-C14 bonds have equal lengths (1.47 Å) and the C3-C4/C12-C13 distance falls to around 1.53-1.54 Å, showing that the carbons are in a typical sp³ hybridization.





Figure 11. Molecular orbitals (LUMO, HOMO and HOMO-1) of TMPC and their energy levels with respect to HOMO at gaseous state: a) TMPC, TMPCN17H⁺ and TMPCN17N17'H₂²⁺; b) TMPC,TMPCN1H⁺ and TMPCN1N4H₂²⁺; c) TMPC, TMPCN1H⁺ and TMPCN17H⁺; d) TMPC, TMPCN1H⁺ and TMPCN17H⁺ using PBE/6-311++G** in the aqueous medium (dielectric constant $\varepsilon = 78.39$) using PCM method.

Besides, there are two forms of pronotonation, namely amine or pyridyl nitrogens; however, the first protonation occurs preferably at pyridyl nitrogen since it stabilizes more than that at amine nitrogen. The theoretical data show that for TMPC (Fig. 10), a more stable structure was obtained when the protonation occurred at nitrogen and the resulting energy difference between TMPCN1H⁺

and TMPCN7H⁺ moieties was 10.38 kJ mol⁻¹ in the gaseous state; for the second proton addition at the molecule, particularly at N4, the energy difference between the two isomers decreased to 5.07 kJ mol⁻¹ in the gaseous state (Fig.11), showing that the second proton addition prefers amine nitrogens to the pyridyl nitrogen. Hirshfeld charges (see Suppl. Table S2) and the structural parameters show that moiety of both nitrogens (pyridyl and amine) have excess electron densities, compared with the other atoms, suggesting that both nitrogens act as nucleophiles because of a small charge density difference between the nitrogens. On the other hand, the excess electron densities over the nitrogens [(N17) -0.2488 and (N1) -0.0696] was detected, showing that the pyridine nitrogen has more electron density than the tertiary nitrogen and the double bond (C16=N17) delocalizes by the overlapping of its σ orbital with the π orbital of N17 to form a delocalization region in the pyridyl ring that has the ability to transmit the electron clouds toward the metallic center. The pyridyl protonated structure gives up the electron density (C=N) through its HOMO orbital to the metal LUMO, leading to an adsorption phenomenon on the metallic surface (Table 11 a, b, c, d). This proposal is consistent with the report [4, 29] that the occupied molecular orbitals of the aromatic derivatives are involved in the chemisorption reaction with the metallic orbitals and the adsorption efficiency depends on how the ligand molecular occupied orbitals overlaps with the unoccupied metal orbitals. For effective overlapping, the energy difference between the orbitals generally must be low; in this case, the overall energy difference between the orbitals (HOMO and HOMO -1) is 0.44 eV for TMPC (Fig. 11 a, b, c, d), showing that the energy difference decreased for the protonated structures.

4. CONCLUSION

1. Compound TMPC turns out to be a good corrosion inhibitor for the steel iron surface in an acid medium at high concentrations, forming an adsorption film over metallic surface, observing that the adsorption model follows the Langmuir isotherm with $\Delta G^{\circ}_{ads} = -32.96 \text{ kJ mol}^{-1}$.

2. The charge capacity of the double layer is maximum in the absence of the inhibitor and it decreases in its presence, thus suggesting that there is a continuous decrease in the speed of the loading and unloading of the capacitor when the inhibitor (TMPC) concentration is increased, there is an indication that since the τ value is high, the charge transfer of electrochemical corrosion reaction is continuously delayed.

3. In the surface fractal dimension (D_s) studies, it is observed that in the presence of the inhibitor TMPC, a high fractal dimension (D_s) value is obtained, suggesting that the organic material is present on the metal surface.

4. The structural, electronic and molecular parameters suggest that the molecule gives up the electron density (C=N) through its HOMO orbital to the metal LUMO, forming adsorption over the metallic surface.

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