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Benzimidazole ligands in the corrosion inhibition for carbon steel in acid medium: DFT study of its interaction on Fe₃₀ surface

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Abstract

The corrosion inhibition of N,N'-bis(benzimidazole-2-yl-methyl)amine (L¹) and N, N'-bis(benzimidazole-2-yl-methyl)hydroxyethylamine (L^2) was analyzed by electrochemical and theoretical methods. The data show that ligands form an adsorption layer over an iron surface, obeying the Langmuir isotherm ($\Delta G^{\circ}ads$ of -32.96 kJ mol⁻¹); the value are higher than -20 kJ mol⁻¹ but less than -40 kJ mol⁻¹, belonging to a conversion stage of physical adsorption to chemical adsorption or a comprehensive adsorption. This is consistent with the fractal dimension of the electrode surface, estimated by an impedance depression angle of a semicircle that the surface is homogeneously covered by the formation of an inhibitor film. Furthermore, the electronic parameters of the ligands were analyzed by DFT, showing that L^1 and L^2 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, and this has been proved theoretically by the interaction of ligands with Fe₃₀. In addition, we have collected corrosion inhibition data for around 70 organic compounds reported in the literature, and the inhibition data plotted against different inhibitors, showing that amine ligands are good corrosion inhibitors.

Keywords: Corrosion inhibition, benzimidazole, DFT, iron cluster, electrochemical

1. Introduction

Corrosion problems represent a serious problem in industries, especially petroleum industry where acids are being used to stimulate the carbonate reservoir or for dissolving fines. Although acids such as hydrochloric, hydrofluoric, acetic, or formic acids are common to be injected into the well during the acidizing stimulation process, mostly HCl at concentrations of 5–28% is being employed in acidizing treatments [1] because sulphate, nitrate, and phosphate salts have lower solubility than chlorides in aqueous media [2]. Thus the corrosion problem in the industries is unavoidable, and the general Corrosion rate is extremely high (>100 mm/y) and it can increase exponentially with increasing temperatures and acid concentrations[3]. To control the corrosion damage of well tubulars, mixing tanks, coiled tubings, and other metallic surfaces, the corrosion process need to be inhibited by the use of an effective corrosion inhibitor[4, 5]. The study of corrosion inhibition of mild steel using organic inhibitors mainly in acidic media is one of the most important subjects in the current industrial research [6-8]. It is common to use organic compounds having π -electrons and hetero-atoms like nitrogen, sulfur, and oxygen as inhibitors in order to impart resistance towards the aggressive [9-12] and they can interact to get adsorbed on to the metal surface [13-15]. The efficiency and suitability of the inhibitors are mainly depend on the nature and surface charge on metal, the type of aggressive electrolyte and the chemical structure of inhibitor. Most of these inhibitors possesses at least one functional group which is considered to be the reaction centre for the adsorption process as the relationship between the inhibitive properties and the their molecular structures is crucial for the corrosion inhibition efficiency. Sometimes, one inhibitor works in one well may not suitable in another well [16] because the mechanism of the inhibition is usually not known, in spite of some proposed models for forecasting corrosion inhibition[17-19]. Thus, there is a great need to investigate the influence of substituent on the inhibitive performance inhibitors; for example, long chain organic compounds are believed to be stronger corrosion inhibitors due to the good hydrophobicity, but they are also poor watersolubility.

In the context, several following compounds were tested as corrosion inhibitors: benzoin and benzil compounds [20]; sodium N-alkylphthalamates (alkyl = $n-C_6H_{13}$, $n-C_{10}H_{21}$, $n-C_{14}H_{29}$)[21]; tributylamine, some alcohols, aniline, n-octylamine,

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diphenylamine, dodecylamine, di-n-butylamine, cyclohexylamine, and 1,3-dibutyl-2-thiourea [4]; furfuryl alcohol[22]; octyl alcohol and propargyl alcohol[23]; 2butyn-1-ol, 3-butyn-1-ol, 3-pentyn-1-ol, and 4-pentyn-1-ol[24]; benzimidazole, 2aminobenzimidazole, 2-mercaptobenzimidazole, 1-benzylbenzimidazol, and 1,2dibenzylbenzimidazole and different azole [25]; 3-(4-amino-2-methyl-5-pyrimidyl methyl)-4-methylthiazoliumchloride[26]; $2-(alkyl(C_nH_{n+1})dimethylamonio)butanol$ bromides (n = 11-15) [27]; 1-(2-pyridylazo)-2-naphthol[28]; 1-(2-ethylamino)-2methylimidazoline-N-[3-(2-aminoethylaminoethyl)]-acetamide, 1-(2and ethylamino)-2-methylimi[29]; pyridoin and 2,20-pyridil [28]; and 1-1,10-dicinnamylidine-3cinnamylidine-3-thiocarbohydrazide and thiocarbohydrazide[30].

Although the above compounds were studied for the corrosion inhibition, The benzimidazole containing inhibitors could be effective due to the following properties: (i) its hydrophobic nature, (ii) the planarity of benzimidazole moiety; (iii) delocalized π - electrons in the aromatic ring, (iv) hetero-atoms like nitrogen. In previous studies [31-34], compounds containing benzimidazole/imidazole groups have been shown as competent corrosion inhibitors in acid medium [3-5, 22-25]. Thus, in this paper, we evaluate the inhibition effectiveness of N,N'-bis(benzimidazole-2-yl-methyl)amine and N, N'-bis(benzimidazole-2-yl-methyl)-hydroxyethylamine on the corrosion of mild steel in 0.5 M HCl solution; to analyze their structural nature for the corrosion inhibition, the interaction studies with different metal clusters Fe₁₅, Fe₁₆ and Fe₃₀ is performed by DFT which has been proved as an efficient theoretical method to probe the inhibitor /surface interaction.

2. Experimental Section

2.1 Synthesis of ligands

The ligand has been prepared as reported elwhere indicated in literature [35-37].

N,N-bis(benzimidazole-2-yl-methyl)amine (L^1): Iminodiacetic acid (13.6 g 100 mM) and 1,2-phenylenediamine (21.6 g, 200 mM) were refluxed for 24 hours in 4N HCl (80 mL), the resulting solution was cooled to isolate the hydrochloride of the compound, then it was neutralized using aqueous ammonia. The product obtained was re-crystallized from aqueous methanol. Yield: 72%, M.P 248 ± 2°C. Elemental analysis for C₁₆H₁₅N₅; Calc C 69.30, H 5.45, N.25.30; found: C 69.18; H, 5.32, N. 25.24. MS (IE, m/z %): 275 [M]⁺, 276 [M+1], 132 (100) [C₈H₈N₂]⁺, 118 (8.9) [C₇H₆N₂]⁺, 146 (24.6%) [C₈H₈N₃]⁺: ¹H NMR (300, MHz, CD₃OD): δ = 3.310-4.111 (m, 4H, bzim-CH₂-N.), 4.917 (s, H, -CH₂-NH-CH₂-) and 7.200-7.550 (m, 8H, bzim-rings). ¹³C NMR (300, MHz, CD₃OD): δ = 48.860-49.428 (CH₂-N-) and 123.628-155.124 (bzim-rings).

N,N- bis (benzimidazole-2yl-methyl) hydroxyethylamine (L²): The above procedure was adopted to prepare N,N- bis (benzimidazole-2yl-methyl) hydroxyethylamine (L²) using N-(2-hidroxyethyl) iminodiacetic acid (2.65 g, 15 mmol) and 1,2-phenylenediamine (3.24 g, 30 mmol). Yield: Yield: 87%, M.P 198 \pm 2 °C: Elemental analysis: Calc. (%) for C₁₈H₁₉N₅O'H₂O: C, 63.79; H, 6.19; N, 20.64. Found (%): C 64.27, H 6.43, N 20.64%. MS, (IE, m/z (%)): 322 [M]⁺, 132 (100) [C₈H₈N₂]⁺, 77 (8.5%) [C₃H₉NO]⁺, 160 (42.5%) [C₉H₁₀N₃]⁺. ¹H NMR (300, MHz, CD₃OD): δ = 2.736-4.058 (s, 4H, -N-CH₂-CH₂-OH), 4.930 (m, 4H, bzim-CH₂-N-) and 7.208-7.563 (m, 8H, bzim-rings). ¹³C NMR (300, MHz, CD₃OD): δ = 48.858-49.427 (CH₂-N-), 53.891-60.494 (-CH₂-CH₂-OH) and 123.759-154.180 (bzim-rings).

2.2 Electrochemical Procedure

A standard electrochemical Princeton Applied Research (PARC) cell (1.0 L) assembled by a carbon steel working electrode (WE) and two-graphite counter electrodes (CE), and a saturated calomel electrode (SCE) as the reference electrode, was used in the experiment. The carbon steel working electrode (WE) was a flat specimen with an exposure area of 1.0 cm^2 and then it was mechanically polished using different grades of emery paper (120-1200). The specimens must be degreased with acetone and then washed with bi-distilled water to avoid carbon pollution. The composition of the carbon steel was: w%: 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 Solartron 1280Z controlled through a Computer having CorrWare and Zplot program. The organic inhibitor was added to the aggressive HCl medium (0.5M) which was first purged with nitrogen gas for 45 min to eliminate dissolved oxygen in the medium. The electrochemical tests were carried out at room temperature under static conditions. All the experiments were performed after dipping the working electrode into a HCl (0.5 M) containing the inhibitor at the open-circuit potential, E_{corr}, with respect to a SCE reference electrode. Two independent experiments were carried out for each concentration and the data were collected.

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 -400 mV to + 400 mV versus the open circuit potential; the scan rate (1.0 mV/seg) allows the quasi-stationary state measurements. Electrochemical impedance spectroscopy (EIS) was carried from 20 kHz to 50 mHz, with a 15 mV peak-to-peak.

2.3 Computational details

To study the adsorption mechanism of ligands L^1 and L^2 , the iron surface was modeled with finite cluster of 30 Fe atoms as this contain more than 25 atoms bulk – like form an electronic point of view[38]. The ground state geometry of the cluster was optimized through Born-Oppenheimer Molecular Dynamics (MD) simulations as indicated previously for other metal clusters[39, 40]. To test the accuracy of our methodology, the ground state geometries of two smaller iron clusters Fe₁₅, and Fe₁₆ were optimized[41]. The molecular dynamics were performed for 150 ps with a time step of 1 fs at the DFTB-SCC spin polarized level of theory using the DFTB+ software [42]. Linear cooling of the system was performed from 1200 K to 10 K using the Nosé-Hoover chain thermostat, following the annealing technique. Multiplicity of 49, 51, and 91 were selected for the optimization of the clusters Fe₁₅, Fe₁₆, Fe₃₀, respectively, in order match the experimental magnetic moments[42].

To determine the interaction energy of the Fe_{30} cluster accurately with the inhibitor molecules L¹ and L², multiple configurations for the interaction of Fe_{30} with the inhibitors were determined from Born-Oppenheimer molecular dynamics at the DFTB-SCC spin polarized level of theory. The simulations were run for 50 ps with a time step of 2.0 fs, cooling the system linearly from 600 K to 10 K. Then local optimizations were performed for both systems with a quasi-Newton root search method at the DFT VWN/DZVP/GEN-A2 [43] level of theory using the deMon2k software [44].

In order to understand the reactivity of the ligands, HOMO and LUMO energies, ionization potential, electron affinity, electronegativity, hardness, electrophilicity, electroaccepting and electrodonating powers, Fukui functions, condensed Fukui functions and electrostatic potential of L^1 and L^2 inhibitors were calculated at the DFT B3LYP/cc-pVDZ level of theory using the Gaussian 09^[56] and MultiWFN software [45]. For calculation of condensed Fukui functions Hirshfeld charges were employed to define the atomic electron populations.

3. Results and Discussion

3.1 Corrosion inhibition studies

The electrochemical inhibition properties of N,N'-bis(benzimidazole-2-ylmethyl)amine (L^1) and N,N'-bis(benzimidazole-2-yl-methyl)hidroxyethylamine (L^2) were analyzed by the polarization Tafel extrapolation and Faradaic impedance spectroscopy [9, 10, 46-48]. The polarization experiments were carried at different concentrations of compounds in order to estimate the corrosion rate in the electrode surface. The Tafel extrapolation was applied to determine the rate of corrosion or corrosion inhibition. The data show that in the presence of the inhibitor, the polarization current is considerably decreased, meaning that the intensity of corrosion is decreased. For instance, for the curve before the addition of L^1 or L^2 to the corrosive medium (0.0 mM), the current density was $5.89 \times 10^{-4} \text{ A/cm}^2$, and it was considerably reduced to 2.40×10^{-4} A/cm² for L¹ (0.2 mM), and for L², it was reduced to 1.81×10^{-4} A/cm², observing that the current density is decreased in both cathodic and anodic branches (Fig.1). It shows that the compounds perform as a mixed inhibitor. The corrosion rates (Table 1) were measured after the metal surface exposure to corrosive medium for 4.0 hours in the presence of compounds at different concentrations, manifesting that with the increasing inhibitor concentration, the corrosion rate continuously decreases; particularly, the corrosion potential does not suffer significantly. It indicates that the mechanism of corrosion inhibition in the metal surface is merely presenting an adsorption phenomenon that hampers both anodic and cathodic reactions.



Fig.1. Polarization curves of carbon steel immersed in HCl (0.5 M) at different concentrations: a) L^1 ; b) L^2

Inhibitor L ¹	$\beta a(mV dec^{-1})$	$\beta c(mV dec^{-1})$	Ecorr (V)	Icorr (A/cm ²)	θ	%E
(mM)						
0.0	194	133	-0.5340	5.89x10 ⁻⁴	-	-
0.01	211	135	-0.5284	5.194x10 ⁻⁴	0.1183	11.83
0.03	241	133	-0.5470	3.977x10 ⁻⁴	0.3249	32.49
0.07	229	115	-0.5472	3.577x10 ⁻⁴	0.3928	39.28
0.2	176	91	-0.5433	2.399x10 ⁻⁴	0.5927	59.27
Inhibitor L ²						
0.0	194	133	-0.5340	5.89x10 ⁻⁴	-	-

Table 1. Electrochemical polarization data of the inhibitors

0.01	151	117	-0.5214	3.46x10 ⁻⁴	0.4126 41.26
0.03	153	112	-0.5309	3.29x10 ⁻⁴	0.4415 44.15
0.07	171	119	-0.5332	2.881x10 ⁻⁴	0.5109 51.09
0.2	166	95	-0.5296	1.813x10 ⁻⁴	0.6922 69.22

The degree of inhibitor coating over the metal surface at different concentrations, which is directly related to the efficiency of the inhibitor [49, 50] is determined as follows:

$$\theta = \frac{i_{corr} - i_{corr(inhi)}}{i_{corr}}$$

% $E = \theta x 100$

 θ = degree of inhibitor coating over the metalic surface; i_{corr} = corrosion rate without inhibitor and $i_{corr(inh)}$ = rate of corrosion with inhibitor.

Furthermore, it is found that the adsorption process of L^1 and L^2 over the metal surface follows Langmuir isotherm model [49, 51] with yielding a straight line

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

for the plot of C_{inh}/θ vs. C_{inh} (Fig. 2). The slope of the plot was nearly 1.0,



Fig.2. Adsorption isotherms of inhibitor on mild steel surface in 0.5 M HCl.; a) L1; b) L2

indicating that the L¹ or L² molecule interacts significantly with metallic surface to form an inhibitor film over the iron surface that corresponds to single layer[52]. Furthermore, with using this model (Langmuir isotherm adsorption), the Gibbs free energy (ΔG^{o}_{ads}), which can be used to describe the stability of the adsorption bond between compound and metal, was determined by using K_{ads} in the following equation.

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

Generally, if the ΔG value is resulted 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; otherwise, if the ΔG is around -40.0 kJ mol⁻¹ or above, there is presence of chemisorptions between ligand and metal, 11

where a covalent bond is formed between the donor atom of the inhibitor and iron [53]. The ΔG^{o}_{ads} value resulted for the adsorption of inhibitor (L¹) was -33.75 KJ mol⁻¹ and its adsorption constant was 14887 M⁻¹, indicating that a strong bond formed between L¹ and metal through chemisorption. Similarly, for L², the values were, ΔG^{o}_{ads} = -36.20 KJ mol⁻¹ and adsorption constant= 39988 M⁻¹. This suggests that the ligand L² is stronger than L¹ due to the difference of -2.45 Kj M⁻¹.

The impedance diagram (Fig. 3) describes the behavior of inhibitors at different concentrations in the corrosive medium and it is seen that there is present a single capacitive semicircle, corresponding to one time constant (τ),



Fig. 3. Impedance diagram of carbon steel in HCl (0.5 M) at different inhibitor concentrations a) L^1 ; b) L^2 .

equivalent to an electric circuit, (Rs(Rt CPE)) (Fig 4) of corrosion process, which is similar to the proposal of many researchers[54, 55]. For the inhibitors (L^1 and L^2),



Fig. 4. Circuit electrical equivalent with one CPE.

there exists an agreement between capacitance and time constant to determine the amount of substance that reacts in a unit of time. For example, the resistance transfer increases with the increasing concentrations, consequently, decreases the capacitance and increases the time constant (see Table 2). In the electric circuit, constant phase element (CPE) represents the electrochemical metal interface. corresponding to the solution resistance (Rs) and Rt represents the resistance transfer. The CPE is determined by the following equation[56, 57]:

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

Z(cpe) = impedance of CPE; Q corresponds to a proportionality factor, j is $(-1)^{\frac{1}{2}}$; ω = angular frequency. n = surface irregularity estimation [25, 57, 58].

The CPE is considered to be a surface irregularity of the electrode[59] and it causes a depression in the Nyquist semicircle diagram for the inhibitor presence in the corrosive medium [60]; thus, we could not draw a conclusion that the metal solution interface performs as a capacitor, for which the metal surface should be flat and homogeneous. If the electrode surface is considered as homogeneous and plane, the exponential value (*n*) becomes equal to 1.0 and the metal-solution interface acts as a capacitor with regular surface. The time constant (τ) and the capacitance value (*C*) of the CPE can be calculated by the following equations [61, 62].

$$Q = \frac{\tau^{n}}{Rp}$$
$$C = (QRp^{1-n})^{\frac{1}{n}}$$

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

L^{1} (mM)	Rs (Ω)	$Q(\Omega^{-1}\mathrm{cm}^{-2}\mathrm{s}^{\mathrm{n}})$	n	Ds	$\operatorname{Rt}\left(\Omega ight)$	$C (\mathrm{F cm}^{-2})$	$\tau(s)$
0.0	3.83	1.061 x 10 ⁻³	0.815	2.22	42	5.296 x 10 ⁻⁴	0.023
0.01	3.65	1.020 x 10 ⁻³	0.766	2.30	60	4.173 x 10 ⁻⁴	0.025
0.03	3.63	9.805 x 10 ⁻⁴	0.724	2.38	72	$3.310 \text{ x}10^{-4}$	0.025
0.07	3.90	8.495 x 10 ⁻⁴	0.773	2.29	79	3.661 x 10 ⁻⁴	0.030
0.20	3.09	1.578 x 10 ⁻³	0.685	2.46	87	5.456 x 10 ⁻⁴	0.049
L ² (mM)	Y.						
0.0	3.83	1.061 x 10 ⁻³	0.815	2.22	42	5.296 x 10 ⁻⁴	0.023
0.01	3.12	1.054 x 10 ⁻³	0.785	2.27	62	4.805 x 10 ⁻⁴	0.030

Table 2. Electrochemical impedance data of the inhibitors

0.03	3.32	1.215 x 10 ⁻³	0.789	2.26	66	6.037 x 10 ⁻⁴	0.040
0.07	3.97	9.588 x 10 ⁻⁴	0.787	2.27	84	4.715 x 10 ⁻⁴	0.040
0.20	3.91	8.778 x 10 ⁻³	0.772	2.29	117	4.227 x 10 ⁻⁴	0.051

The resistance transfer (Rt) at different concentrations of inhibitor during the period of 4.0 hours is shown in Fig 5, observing clearly that the resistance was minimum value in the absence of the compound in the corrosive medium, the speed of corrosion is high without inhibitor over metal surface. However, in the presence of the inhibitor, the Rt value increases steadily, suggesting that L^1 or L^2 form a protective layer over the metal surface immediately and it stabilizes within a



Fig. 5. Resistance variations (Rt) of charge transfer over 6 hours at different concentrations: a) L^1 ; b) L^2

short period of time; this is an agreement with the results obtained from the polarization curves.

The behavior of resistance transfer (Rt) led to a study of the performance of the double layer caused by CPE. Thus the Rt values were plotted against time over perioiod of 4.0 hours (Fig. 5) and it shows that the capacitance is maximum in the absence of inhibitor (Table 2) and it steeply decreases in the presence of inhibitor until its concentration to 0.2 mM. The time constant CPE (τ) against time, over period of 4.0 hours shows that there is a continuous decrease in the speed of loading and unloading of the capacitor when increasing the inhibitor (L¹ or L²) concentration, manifesting that since the τ value is high, the charge transfer of electrochemical corrosion reaction is continuously delayed.

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 [64] with the following equation:

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

Ds= fractional dimension of metallic surface

The Ds data show that the fractional dimension is lower in the absence of inhibitor in the corrosive medium and it suggests that the high energy regions are caused by the roughness of the surface of the electrode. This is entirely logical because on a rough surface, the surface peaks are high-energy points which preferably dissolve into the solution to give a more homogeneous surface. On the other hand, in the presence of inhibitors, a high fractal dimension (Ds) value was obtained, suggesting that the inhibitors are being covered the electrode surface uniformly, and it inhibits the corrosion process in the acid medium. Furthermore, in the study, compound L^2 inhibits strongly by forming a uniform film over metal surface, because of its addition functional groups. Thus a higher Ds value resulted for L^2 than L^1 .

The corrosion inhibition efficiency of different compounds reported in the literature was analyzed (Table 3 and Fig. 6), and it show that amine compounds are generally more efficient for the corrosion inhibition than other compounds; however, some benzimidazoles exhibit high corrosion inhibition efficiency, for example, 1,8-bis (1-chlorobenzyl-benzimidazolyl)–octane or 2,2′-bis(benzimidazole) are good corrosion inhibitors.



Fig. 6. The current density of compounds for the range of 0.1-0.2 mM plotted against different inhibitors.

Table 3. Efficiency of corrosion inhibition of different organic compounds (0.1 - 0.2 mM) reported in the literature

Compounds	Conc.	Icorr	Rp	%ղ	Ref.
	(mM)	(A/cm ²)	$(\Omega \ \mathrm{cm}^2)$		
Amines					7
Benzylidene-pyridine-2-yl-amine	0.2	0.220 x10 ⁻⁴	58	35	[63]
4-Methyl-benzylidene)-pyridine-2-yl-amine	0.2	0.156 x10 ⁻⁴	19	54	[63]
4-Chloro-benzylidene)-pyridine-2-yl-amine	0.2	0.110 x10 ⁻⁴	18	67	[63]
Methyl-1-[((methylphenyl){[3-methoxycarbonyl)-5- methyl-1H-pyrazol-1-yl]methyl}	0.1	1.22 x10 ⁻⁴	547	87	[64]
amino)methyl]-5-methyl-1H-pyrazole-3carboxilate					
N,N-bis[3,5-dimethyl-1H-pyrazol-1-yl)methyl]-N-(4- methylphenyl)amine	0.1	2.72 x10 ⁻⁴	273	71	[64]
N,N,N-tris[(3,5-dimethyl-1H-pyrazol-1-yl)methyl] amine	0.1	0.47 x10 ⁻⁴	679	89	[65]
N,N,bis(methyl 1-[({[3-(methoxycarbonyl)-5-methyl-1H- pyrazol-1 yl]methyl}amino)methyl])-5-methyl-1H- pyrazole-3-carboxylate	0.1	3.27 x10 ⁻⁴	339	65	[65]
2-[{2-[bis-(2-hydroxyethyl)amino]-ethyl}(2- hydroxyethyl)amino]ethanol	0.1	3.48 x10 ⁻⁴		72	[66]
4-(N,N,N-dimethyldodecylammonium bromide)benzylidene-4-methoxybenzene-2-yl-amine	0.1	0.25 x10 ⁻⁴	758	90	[67]
4-(N,N,N-dimethyldodecylammonium bromide)benzylidene-4-aminobenzene-2-yl-amine	0.1	0.26 x10 ⁻⁴	748	89	[67]
4-(N,N,N-dimethyldodecylammonium bromide)benzylidene-4-hydroxybenzene-2-yl-amine	0.1	0.28 x10 ⁻⁴	743	88	[67]
4-(N,N,N-dimethyldodecylammonium bromide)benzylidene-4-chlorobenzene-2-yl-amine	0.1	0.29 x10 ⁻⁴	734	88	[67]
4-(N,N,N-dimethyldodecylammonium bromide)benzylidene-4-nitrobenzene-2-yl-amine	0.1	0.32 x10 ⁻⁴	693	87	[67]
N-[(Z)-1-phenylemethyleidene]-N-{2-[(2-{[(Z)-1phenyl-	0.1	0.369 x10 ⁻⁴	220	91	[68]

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methylidenejamino{pnenyl)disulfanyl]pnenyl} amine					
2-[({2-[(2-{[(Z)-1-(2-hydroxyphenyl)methylidene] amino} phenyl) disulfanyl]phenyl} imino)methyl]phenol	0.1	1.004 x10 ⁻⁴	123.5	87	[68]
N-[(Z)-1-(4-methylphenyl)methylidene]-N-{2-[(2-{[(Z)-1- (4-methylphenyl) methylidene]amino}phenyl) disulfanyl]phenyl} amine	0.1	0.795 x10 ⁻⁴	145.8	86	[68]
(E,E)-N,N'-dibenzo[b,d]thiene-2,8-diylbis[1-(thiophen-2-yl)methanimine]	0.1	0.655 x10 ⁻⁴	759.4	91	[69]
Dibenzo[b,d]thiophene	0.1	1.067 x10 ⁻⁴	499.9	85	[69]
Decylamine ethoxylate	0.2	0.1972 x10 ⁻⁴	427	60	[70]
Decylamine ethoxylate	0.13	0.5705 x10 ⁻⁴	601	71	[70]
	0.17	0.4082x10 ⁻⁴	840	79	[70]
Decylamine ethoxylate	0.19	0.2815x10 ⁻⁴	1243	86	[70]
Hexadecylamine ethoxylate	0.18	0.2345x10 ⁻⁴	1505	88	[70]
N-benzyl-N,N-bis[(3,5-dimethyl-1H-pyrazol-1- yl)methyl]amine	0.1	0.76x10 ⁻⁴	230	70	[71]
nvridines					
pyridines (5 methyl 1 pyridin 2 yl 1H pyrazol 3 yl)methanol	0.1	0.79×10^{-4}	453	74	[72]
pyridines (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol	0.1	0.79×10^{-4}	453	74	[72]
pyridines (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol ethyl 5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate	0.1	0.79 x10 ⁻⁴ 0.91 x10 ⁻⁴	453 315	74 70	[72] [72]
pyridines (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol ethyl 5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate (2Z)-3-imino-4-methyl-2-(pyridin-3-ylhydrazono) pentanenitrile	0.1 0.1 0.91 x10 ⁻⁴	0.79 x10 ⁻⁴ 0.91 x10 ⁻⁴ 4.04 x10 ⁻⁴	453 315	74 70 69	[72] [72] [73]
 pyridines (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol ethyl 5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate (2Z)-3-imino-4-methyl-2-(pyridin-3-ylhydrazono) pentanenitrile 4-(3,4-dichlorophenyl)-2,6-dimethyl-1,2-dihydropyridine-3,5-dicarbonitrile 	0.1 0.1 0.91 x10 ⁻⁴ 0.1	0.79 x10 ⁻⁴ 0.91 x10 ⁻⁴ 4.04 x10 ⁻⁴ 3.34 x10 ⁻⁴	453 315	74 70 69 75	[72] [72] [73] [73]
 pyridines (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol ethyl 5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate (2Z)-3-imino-4-methyl-2-(pyridin-3-ylhydrazono) pentanenitrile 4-(3,4-dichlorophenyl)-2,6-dimethyl-1,2-dihydropyridine-3,5-dicarbonitrile 1,4-diamino-5-cyano-2-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylic acid 	0.1 0.1 0.91 x10 ⁻⁴ 0.1 0.1	0.79 x10 ⁻⁴ 0.91 x10 ⁻⁴ 4.04 x10 ⁻⁴ 3.34 x10 ⁻⁴ 2.37 x10 ⁻⁴	453 315	74 70 69 75 82	[72] [72] [73] [73] [73]
 pyridines (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol ethyl 5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate (2Z)-3-imino-4-methyl-2-(pyridin-3-ylhydrazono) pentanenitrile 4-(3,4-dichlorophenyl)-2,6-dimethyl-1,2-dihydropyridine-3,5-dicarbonitrile 1,4-diamino-5-cyano-2-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylic acid Ethyl 4-amino-5-cyano-2-(dicyanomethylene)-6-phenyl-1,2-dihydropyridine-3-carboxylate 	0.1 0.1 0.91 x10 ⁻⁴ 0.1 0.1	0.79 x10 ⁻⁴ 0.91 x10 ⁻⁴ 4.04 x10 ⁻⁴ 3.34 x10 ⁻⁴ 2.37 x10 ⁻⁴ 1.19 x10 ⁻⁴	453 315	 74 70 69 75 82 91 	 [72] [72] [73] [73] [73] [73]
 pyridines (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol ethyl 5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate (2Z)-3-imino-4-methyl-2-(pyridin-3-ylhydrazono) pentanenitrile 4-(3,4-dichlorophenyl)-2,6-dimethyl-1,2-dihydropyridine-3,5-dicarbonitrile 1,4-diamino-5-cyano-2-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylic acid Ethyl 4-amino-5-cyano-2-(dicyanomethylene)-6-phenyl-1,2-dihydropyridine-3-carboxylate Bis-2,6-(3,5-dimethylpyrazolyl)pyridine 	0.1 0.1 0.91 x10 ⁻⁴ 0.1 0.1 0.1	0.79 x10 ⁻⁴ 0.91 x10 ⁻⁴ 4.04 x10 ⁻⁴ 3.34 x10 ⁻⁴ 2.37 x10 ⁻⁴ 1.19 x10 ⁻⁴ 3.319 x10 ⁻⁴	453 315 56	 74 70 69 75 82 91 75 	 [72] [72] [73] [73] [73] [73] [73] [73]
 pyridines (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol ethyl 5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate (2Z)-3-imino-4-methyl-2-(pyridin-3-ylhydrazono) pentanenitrile 4-(3,4-dichlorophenyl)-2,6-dimethyl-1,2-dihydropyridine-3,5-dicarbonitrile 1,4-diamino-5-cyano-2-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylic acid Ethyl 4-amino-5-cyano-2-(dicyanomethylene)-6-phenyl-1,2-dihydropyridine-3-carboxylate Bis-2,6-(3,5-dimethylpyrazolyl)pyridine Benzylidene-pyridine-2-yl-amine 	0.1 0.91 x10 ⁻⁴ 0.1 0.1 0.1 0.1 0.2	0.79 x10 ⁻⁴ 0.91 x10 ⁻⁴ 4.04 x10 ⁻⁴ 3.34 x10 ⁻⁴ 2.37 x10 ⁻⁴ 1.19 x10 ⁻⁴ 3.319 x10 ⁻⁴ 0.22 x10 ⁻⁴	453 315 56 58	 74 70 69 75 82 91 75 35 	 [72] [72] [73] [73] [73] [73] [74] [63]

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(4-chloro-benzylidene)-pyridine-2-yl-amine	0.2	0.111 x10 ⁻⁴	18	67	[63]
2-(3-methyl-1H-pyrazol-5-yl) pyridine	0.1	0.21 x10 ⁻⁴	420	73	[75]
2-phenylimidazo[1,2-a]pyridine	0.1	1.241 x10 ⁻⁴	147.4	85	[76]
2-(m-methoxy phenyl) imidazo[1,2- a] pyrimidine	0.1	1.194 x10 ⁻⁴	157.7	85	[76]
3-bromo-2-phenylimidazol[1,2- α] pyridine	0.1	1.08 x10 ⁻⁴	90	70	[77]
2,6-bis-(hydroxy)-pyridine	0.1	2.62 x10 ⁻⁴		51	[78]
2,6-bis-(chloro)-pyridine	0.1	1.76 x10 ⁻⁴		67	[78]
Diethyl 1,1'-(pyridine-2,6-diyl)bis(5-methyl-1H-pyrazol2- 3-carboxylate	0.1	1.25 x10 ⁻⁴		77	[78]
imidazoles					
2-(2-trifluoromethyl-4,5-dihydro-imidazol-1-yl)- ethylamine	0.1	4.63 x10 ⁻⁴	28.5	49	[73]
2-(2-trichloromethyl-4,5-dihydro-imidazol-1-yl)- ethylamine	0.1	1.87 x10 ⁻⁴	53.7	79	[73]
N´-(phenylmethylidene)-2-(2-methyl-1H-benzimidazol-1- yl) acetohydrazides	0.17	1.48 x10 ⁻⁴	102	74	[79]
N´-(4-methylphenylmethylidene)-2-(2-methyl-1H- benzimidazol-1-yl)acetohydrazides	0.17	1.77 x10 ⁻⁴	77	69	[79]
N´-(4-methoxyphenylmethylidene)-2-(2-methyl-1H- benzimidazol-1-yl)acetohydrazides	0.16	1.96 x10 ⁻⁴	74	65	[79]
Benzimidazoles					
2,2´-bis(benzimidazole)	0.1	6.0×10 ⁻⁴		96	[80]
tris(benzimidazole-2-ylmethyl)amine	0.1	1.17×10 ⁻⁴	150	87	[11]
tris(benzimidazole-2-ylmethyl)amine	0.15	1.40×10 ⁻⁴	146	85	[11]
1,8-bis (1-chlorobenzyl-benzimidazolyl) -octane	0.13	0.31×10 ⁻⁴	639	98	[81]
2-(4-pyridyl)-benzimidazole	0.1	2.88×10 ⁻⁴	48.63	80	[82]
2-(4-pyridyl)-benzimidazole	0.25	2.57×10 ⁻⁴	52.12	82	[82]
2-aminomethyl benzimidazole	0.1	7.14×10 ⁻⁴	46.6	58	[83]
Bis (2-benzimidazolylmethyl) amine	0.1	2.21×10 ⁻⁴	148.9	84	[83]

Tri (2-benzimidazolylmethyl) amine	0.1	1.95×10 ⁻⁴	212.7	88	[83]
2,6-Bis-(2-benzimidazolyl) pyridine	0.1	2.47×10 ⁻⁴	40.5	79	[84]
Bis-(2-benzimidazolyl methyl) sulphide	0.1	3.49×10 ⁻⁴	32.5	71	[84]
Bis-(2-benzimidazolyl methyl) oxide	0.1	4.53×10 ⁻⁴	25	63	[84]
1,2-Bis-(2-benzimidazolyl) ethylene	0.1	5.99×10 ⁻⁴	17.5	50	[84]
Benzimidazole	0.42	1.30×10 ⁻⁴	90	36	[85]
2-Methylbenzimidazole	0.38	1.15×10 ⁻⁴	98	44	[85]
2-Mercaptobenzimidazole	0.33	0.56×10 ⁻⁴	213	73	[85]
2-mercaptobenzimidazole	0.1	0.288×10 ⁻⁴	464	87	[86]
2-mercaptobenzoxazole	0.1	0.484×10 ⁻⁴	196	79	[86]
1, 4-bis-benzimidazolyl-butane	0.1	0.520×10 ⁻⁴	262	82	[87]
1, 4-bis-benzimidazolyl-butane	0.2	0.390×10 ⁻⁴	372	87	[87]
1-Butyl-2-(4-methylphenyl)benzimidazole	0.19	3.700×10 ⁻⁴		75	[88]
	0.2	2.399x10 ⁻⁴	87	59	Present work L ¹
	0.2	1.813x10 ⁻⁴	117	69	Present work L ²

3.2 Theoretical studies

The geometries of Fe₁₅, Fe₁₆ and Fe₃₀ clusters are fully optimized (Fig. 7) with the total multiplicity of M = 49, 51, and 91 respectively (M = 2S + 1, S =total spin), and the global minimum energy of Fe₁₅ and Fe₁₆ clusters data derived from our methodology matches with the reported in the literature[41]. The global reactivity descriptors, i.e HOMO and LUMO energies, ionization potential, electron affinity, electronegativity, hardness, electrophilicity, electroaccepting and electrodonating

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powers of L^1 and L^2 inhibitors are presented Table 4, showing that both inhibitors are expected behave almost similar in their interaction with metal surface.



Fig. 7 Optimized geometries of Fe_{15} (left), Fe_{16} (center) and Fe_{30} (right) clusters obtained by simulated annealing at the DFTB-SCC spin polarized level of theory.

Table 4. HOMO, LUMO, gap, ionization potential (IP), electron affinity (EA), electronegativity (χ), hardness (η) and electrophilicity (ω) of L¹ and L² inhibitors calculated at the DFT B3LYP/cc-pVDZ level of theory. All values are given in eV.

Inhibitor	E _{HOMO}	E_{LUMO} ΔE	IP	EA	χ	Н	Ω	ω^+	ω¯
L^1	-4.75	-0.76 3.99	6.21	0.58	3.39	2.81	2.05	0.06	6.85
L^2	-4.78	-0.84 3.94	6.10	0.47	3.29	2.81	1.92	0.04	6.61

To rationalize chemical reactions in analyzing the reactive site in a ligand molecule, although several local and global descriptors are being considered [89-93], the condensed-to atom Fukui indexes (CAFI) f(r) was used to identify the local reactivity of the ligand [90, 94, 95]. In the study, the most suitable descriptor, Hirshfeld charge was employed to calculate the CAFI as suggested in the previous reports [96, 97]. The calculation yielded reliable NPA charges at different basis sets

(DGDZVP and 6-31G^{**}) in the B3LYP framework. The Fukui function f(r) defines as the derivative of the electronic density $\rho(r)$ with respect to the number of electrons N at a constant external potential v(r) and it allows to identify the most active sites in the ligand:

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]$$

If the effects of relaxation associated with the addition or removal of electronic charges are not considered, then

 $f^+(r) \approx \rho_{LUMO}(r)$

 $f^{-}(r) \approx \rho_{HOMO}(r)$

$$f^{0}(r) \approx \frac{1}{2} \left[\rho_{HOMO}(r) + \rho_{LUMO}(r) \right]$$

 $\rho_{\text{LUMO}}(r)$ = density of the first unoccupied molecular orbital; $\rho_{\text{HOMO}}(r)$ = density of the highest occupied molecular orbital [98]. The condensed Fukui functions[94] are found by taking the finite difference approximations from the population analysis of atoms in molecules, depending on the direction of the electron transfer.

- $f_x^- = [q_x(N) q_x(N 1)]$ electrophilic attack
- $f_x^{+} = [q_x (N + 1) q_x (N)]$ nucleophilic attack

 $f_x^0 = \left[\frac{f_x^+ + f_x^-}{2}\right]$ radical attack

 $(q_x = charge on atom x in the molecule); are being employed.$

The Fukui indices data (Table 5, Fig.8 and Fig. 9) show that the reactive sites are located over the aromatic rings of the ligands. For all atoms in the ligand, the CAFI f(r) data calculated for ligand with B3LYP at different basis sets (DGDZVP and 6-31G**) show that the Hirshfeld Population Analysis and natural population analysis (NPA) predict positive values; the Fukui Functions indicate that those atoms having the largest Fukui values are the most reactive site; for instance, the most reactive ones for L¹ are N5, C3, C6, C9, C10, and C11; while that L² are O1, N4, C5, C8, C10, C13 and C14. These results indicate that the oxygen atom of L² inhibitor has the capacity to donate charge. Moreover the electrostatic potential map shown in Fig. 8c that the nitrogen (N5) for L¹ and (N4) for L² have the most negative potential on the isosurface



Fig.8. a) f^+ Fukui function of L^1 inhibitor (left) and L^2 inhibitor (right); b) f Fukui function of L^1 inhibitor (left) and L^2 inhibitor (right); c) Electrostatic potential plotted on a 0.0001 electron density isosurface of L^1 inhibitor (left) and L^2 inhibitor (right). In the electrostatic potential: blue color= positive electric charge; red color = negative electric charge; green = potential close to zero. All the plots were calculated at the DFT B3LYP/cc-pVDZ level of theory.



Fig. 9. Atom numbering of L^1 inhibitor (left) and L^2 inhibitor (right) corresponding to the condensed Fukui indices.

Table 5. Condensed Fukui indices calculated with Hirshfeld charges of heavy atoms in L^1 and L^2 inhibitors. The electron density was calculated at the DFT B3LYP/cc-pVDZ level of theory. Note that the largest f+ or f- values of L^2 inhibitor are not located on the oxygen atom.

	L			L^2	
Atom	f-	f+	Atom	f-	f+
C1	0.015	0.026	C1	0.009	0.002
C2	0.015	0.010	C2	0.006	0.023

C3	0.063	0.012	C3	0.020	0.013
C4	0.017	0.019	C4	0.014	0.004
C5	0.014	0.023	C5	0.052	0.012
C6	0.060	0.004	C6	0.011	0.018
C7	0.013	0.071	C7	0.015	0.022
C8	0.036	0.035	C8	0.043	0.003
C9	0.056	0.016	C9	0.003	0.073
C10	0.075	0.029	C10	0.046	0.017
C11	0.076	0.025	C11	0.038	0.033
C12	0.033	0.024	C12	0.029	0.019
C13	0.023	0.044	C13	0.052	0.024
C14	0.039	0.067	C14	0.074	0.028
C15	0.011	0.074	C15	0.018	0.045
C16	0.022	0.075	C16	0.029	0.063
C17	0.030	0.001	C17	0.008	0.072
N1	0.030	0.001	N1	0.018	0.074
N2	0.013	0.030	N2	0.018	0.001
N3	0.033	0.008	N3	0.012	0.031
N4	0.000	0.041	N4	0.083	0.003
N5	0.044	0.026	N5	0.000	0.041
			01	0.047	0.027

The interaction energies resulted from the adsorption of the inhibitors on the metal cluster i.e. the energy difference between the cluster—inhibitor system and the

isolated cluster and inhibitor. In the study, three configurations of L¹ inhibitor and five configurations of L² inhibitor were adopted for their adsorption on the Fe₃₀ cluster by the simulated annealing technique. The results show that both L¹ and L² inhibitors are adsorbed mainly through π interactions with the cluster. The annealed geometries were then optimized at the DFTB and VWN levels of theory with spin multiplicity of 91. The interaction energies of these configurations (Table 6) indicate that the adsorptions energies of L² are greater than those of L¹ at both levels of theory, but the magnitude of the difference is significantly smaller with VWN. These values are comparable to the energies for the adsorption of benzene on iron oxide surfaces[99]. To quantify the magnitude of the adsorption energy, we chose the VWN values as DFT is more reliable than DFTB. The interaction energy resulted for L² (122.1 kcal/mol) is greater than that for L¹ (101.9 kcal/mol) (Table 6). Thus adsorption of L² over the metal cluster much stronger (around 20 kcal/mol) than that with L¹, agreeing with the experimental results that that L² inhibitor binds more efficiently to the Fe surface.

Interaction		Multiplicity	Interaction energy (kcal/mol)				
Inter	action		DFTB	VWN			
Fe ₃₀ L ₁		91	-63.6	-95.9			
Fe_{30} — L_1		91	-67.1	-101.9			
Fe_{30} — L_1		91	-72.0	-100.3			
Fe ₃₀ L ₂		91	-116.1	-113.3			
Fe ₃₀ L ₂		91	-116.1	-108.5			
Fe_{30} — L_2		91	-119.4	-96.1			
Fe_{30} — L_2		91	-132.8	-117.3			
Fe_{30} — L_2		91	-132.8	-122.1			

Table 6. Interaction energies of L1 and L2 inhibitors on the Fe_{30} cluster calculated at the DFTB-SCC and VWN/DZVP/GEN-A2 levels of theory.

The preferred interaction of L^1 and L^2 inhibitors with the Fe₃₀ cluster is shown (Fig.10), showing that the interaction occurs through π electrons of the aromatic rings over the cluster. The additional energy acquired for L^2 during the interaction with the cluster (L^2 -Fe₃₀) is believed from the presence of oxygen atom although this O····Fe interaction was not observed in all the five annealed configurations, reducing significantly the energetic difference between the interaction energies of L^1 -Fe₃₀ and L^2 -Fe₃₀ systems.



Fig. 10. a) Optimized geometry of most stable L^1 inhibitor adsorbed on the Fe₃₀ cluster. b) Optimized geometry of most stable L^2 inhibitor adsorbed on the Fe₃₀ cluster. Optimizations were performed at the VWN/DZVP/GEN-A2 level of theory.

Conclusion

Both inhibitors perform as mixed inhibitor as they affect both anodic and cathodic branches by decreasing current density. The efficiency of inhibitors increases with increasing their concentration in the corrosion medium. Furthermore, the presence of additional functional group of the inhibitor L^2 conferred greater stability to the film

(-36.20 Kj M⁻¹) than inhibitor L¹ (- 33.75 Kj M-) with the difference of - 2.45 Kj M⁻¹. This is consistent with the fractal dimension data where a greater value is resulted for L² than L¹, showing that the former adsorbs uniformly on the metal surface. DFT and electrochemical studies clearly show that there is a formation of an adsorption layer over the metallic surface by giving the π -electron density from delocalization region through its HOMO orbital to the metal LUMO. Thus adsorption of L² over the metal cluster much stronger (around 20 kcal/mol) than that with L¹, agreeing with the experimental results that that L² inhibitor binds more efficiently to the Fe surface. In addition, the corrosion inhibition data collected for around 70 organic compound reported in the literature show that amine ligands are mostly good corrosion inhibitor, and exceptionally some benzimidazoles perform as efficient inhibitors.

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Highlights

- Corrosion inhibition by benzimidazole in acid medium
- DFT study on interaction of benzimdazole with on Fe₃₀
- Elelectrochemical impedance and polarization curves of inhibitor on mild steel in acid medium
- Comparative analysis of amine, pyridine, and benzimidazole ligands