

Experimental and Theoretical Studies of New Schiff Base as a Corrosion Inhibitor in Acidic Media and Study Antioxidant Activity

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ABSTRACT: In the present study, the Schiff base was synthesized [1,1'-((1E,1'E)-((4,5-dimethyl-1,2-phenylene)bis(azanilylidene))bis(methanylylidene))bis(naphthalen-2-ol)] derived from the reaction of 2-hydroxy-1-naphtha-aldehyde with, 4,5-Dimetyl-1,2-penylenediamine for 4hr. and yield was 90.09%. The prepared compound was identified by C.H.N, UV-Vis, FT-IR ¹H-NMR, and mass spectroscopy and was studied also theoretically using Gaussian 09 software based on the DFT method at B₃LYP/6-31G (d,p). Quantum chemical calculations were performed to provide further insight into the inhibition efficiencies that were conducted experimentally. The weight loss method was used to measure the efficiency of the prepared compound as a corrosion inhibitor in an acid medium. It was found that the inhibition efficiency was increased with decreasing temperature and the concentration increase of synthesized Schiff base and the highest inhibition efficiency was obtained at an optimum concentration of (1×10⁻³ M) for inhibitor at 298 K. Moreover, it was found that the adsorption process of the inhibitor on the surface of the brass is obeyed by the Langmuir isotherm of adsorption. The value of the free energy change was found to be -28.28 kJ/mol, which indicates that the prepared compound adsorbed on the surface of the metal. The antioxidant activity of the prepared Schiff base was investigated on the basis of the radical scavenging effect of 1,1-diphenyl-2-picryl-hydrazyl (DPPH)-free radical activity was also studied. The ligand (S₁) exhibited excellent activity.

KEYWORDS: Schiff Base; Corrosion; Brass alloy; Inhibitor; Antioxidant activity.

INTRODUCTION

Schiff bases are formed by the reaction of aldehydes or ketones with amines to form an imine or azomethine group [1,2]. Schiff bases of aromatic aldehydes have an effective and significant conjugated system [3]. The flexibility of the imine group associated with this group of compounds, which enables attachment and extension of p-donating groups has interestingly widened the scope of Schiff bases. This property increases the interest of corrosion chemists

for their possible use in the metal surface protection [4]. Schiff bases were used as corrosion inhibitors because they can be easily synthesized, contain aromatic rings that offer electron cloud, and can incorporate some electronegative atoms as substituents, which could determine their overall potency and help in the technological advancement of better corrosion inhibitors [5]. The C=N group, planarity of p-bonding orbitals and electrons from the attached

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1021-9986/2022/10/3351-3364

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electronegative atoms afford them the great opportunity of being adsorbed on metal surfaces [6]. Corrosion problems have received a considerable amount of attention because of their economic and safety consequences. The use of inhibitors is one of most practical methods to eliminate or prevent corrosion [7]. There is an increasing desire to combat corrosion of metals as recent survey reported worldwide cost of corrosion control to the estimated sum of US \$2.5 trillion [8,9]. It is therefore a significant to material scientists. There is a need to develop high yield, cost effective, low toxic and efficient corrosion inhibitors that can be exploited as additives in many industrial applications. It was showed that Schiff base compounds have been reported as efficient corrosion inhibitors for metals in acidic media [10-12]. These inhibitors act through a process of surface adsorption, so the efficiency of any inhibitor depends on the characteristics of the environment in which it acts the nature of the metal surface, and electrochemical potential at the interface. The chemical structure of inhibitor itself, which includes the number of adsorption active centers in the molecule and their charge densities, the molecule size, the mode of adsorption and the protected area of the inhibitor on the metal surface, have an effect on the efficiency of the inhibitor [13,14]. The Schiff base 1,1'-((1E,1'E)-((4,5-dimethyl-1,2-phenylene)bis(azanylylidene)) bis(methanylylidene))bis(naphthalen-2-ol) was synthesized and their molecular structure was determined by many devices including elemental analysis (C.H.N analysis), UV-visible, Fourier transform infrared FT-IR spectroscopy, nuclear magnetic resonance ($^1\text{H-NMR}$) and mass spectroscopy. The ability of this molecule to inhibit brass corrosion in an acidic media (1M HCl) was determined by utilizing the weight loss method. To elucidate the inhibition mechanism and the relationship between the structure and the inhibition efficiency of the inhibitor, quantum chemical calculations of Schiff base (S_1) were performed. Theoretical calculations using DFT models were also performed to clearly the basic sites of electron transfer involved in the inhibition process and use the compound prepared for antioxidant activity.

EXPERIMENTAL SECTION

Instrumentation

The device of UV-Vis spectrophotometer model T 60, PG Instruments Ltd, (Germany) was used. IR spectra were

recorded by using by the utility of FT-IR affinity Spectrophotometer (Shimadzu) Japan, using KBr discs. The device is available in the Department of Chemistry, College of Science, University of Thi-Qar, Iraq. $^1\text{H-NMR}$ with using DMSO-d_6 as a solvent, Mass spectra are recorded of compound using Agilent Technology (HP)/MS Model 5973 network mass selective detector and element analysis model Eager 300 for EA1112 in the University of Tehran, Iran. Melting points were determined by the utility of a digital Stuart SMP31 melting point apparatus available at the same mentioned department.

Materials

All chemical substances; 2-hydroxy-1-naphthaldehyde, 4,5-Dimethyl-1,2-penylene-diamine and solvents were of commercial analytical grade, they were purchased from Aldrich and BDH. Chemicals were used with no any purification process.

Synthesis of corrosion inhibitor

4,5-Dimethyl-1,2-penylenediamine (10mmol, 1.360gm) in 25mL ethanol was added to a hot ethanolic solution of 2-hydroxynaphthaldehyde (20mmol, 3.440gm). Two drops of glacial acetic acid were added. The formed solution was refluxed for 4 hr. and then lefts overnight in a refrigerator. The collected solid product was filtered and washed with acetone and was recrystallized by using chloroform: ethanol (8:2, v:v) as a solvent [15]. The obtained crystals had yellow-orange color with a percentage yield of 90.09%, m.p:252-254°C.

Weight loss measurements

Corrosion tests were performed using coupons prepared from brass alloy. The chemical composition (wt%) of the brass alloy sample is shown in Table 1.

The corrosive acid solutions were prepared from hydrochloric acid with a concentration of 1M. The required concentration of acid (1M HCl) was prepared by using deionized water. The tests were performed in the absence and presence of certain inhibitor concentrations ($1 \times 10^{-3}\text{M}$ - $1 \times 10^{-6}\text{M}$) with a range of immersion time (1-5) hr. Many temperatures (298, 308, 318) K were used in the experiments. The corrosion rate (W), the percentage inhibition efficiency (IE %), and the degree of surface coverage (θ) were calculated using Equation (1) [16]:

Table 1: The chemical composition (wt%) of the brass alloy sample.

Metals	Wt%
Cu	68.75
Zn	28.00
Al	1.20
Fe	1.00
As	0.05
Other	1.00

$$W = \frac{WL \cdot K}{A \cdot t \cdot D} \quad (1)$$

Where WL is the weight losses (gm) before and after immersion in the test solutions, W is the corrosion rate, A is the area of the specimen (Inch²), D is the density of the alloy in g/cm³, K is a constant (543) (giving rate in mpy) and t is the immersion time (hours). The inhibition efficiency (IE%) was computed using Eq. (2) [17]:

$$E\% = \frac{W_a - W_b}{W_a} \times 100\% \quad (2)$$

Where W_a and W_b are the corrosion rates in the absence and presence of the inhibitor, respectively and the surface coverage, θ of the metal surface covered by the adsorbed inhibitor was evaluated from weight loss measurements using Eq. (3):

$$\theta = 1 - \frac{W_a}{W_b} \quad (3)$$

Antioxidant activity Ttest

The antioxidant activity of Schiff base and the standard were assessed on the basis of the radical scavenging effect of 1-diphenyl-2-picryl-hydrazyl (DPPH)-free radical activity by modified method. A freshly prepared DPPH solution exhibited a deep purple color with a maximum absorption at 517 nm. This purple color disappears when an antioxidant is present in the medium. Therefore, antioxidant molecules can quench DPPH free radicals and convert them to a colorless product.

The diluted solutions of the test sample were carefully prepared in methanol. Ascorbic acid was used as a standard solution. A solution of 0.002% of DPPH was prepared in methanol. A volume of 2 mL of this solution was mixed with 1mL of the sample solution and standard

solution separately. These solution mixtures were kept in darkness for 30 min and absorbance was measured at 517nm using UV-Visible spectrophotometer. Methanol (1mL) with DPPH solution (0.002%, 1mL) was used as a blank. The free radical scavenging activities are expressed as the ratio percentage of the sample absorbance decrease and the absorbance of tested compound at 517nm. The absorbance was recorded and % inhibition was calculated using Equation (4) [18]:

Inhibition of DPPH radical (I%) was calculated using the following relation.

$$I\% = \frac{A_{\text{Blank}} - A_{\text{Sample}}}{A_{\text{Blank}}} \times 100 \quad (4)$$

Where A Blank = Absorbance of the blank and A Sample = Absorbance of the sample. DPPH free radical scavenging activity % was proportional to the concentration of the tested compound.

RESULTS AND DISCUSSION

Elemental analysis

The results of elemental analysis of synthesis compound (S₁) shown in Table 2 are in acceptable agreement with those required by the proposed formula.

UV-Vis spectrum analysis

The electronic absorption spectra of Schiff base (S₁) in DMF solution were recorded in the range of 250-450 nm at room temperature. The results are shown in Fig.1. In the spectrum of the ligand, four absorption bands were observed. The three first bands, which appear at 291, 302, and 347 nm are attributable to $\pi \rightarrow \pi^*$ electronic transitions associated with the naphthalene and phenyl units [19-21]. The four absorption bands located at 386nm are attributed to $n \rightarrow \pi^*$ transitions of conjugation between the lone pair of electrons and the conjugated bond of the aromatic cycle [19].

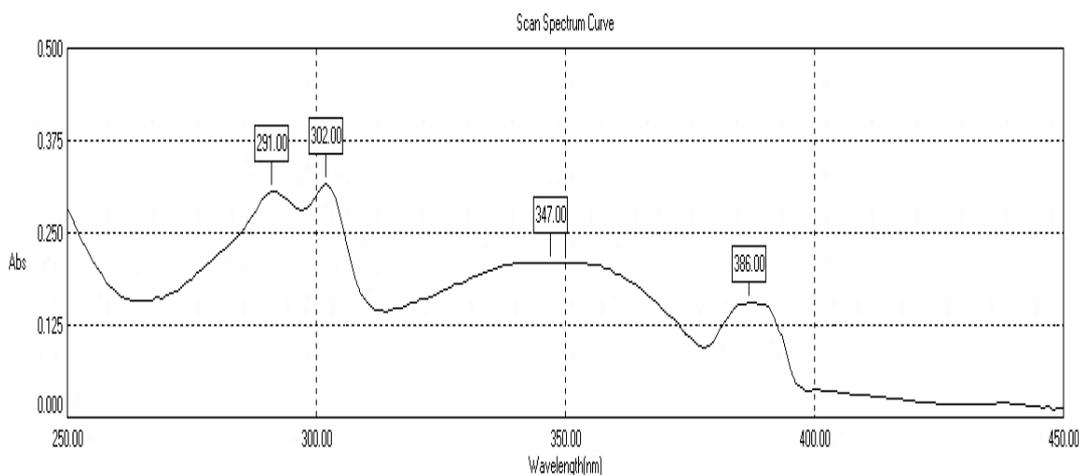
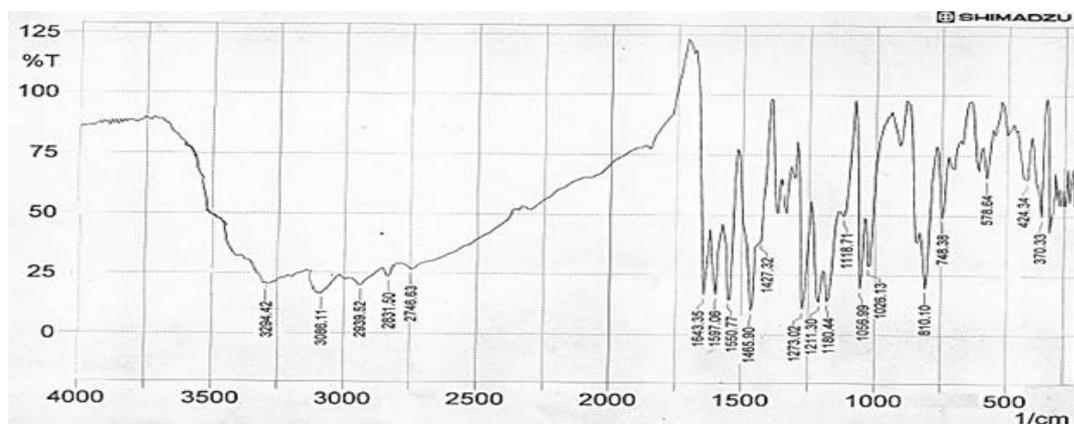
FT-IR spectrum

A strong band at 1643.35 in the IR spectrum of the Schiff base (Fig. 2) is assigned to $\nu(\text{C}=\text{N})$ of azomethine vibration. The band in the spectra at 1597.06cm⁻¹ is due to $\nu(\text{C}=\text{C})$ of aromatic rings.

While the band at 2831.50-2939.51cm⁻¹ is attributed to (C-H aliph.). Furthermore, the band at 3086.11cm⁻¹ is attributed to (C-H Ar.) and the band at 3294.42cm⁻¹ is attributed to OH [22-24].

Table 2: Elemental analysis data of the Schiff base (S₁).

Compound	Molecular Weight	Experimental			Theoretical		
		C%	H%	N%	C%	H%	N%
S ₁	444	81.081	5.405	6.306	81.064	5.383	6.281

Fig.1: UV-Vis spectrum for compound (S₁).Fig. 2: FT-IR spectrum for compound (S₁).

¹H-NMR spectrum analysis

¹H NMR spectra of the synthesized compound were recorded in DMSO-d₆ (500MHz) as the solvent δ at 2.51 in Fig. 3. ¹H NMR spectra show a signal at 3.36 (s, 6H, 2CH₃-Ar) [25]. The region at δ 7.34-7.89 ppm (s, 14H, aromatic rings) is due to aromatic protons [26,27]. δ at 8.08ppm (s, 2H, 2CH=N) [26,27]. ¹H NMR spectra of the synthesized compound shows a signal at δ 11.45 ppm (b, 2H, 2OH) [25] due to phenolic OH.

Mass spectrum analysis

The mass spectrum of the synthesized compound (S₁) was recorded and the obtained molecular ion (m/z) peaks confirm for a proposed formula that behaves as a bidentate ligand. The ligand shows a peak at M⁺=444 corresponding to the molecular ion peak (C₃₀H₂₄N₂O₂) as illustrated in Fig. 4. It also showed a series of peaks at m/z=427, 301, 288, 274, 259, 244, 170, 156, 143, 119, 105, 91 and 77 corresponding to [C₃₀H₂₃N₂O]⁺, [C₂₀H₁₇ N₂O]⁺,

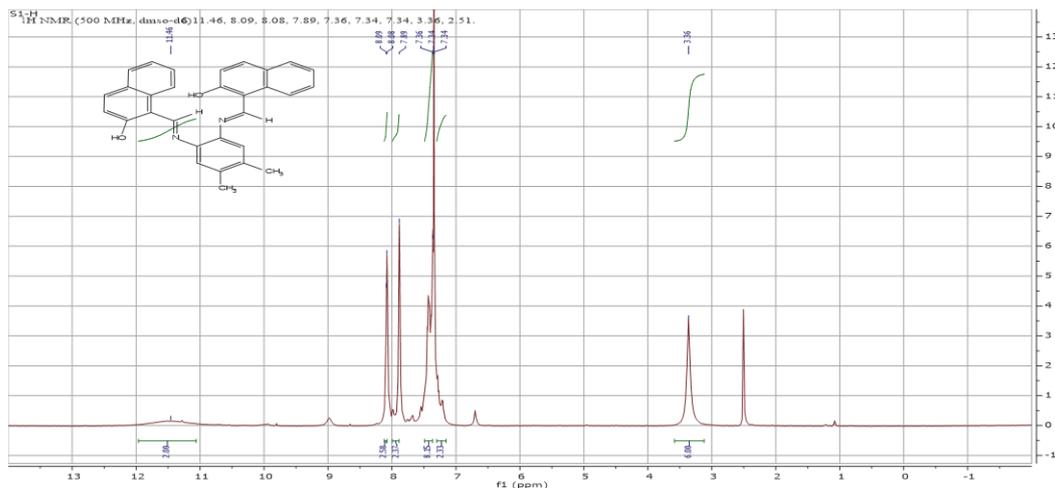


Fig. 3: $^1\text{H-NMR}$ spectrum for compound (S1).

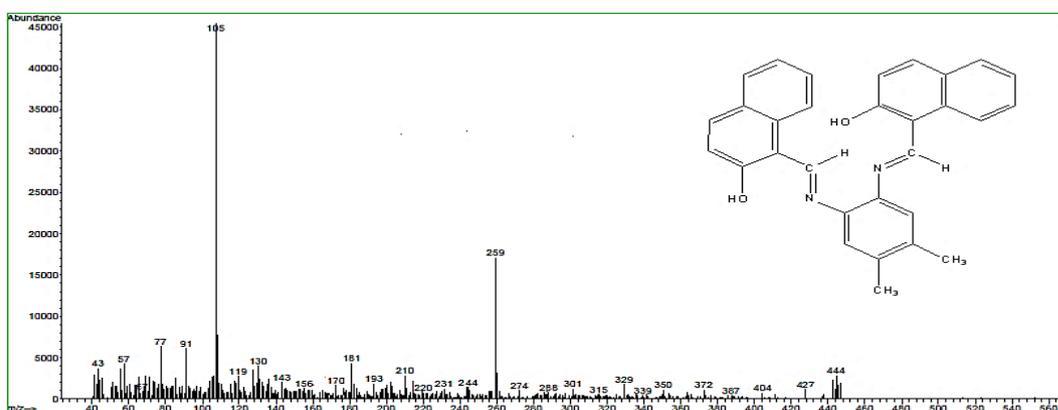


Fig. 4: Mass spectrum for compound (S1).

$[\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}]^+$, $[\text{C}_{19}\text{H}_{16}\text{NO}]^+$, $[\text{C}_{18}\text{H}_{13}\text{NO}]^+$, $[\text{C}_{17}\text{H}_{10}\text{NO}]^+$, $[\text{C}_{11}\text{H}_8\text{NO}]^+$, $[\text{C}_{11}\text{H}_8\text{O}]^+$, $[\text{C}_{10}\text{H}_7\text{O}]^+$, $[\text{C}_8\text{H}_9\text{N}]^+$, $[\text{C}_8\text{H}_9]^+$, $[\text{C}_7\text{H}_7]^+$ and $[\text{C}_6\text{H}_5]^+$ respectively.

Weight loss measurements

Effect of exposure time on the corrosion process

The effect of the addition of the inhibitor on the corrosion of brass alloy in 1M HCl solution was studied by the weight loss method at a temperature of 298K after (1-5) hr. of exposure time in the absence and presence of (10^{-3}M) of the prepared Schiff base as a corrosion inhibitor. The results are shown in Figs. 5 and 6. The two figures clearly show a great reduction in the weight loss and the rate of corrosion with the increase in immersion from 1h. to 5hr. at different temperatures of the metal coupons in

the presence of the inhibitor compared to the hydrochloric solutions alone. This is due to the formation of strong passive protective layer on the surface of the metal when exposed to electrolyte for more time [16,17,28]. The values of Weight loss (gm) and corrosion rate (mpy) are summarized in Table 3.

Effect of inhibitor concentration on the corrosion process

Weight loss data and the rate of corrosion of brass alloy in 1M HCl in the absence and presence of various concentrations of inhibitors at 298 K after 3 hr. exposure were obtained and are given in Table 4. The results show that the weight loss data and the rate of corrosion decrease with increasing inhibitor concentration (Figs.7 and 8) [29-31].

Table 3: Weight loss and corrosion rate for brass alloy in 1M HCl alone and in presence of inhibitor ($C=1\times 10^{-3}$ M) at different exposure time and different temperature.

The Variable	Corrosion medium	Exposure time (hours)				
		1	2	3	4	5
Weight loss (gm)	HCl only	0.0042	0.0065	0.0074	0.0084	0.0085
Corrosion rate (mpy)	HCl only	95.032	73.53	55.81	47.51	38.46
Weight loss (gm)	HCl + inhibitor	0.0015	0.0025	0.0035	0.0040	0.0041
Corrosion rate (mpy)	HCl + inhibitor	33.94	28.28	26.39	22.62	18.55

Table 4: Weight loss and corrosion rate for brass alloy in 1MHCl absence and in presence of various concentrations of inhibitor.

Inhibitor conc. (M)	Weight loss (gm)	Corrosion rate (mpy)
0	0.0074	55.81
1×10^{-6}	0.0060	45.3
1×10^{-5}	0.0045	33.9
1×10^{-4}	0.0040	30.1
1×10^{-3}	0.0035	26.3

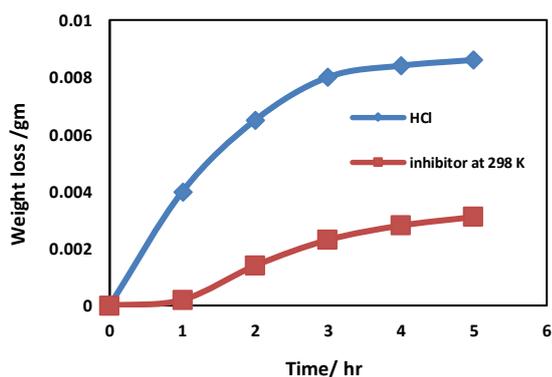


Fig. 5: Weight loss Vs. Exposure time at 298K.

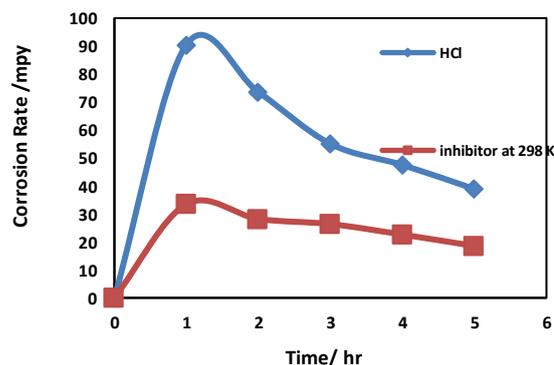


Fig. 6: Corrosion rate Vs. Exposure time at 298K.

Effect of temperature

To evaluate the adsorption of inhibitor and activation parameters of the corrosion process of brass alloy in an acidic medium, weight loss measurements were performed at (298,308,318)K, in the absence and presence of the inhibitor at a concentration (1×10^{-3} M) during 4 hr. immersion time. The variation of inhibition efficiency and Surface coverage with inhibitor with temperature are given in Figs. 9 and 10. The effect of temperature on the inhibited acid-metal reaction is very complex. Many changes such as rapid etching desorption of inhibitor, as well as inhibitor decomposition occur on the metal surface [32]. The results

revealed that, on increasing temperature, there is a decrease in inhibition efficiency for the compound used. Generally, the metallic corrosion in acidic media is accompanied by the evolution of hydrogen gas, and a rise in the temperature usually accelerates the corrosion reactions resulting in a higher dissolution rate of the metal [33]. A decrease in inhibitor efficiency with temperature can be attributed to the increased desorption of inhibitor molecules from the metal surface, or decreased adsorption process strength at elevated temperature suggesting a physical adsorption mode. Temperature investigations are also required, although they do not furnish all of the information

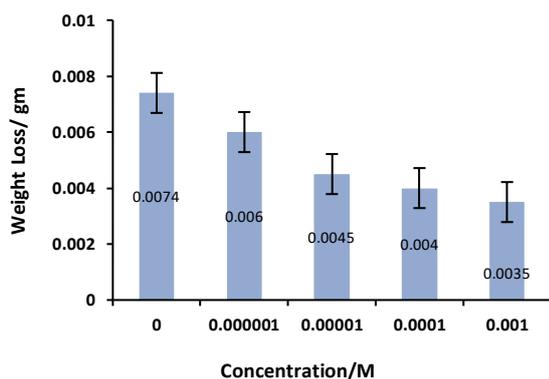


Fig. 7: Weight loss Vs. Concentration at 298K after 3hr. exposure time.

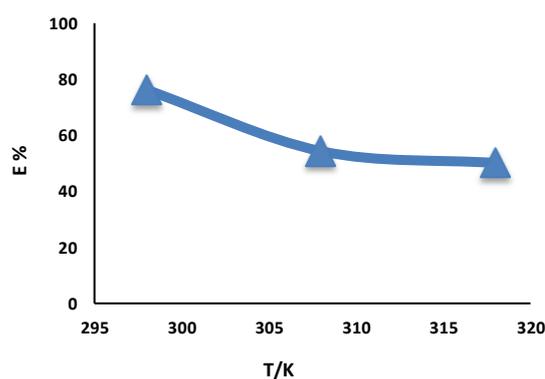


Fig. 9: Inhibition efficiency of inhibitor ($1 \times 10^{-3} M$) in 1M HCl at different temperatures after 3 hr. exposure.

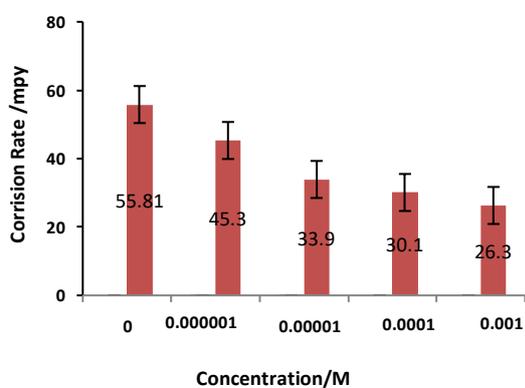


Fig. 8: Corrosion rate Vs. Concentration at 298K after 3hr. exposure time.

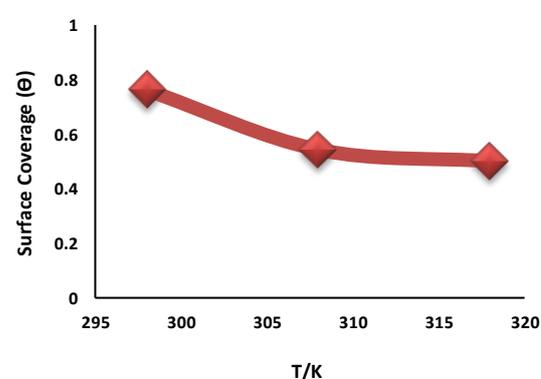


Fig. 10: Surface coverage with inhibitor ($1 \times 10^{-3} M$) in 1M HCl at different temperatures after 3hr. exposure time.

needed for the elucidation of adsorption character. There are cases in which chemical adsorption is accepted, although inhibition efficiency decrease with increasing temperature [34].

Thermodynamics parameters activation energy (E_a)

The values of activation energy (E_a) for brass alloy corrosion reaction were obtained from Arrhenius equation (4):

$$\text{Log} \frac{W_b}{W_a} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

Where W_a and W_b are corrosion rates at temperatures T_1 and T_2 , respectively and E_a is the apparent activation energy for corrosion process which represents the energy necessary for a molecule to possess in order to react [35]. The values of E_a are given in Table 5. It is found that E_a values for inhibited systems are higher than E_a for uninhibited systems. The increase in activation energy after the addition of the inhibitor to acid solutions can

indicate that physical adsorption (electrostatic) occurs in the first stage. Physical adsorption is small but significant because it is preceding stage of chemisorption of investigated organic compounds on brass alloy surface [36]. The increase in the activation energy indicates a strong adsorption of the inhibitor molecules on brass alloy surface.

Enthalpy and entropy of activation

The values of enthalpy and entropy of activation can be calculated from the alternative form of Arrhenius equation (5) as follows:

$$\text{Log} \frac{W}{T} = \left[\text{Log} \left(\frac{R}{Nh} \right) + \left(\frac{\Delta S^*_a}{2.303R} \right) \right] - \left(\frac{\Delta H^*_a}{2.303RT} \right) \quad (5)$$

Where h is Planks constant, N is Avogadro's number, ΔS^*_a is the entropy of activation, and ΔH^*_a is the enthalpy of activation. A plot of $\log CR/T$ versus $1/T$ should give straight lines (Fig. 11), with a slope of $(-\Delta H^*_a/2.303R)$,

Table 5: Thermodynamics parameters and activation energy for brass alloy dissolution in acid solution in absence and presence of inhibitor for the prepared compound (S1).

Parameter	Corrosion medium	
	HCl	HCl + Inhibitor
ΔH^*a kJ mol ⁻¹	44.75	53.72
E_a^* kJ mol ⁻¹	-78.20	-68.04
ΔS^*a J mol ⁻¹ K ⁻¹	-85.33	-48.13

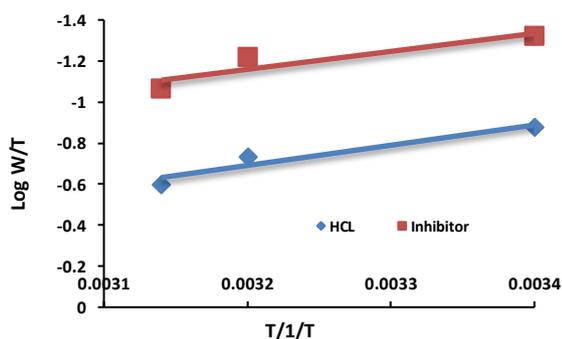


Fig. 11: Alternative Arrhenius plots of brass dissolution in 1M HCl in the absence and presence of 10⁻³ M of inhibitor.

and an intercept of $[\log(R/Nh) + (\Delta S^*a/2.303R)]$, from which the values of ΔH^*a and ΔS^*a were calculated, respectively. The value of ΔH^*a is reported in Table 5 and is positive. The positive sign of the enthalpy reflects the endothermic nature. Also, the value of entropy of activation is negative. The negative value of entropy implies that the activated complex in the rate determining step represents an association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactant to activated complex [37,38].

Adsorption isotherm

Basic information on the interaction between the inhibitor and the brass surface can be provided by the adsorption isotherm. The degree of surface coverage (θ) obtained from potentiodynamic polarization studies were used to explain the adsorption isotherm. In the present study, various adsorption isotherms are tested and it is found that the adsorption of inhibitor on the brass surface in hydrochloric acid medium follows the Langmuir adsorption isotherm, which is given by Eq. (1) [16]:

$$\frac{\theta}{1 - \theta} = K_{ads} \cdot C \quad (1)$$

Where C is the inhibitor concentration in mol dm⁻³, θ the surface coverage and K_{ads} is the equilibrium constant of adsorption process. The equilibrium constant for the adsorption process (K_{ads}) is related to the standard Gibbs free energy of adsorption (ΔG_{ads}) by Equation (2) [17]:

$$\Delta G_{ads} = -RT \ln (55.5 K_{ads}) \quad (2)$$

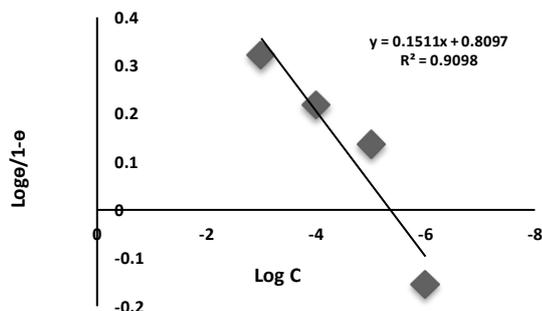
Where 55.5 mol/dm³ is the molar concentration of water in the solution, R is the gas constant and T is the absolute temperature [39]. The negative ΔG_{ads} values (Table 6) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface [40]. It has been reported [41] that the value of ΔG_{ads} up to -20 kJ/mol the adsorption was regarded as physisorption, the inhibition acts due to electrostatic interaction between the charged molecules and the charged metal.

Quantum chemical calculations

Quantum chemical calculation has been widely used to evaluate the inhibition performance of corrosion inhibitors, which can quantitatively study the relationship between inhibition efficiency and molecular reactivity [41–43]. With this method, the analysis of global reactivity parameters, such as the energy gap between HOMO and LUMO ($\Delta E_{LUMO - HOMO}$), Ionization Energy (I), Electron Affinity (A), Global Hardness (η), Electronegativity, Global Softness (σ) and Chemical potential (μ). The reactive abilities of Schiff base are closely related to their frontier molecular orbitals including the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). E_{HOMO} indicates the tendency of an organic molecule to donate electrons. The higher the value of E_{HOMO} , the greater the ability of a molecule to donate electrons while E_{LUMO} indicates the propensity of a molecule to accept electrons. The lower E_{LUMO} is the greater is the ability of that molecule to accept electrons. Thus, the binding ability of organics to the metal surface increases with an increase in energy of the HOMO and a decrease in the value of energy of the LUMO. The energy gap, ΔE , is an important parameter, which indicates the reactivity tendency of organics toward the metal surface [44,45]. In this study, quantum chemical calculations were conducted of the studied compound in order to support

Table 6: Parameters for adsorption of inhibitor in brass / inhibitor/1MHCl system at 298 K.

Temperature (K)	298
$K_{ads} \times 10^4 \text{ M}^{-1}$	1632.016
$\Delta G \text{ kJ mol}^{-1}$	-28.28
R^2	0.9098

**Fig. 12: Langmuir's adsorption plots for brass alloy in 1MHCl with various concentrations of compounds studied at 298K.**

experimental data and to investigate the relationship between molecular structure of the Schiff base and their inhibition effect. Frontier molecular orbital (HOMO and LUMO) theory is useful in predicting the adsorption centers of the inhibitor responsible for the interaction with metal surface [46,47]. The HOMO populations of the studied Schiff base were shown in Fig.13. The HOMO energy indicates the electron-donating ability of the molecule to an appropriated acceptor with empty molecular orbitals [48]. Therefore, increase in the values of E_{HOMO} can facilitate the adsorption and improve the inhibition efficiency. The corrosion rate decreases with increasing E_{HOMO} value (less negative). In the same way, low values of the ($\Delta E_{LUMO-HOMO}$) will provide good inhibition efficiencies, because the excitation energy to remove an electron from the last occupied orbital will be low [49]. The relationship between corrosion inhibition efficiency and HOMO energy, the inhibition efficiency increased with the E_{HOMO} rising. The band gap energy an important parameter as a function of reactivity of the inhibitor molecule toward the adsorption on metallic surface. As ΔE decreases, the reactivity of the molecule increases, leading to an increase in adsorption onto a metal surface. A molecule with low energy gap is more

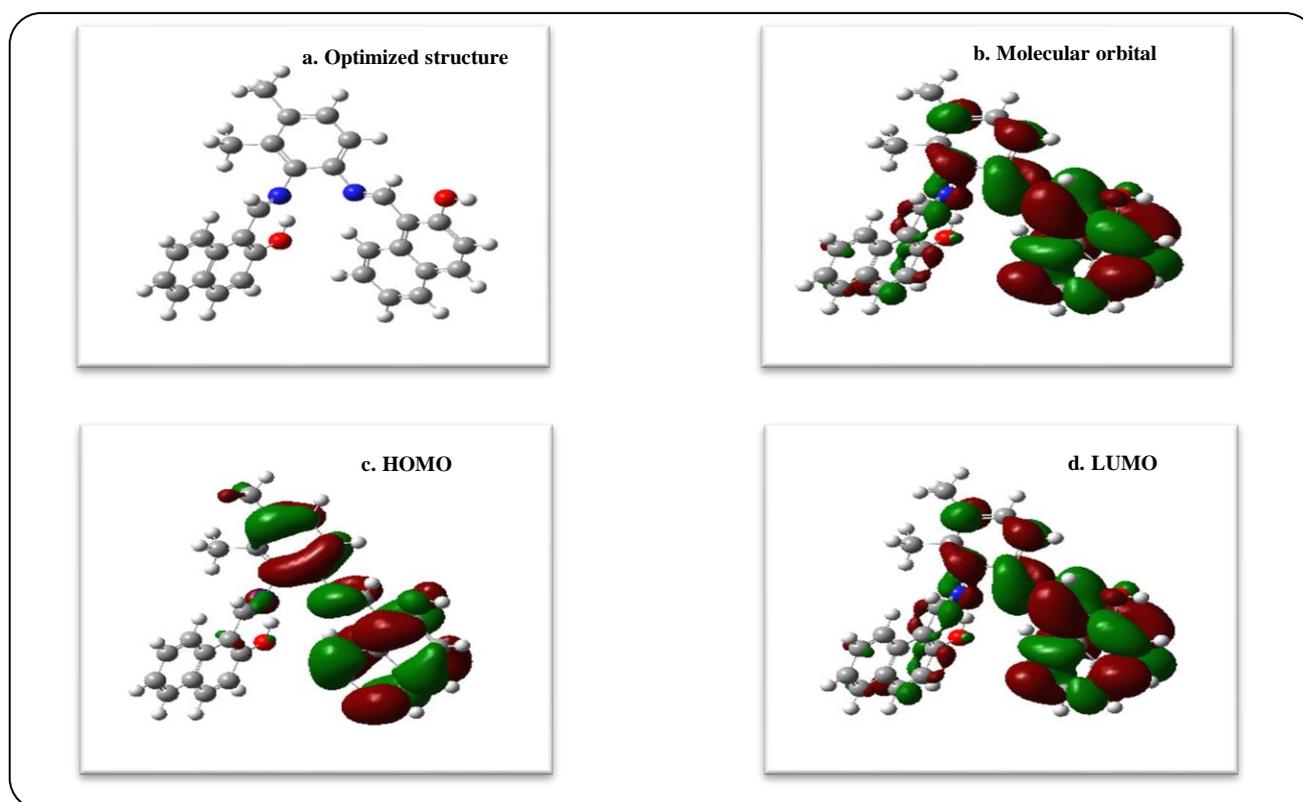
polarizable and is generally associated with high chemical reactivity and low kinetic stability. Thus, ΔE has been used in literature to characterize the binding ability of organics to the metal surface [50]. The reactivity of corrosion inhibitors may also be discussed in terms of chemical hardness and softness parameters. These quantities are often associated with the Lewis theory of acid and bases and Pearson's hard and soft acids and bases theory [51]; a hard molecule has a large ΔE and therefore is less reactive; a soft molecule has a small ΔE and is therefore more reactive. Adsorption occurs most probably at the region of the molecule where softness has the highest value [52]. Fig.13 shows the optimized geometry, the HOMO density distribution and the LUMO density distribution. Table 7 that the highest value of $E_{HOMO} = -7.351\text{eV}$ of the studied compound indicates the better inhibition efficiency. The lowest value of the $E_{LUMO} = -1.965\text{eV}$ indicates the easier of the acceptance of electrons from the d orbital of the metal. As ΔE decreases, the reactivity of the molecule increases leading to increase the inhibition efficiency of the molecule. The calculations indicate that our studied molecule has value of gap energy (5.386eV) which means the highest reactivity and accordingly the highest inhibition efficiency, which agrees well with the experimental observations. Absolute hardness and softness are important properties to measure the molecular stability and reactivity. Adsorption could occur at the part of the molecule where σ [53]. In a corrosion system, the inhibitor acts as a Lewis base while the metal acts as a Lewis acid. Bulk metals are soft acids and thus soft base inhibitors are most effective for acidic corrosion of those metals. In our present work, the studied molecule has softness value 0.371eV.

Antioxidant activity of the Schiff base (S_1)

Two major mechanisms are known for an antioxidant to deactivate radicals: (a) Hydrogen Atom Transfer (HAT) or (b) Single Electron Transfer (SET). DPPH radical test affords an easy and rapid mean to evaluate the antioxidants. Because that the DPPH is a stable free radical, purple colored, and containing an odd electron in its structure, it is usually employed for the detection of the radical scavenging activity in chemical analysis. The DPPH is converted to colorless after its reaction with the antioxidants. The degree of discoloration expresses the radical-scavenging ability of the antioxidant.

Table 7: Molecular properties of Schiff base obtained from the optimized structure using DFT at the B3LYP/6-31G.

Parameters	Value
E_{HOMO} (eV)	-7.351
E_{LUMO} (eV)	1.965 -
ΔE gap (eV)	5.386
$I = -E_{\text{HOMO}}$ (eV)	7.351
$A = -E_{\text{LUMO}}$ (eV)	1.965
$\chi = \frac{I+A}{2}$ (eV)	4.658
$\eta = \frac{I-A}{2}$ (eV)	2.693
$\mu = -\chi$	4.658-
$\sigma = \frac{1}{\eta}$	0.371

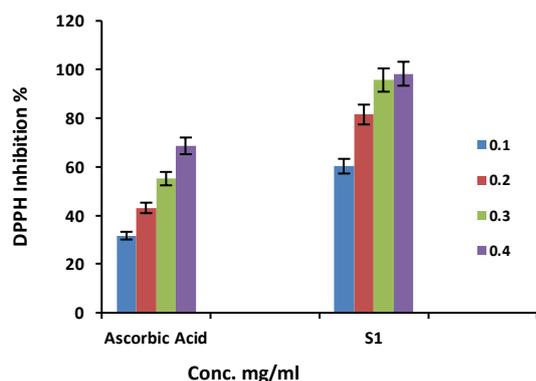
**Fig. 13: Optimized structure, molecular orbital and HOMO-LUMO of Schiff base (S_1).**

The reduction capability of DPPH radicals was evaluated from the decrease in its absorbance at 517nm induced by antioxidants. From the plot of the percentage scavenging ability of an antioxidant versus concentration, the data were obtained [54-56]. The antioxidant assay study was carried out using different concentrations of the Schiff base with DPPH radicals, while ascorbic acid, and was used as standard. The antioxidant activity of Schiff base (S_1), with the standard, was assessed (Table 7) on the basis of the free radical scavenging effect of the stable DPPH

free radical activity. They examined changes in the free radical the scavenging ability of the test samples on the basis of percent inhibition is presented in Fig. 10. The DPPH scavenging the activity of ligand is higher indicating that this is a much better/stronger free radical scavenger and antioxidant but lower when compared to ascorbic acid as standard. Radical scavenging the activity of S_1 , as well as the standards, was increased in a dose-dependent manner, the antioxidant ability of Schiff base (S_1), increased significantly with increase concentration.

Table 7: Values of inhibition of Schiff base (S₁)

Conc. mg.mL ⁻¹	DPPH inhibition %	Ascorbic acid
0.1	60.26	31.70
0.2	81.50	43.11
0.3	91.66	55.15
0.4	98.28	68.62

Fig. 14: Antioxidant of Schiff base (S₁).

The results revealed that the Schiff base (S₁) has good activity as a free-radical scavenger [57].

CONCLUSIONS

In the present study, the synthetic compound of [1,1'-(1E,1'E)-(4,5-dimethyl-1,2-phenylene)bis (azanylylidene) bis(methanylylidene))bis(naphthalen-2-ol)] shows good inhibitive properties for brass corrosion in 1M HCl solution. The results showed that two parameters have affected the inhibition efficiency. The first one was the temperature when it was observed that there was a clear increase with the temperature decrease. The second parameter was the concentration of the synthesized Schiff base. The increase in the concentration led to an apparent increase in the inhibition efficiency. The highest inhibition efficiency was obtained at a concentration of (1×10^{-3} M) for inhibitor at a temperature of 298 K. Moreover, it was concluded that the adsorption process of the inhibitor on the surface of the brass alloy obeyed to the Langmuir isotherm of adsorption. The value of the free energy change was calculated and found to be -28.28 KJ/mol. This indicated that the prepared compound was adsorbed on the surface of the metal by physical and chemical

interferences. The quantum mechanical approach may well be able to foretell molecule structures that are better for corrosion inhibition. The antioxidant activity of the phenolic Schiff base on the basis of the radical scavenging effect of 1,1-diphenyl-2-picryl-hydrazyl (DPPH) free radical activity was also investigated. The Schiff base (S₁) exhibited excellent activity.

Received : Jul. 29, 2021 ; Accepted : Nov. 29, 2021

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