

Experimental and Theoretical Investigation of Clemastine Drug for Corrosion Protection of Carbon Steel in Sulfuric Acid Solution

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ABSTRACT

*P*olarization and electrochemical impedance spectroscopy (EIS) were employed for investigating the behavior of clemastine drug on the corrosion protection of carbon steel in 0.5 M H_2SO_4 solution which was enhanced by increasing the clemastine concentration in acid solution. As evidenced by polarization data, clemastine behaved as a mixed-type inhibitor and retards both anodic and cathodic processes. Adsorption of clemastine on carbon steel in acid solution obeyed the Langmuir adsorption isotherm. A reasonable correlation was observed between the ΔG°_{ads} values obtained from EIS and potentiodynamic polarization measurements. The calculated ΔG°_{ads} values of clemastine confirmed comprehensive adsorption that is a combination of physical and chemical adsorption. The electronic properties of clemastine were calculated via density functional theory (DFT) approach to establish the relationship between the inhibitive effect and molecular structure of the clemastine. According to the obtained quantum chemical parameters, clemastine showed higher E_{HOMO} , lower E_{LUMO} , lower energy gap, and higher dipole moment than some inhibitors earlier reported as good corrosion inhibitors. Prog. Color Colorants Coat. 15 (2022), 37-44 © Institute for Color Science and Technology.

1. Introduction

Corrosion may be defined as an unintentional attack on a material through reaction with the surrounding medium. It is necessary to devote more attention to metallic corrosion nowadays, due to the growing usage of metals within different fields of technology and also the usage of rare and expensive metals for special applications such as atomic energy field. On the other hand, more corrosive environments due to the increasing of air and water pollution necessitate more corrosion control in recent years. There are different materials for corrosion protection such as conducting polymer coatings and

corrosion inhibitors [1-4]. Compounds which decrease the reaction of metallic surfaces with the corrosive media are called corrosion inhibitors. Acid solutions that are used in a wide variety of industrial applications require the inhibitors to reduce their aggressivity [4-16]. Application of sulfuric acid for steel surface treatment is relate to its lower cost and non-corrosive nature of the sulfate ion. However, corrosion inhibitors may cause some negative effects on the environment. Thus, it is important to develop novel inhibitors from both natural sources and non-toxic or low-toxic compounds [5-8]. In this way, many researchers have tried to develop drugs

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as inhibitors for corrosion protection of metallic surfaces [4, 8-16]. Eddy et al. studied the inhibition effects two penicillin compounds as corrosion inhibitors for carbon steels based on physical adsorption [9, 10]. The corrosion protection of stainless steel in hydrochloric solution by ampicillin and benzylpenicillin (penicillin G) has been investigated by Fouda et al. [11]. The inhibition effect of amoxicillin on carbon steel in 1 M sulfuric acid was studied by Kumar et al. [12]. Soltaninejad et al. found that penicillin G showed the best inhibition effect on mild steel at 10 mM concentration in 3.0 M H_3PO_4 solution using potentiodynamic polarization and EIS techniques [4]. Golshani et al. evaluated metoclopramide tablet as corrosion inhibitor for mild steel in sulfuric acid and hydrochloric acid solutions [13]. The effect of penicillin G benzathine drug as green corrosion inhibitor for mild steel in 1.0 M hydrochloric acid solution was studied by Gholamhosseinzadeh et al. [14]. Abdollahi et al. investigated the inhibition effects of meloxicam drug on mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 solutions [15].

In the present paper, the corrosion protection effect of clemastine as corrosion inhibitor was investigated on the corrosion of carbon steel in 0.5 M H_2SO_4 solution by employing potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques.

2. Experimental

2.1. Materials

Concentrated H_2SO_4 solution was obtained from Merck Co. The chemical structure of clemastine is illustrated in Figure 1. Carbon steel with the surface area of 100 mm^2 was used as working electrodes (Wes). The chemical composition of carbon steel was (wt.%): Mn (0.73), C (0.15), Si(0.72) and Fe (balance).

2.2. Methods

The inhibition effect of different concentrations of clemastine on carbon steel was investigated in 0.5 M H_2SO_4 solution by potentiodynamic polarization and EIS techniques. After connecting a copper wire to the

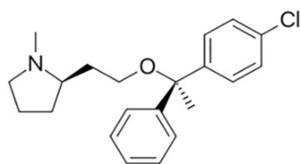


Figure 1: Structure of clemastine.

specimen, it was embedded in a PVC holder using epoxy resin except one side so that this side acted as the surface of the working electrode. Steel samples were polished using SiC emery papers through 600-2500 grades, and then rinsed with distilled water, degreased with ethanol, and dried in air.

2.3. Characterization

Potentiostat/galvanostat Autolab 302N (Eco Chemie, Netherlands) was employed to conduct the potentiodynamic polarization and EIS measurements. Saturated (KCl) Ag/AgCl and platinum rod (100 mm^2) were used as the reference and the counter electrodes (CE), respectively. Three-electrode arrangement was employed to conduct the electrochemical measurements. Each sample was soaked for 30 min in the test solution before measurement to obtain stabilized open circuit potential (OCP).

The EIS measurements were performed at OCP over a frequency range of 100 kHz to 10 mHz. The amplitude of sinusoidal potential perturbation was 5 mV. Nova in amplitude. 1.9 software was employed for analyzing the Nyquist plots of the impedance data. Polarization experiments were done potentiodynamically at the scan rate of 1 mV/s in the potential range of ± 250 mV versus OCP. Polarization data were also analyzed by Nova 1.9 software.

Quantum chemical calculations were employed to determine the reactivity descriptors such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), dipole moment, and the energy gap. These calculations were executed with Gaussian 09 program package using DFT/ (B3LYP) with a basis set of 6-311+G (d,p).

3. Results and Discussion

3.1. Polarization measurements

Polarization plots obtained for carbon steel soaked in 0.5 M H_2SO_4 solution in the absence and presence of various amounts of clemastine are presented in Figure 2.

The polarization parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a , β_c) are listed in Table 1. The i_{corr} decreased as the amount of clemastine increased. Two branches of the potentiodynamic polarization curves were affected by the addition of clemastine to acid medium. Therefore, it is clear that clemastine behaved as a mixed corrosion inhibitor.

Table 1: Polarization parameters and the corresponding inhibition efficiencies for carbon steel in 0.5 M H₂SO₄ solution with different concentrations of clemastine at 25 °C.

C (ppm)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	$-E_{corr}$ (mV)	β_a (mV.dacade ⁻¹)	β_c (mV.dacade ⁻¹)	IE _P (%)
0	699	493	82	142	-
100	140	446	82	123	80.0
200	106	468	90	133	84.8
300	69	446	96	126	90.1
400	59	449	92	124	91.6
500	51	441	78	125	92.7

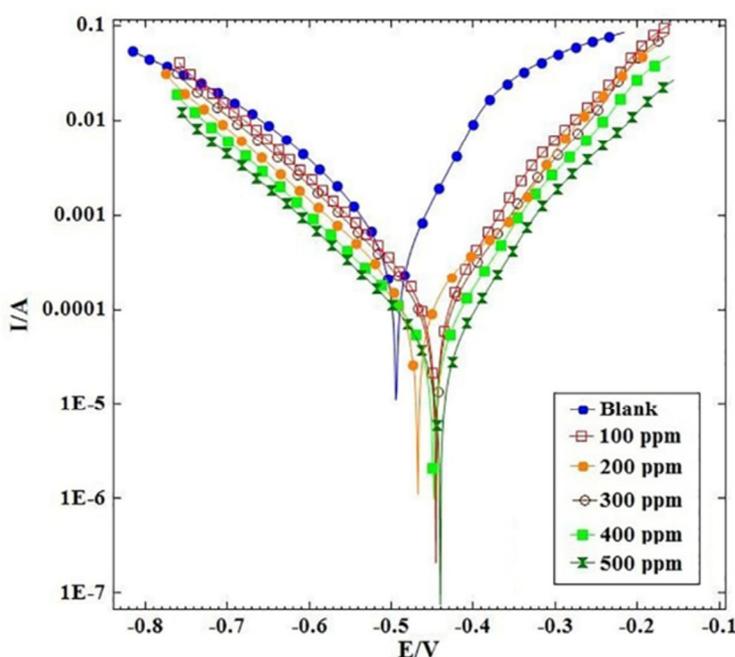


Figure 2: Polarization curves for carbon steel in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations of clemastine at 25 °C.

The inhibition efficiency (IE) values listed in Table 1 were obtained from the following equation (Eq. 1) [17]:

$$IE_P(\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \quad (1)$$

where i_{corr} and i'_{corr} are the corrosion current densities under uninhibited and inhibited conditions, respectively. It is clear that the increase in clemastine concentration increased the IE value. The IE values showed a considerable increase with the increase in clemastine concentration, suggesting that the

adsorption of clemastine on the steel surface effectively retarded the corrosion.

It can be seen that an increase in the concentration of clemastine is accompanied by a decrease in the corrosion current (i'_{corr}) and a corresponding increase in the inhibition efficiency. The increase in the IE value is due to the increased surface coverage (θ) by clemastine [18]. After obtaining surface coverage values by $\theta = IE/100$ equation, an attempt was made to test the Langmuir, Frumkin, Temkin and Freundlich isotherms. The Langmuir adsorption isotherm was found to fit well with the experimental data (Figure 3), which can be expressed as (Eq. 2 and 3):

$$\theta = \frac{KC}{1+KC} \quad (2)$$

or:

$$\frac{C}{\theta} = C + \frac{1}{K} \quad (43)$$

where θ is the surface coverage, C is the inhibitor concentration, and K is the adsorption equilibrium constant. As shown in Figure 3, C/θ plots versus C show a straight line with a correlation coefficient close

to 1.0 which confirms the Langmuir behavior of the clemastine adsorption on the carbon steel surface.

3.2. Impedance measurements

Nyquist diagrams for carbon steel in H_2SO_4 solution without clemastine (blank sample) and with various concentrations of clemastine are presented in Figure 4. It is clear that the impedance values of carbon steel are increased with increasing the amount of clemastine.

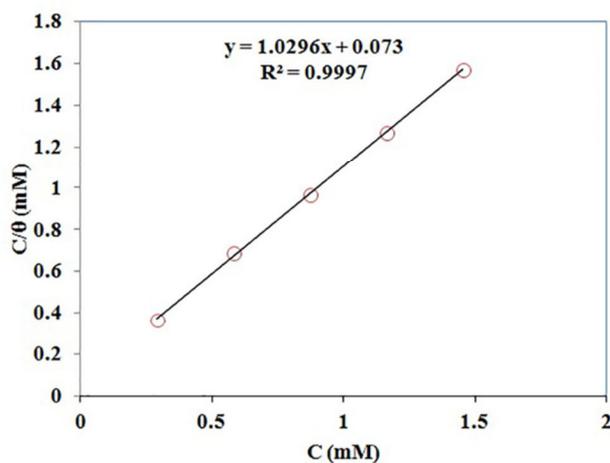


Figure 3: Langmuir adsorption isotherm of the inhibitor in 0.5 M H_2SO_4 solution by using surface coverage values calculated by Tafel polarization results.

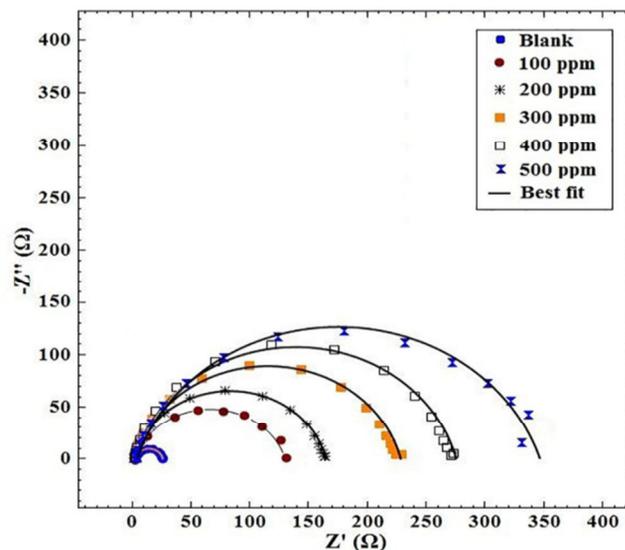


Figure 4: Nyquist plots for carbon steel in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of clemastine at 25 °C.

The impedance data have been fit to the Randles circuit. Solution and charge transfer resistances are represented by R_s and R_{ct} , respectively. The constant phase element (CPE) is characterized by the CPE constant, Y_0 , and the CPE exponent, n . The following equation was employed for determining the impedance of CPE (Eq. 4) [19, 20]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (4)$$

where j equals $\sqrt{-1}$ and ω is the angular frequency.

The impedance parameters obtained from EIS measurements in the absence (blank sample) and presence of different concentrations of clemastine are listed in Table 2. It can be seen that the R_{ct} values are increased with increasing the clemastine concentration.

The following equation was employed for the calculation of inhibition efficiencies in Table 2 (Eq. 5):

$$IE_{EIS}(\%) = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \quad (5)$$

where R_{ct} and R'_{ct} represent the charge transfer resistance of carbon steel in the acidic media without and with clemastine, respectively. The increase in clemastine concentration caused an increase in the inhibition efficiency. According to Tables 1 and 2, a good agreement can be observed between the IE values obtained from the EIS and polarization techniques. EIS plots shown in Figure 5 prove that the adsorption of clemastine on the steel surface follows the Langmuir isotherm. Thus, the EIS results are in good agreement with the polarization results which confirm the Langmuir behavior of the adsorption.

Table 2: Impedance parameters and the corresponding inhibition efficiency values for carbon steel in 0.5 M H_2SO_4 solution with different concentrations of clemastine at 25 °C.

C (ppm)	R_s ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	n	$10^6 Y$ ($\Omega^{-1}.cm^{-2}$)	IE_{EIS} (%)
0	1.8	24	0.906	230	-
100	2.0	128	0.825	39	81.2
200	1.5	163	0.866	37	85.3
300	2.1	226	0.854	33	89.4
400	2.2	273	0.851	30	91.2
500	3.5	343	0.811	28	93.0

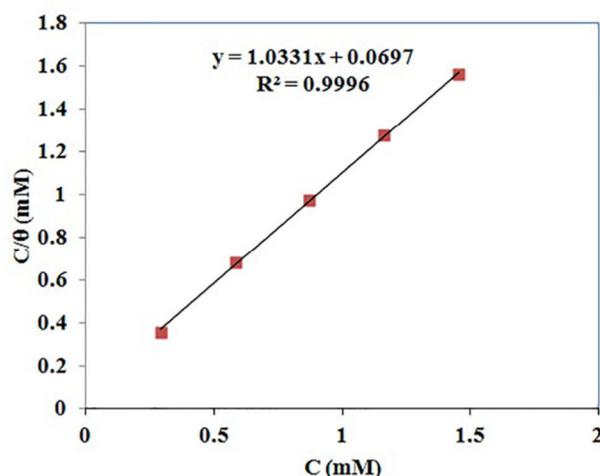


Figure 5: Langmuir adsorption isotherm of the inhibitor in 0.5 M H_2SO_4 solution by using surface coverage values calculated by EIS results.

The adsorption equilibrium constant, K_{ads} , can be determined from the reciprocal of the intercept of the isotherm line shown in Figure 3. The following equation can be used for determining the free energy of the adsorption of inhibitor on carbon steel surface (Eq. 6);

$$\Delta G^{\circ}_{ads} = -RT \ln(K_{ads}) \quad (6)$$

Table 3 lists the K_{ads} and ΔG°_{ads} values for clemastine obtained from Langmuir isotherms through polarization and impedance measurements. A good agreement is observed for ΔG°_{ads} values determined from the polarization and EIS techniques.

Electrostatic interactions between the clemastine molecules and the charged steel surface, known as physisorption, lead to the ΔG°_{ads} values less negative than -20 kJ.mol^{-1} . On the other hand, formation of a coordinate bond between the steel and clemastine molecules, known as chemisorption, leads to the ΔG°_{ads} values more negative than -40 kJ.mol^{-1} [21]. The calculated ΔG°_{ads} values in the present work are between these two cases, confirming the comprehensive adsorption which involves both physical and chemical adsorption.

3.3. Theoretical study

To understand the interaction of clemastine with carbon steel, quantum chemical calculations were carried out using density functional theory (DFT) method. Generally, the adsorption of an organic

inhibitor molecule on a metal surface is reported to occur based on donor-acceptor interactions between the π -electrons of the organic inhibitor and the orbital of the metal atom [22]. Thus, the energies of HOMO and LUMO of the inhibitor molecule are very important in discussing its interaction with a metal surface. The vacant orbital of Fe atom can interact with the HOMO of the inhibitor, while the 4s orbital of Fe atom interacts with the LUMO of the inhibitor. The inhibitor molecule with more HOMO energy (less negative) tends to be more donating and that with the lower LUMO energy (more negative) tends to be more accepting. Therefore, the inhibition efficiency increases by increasing the HOMO energy and decreasing the LUMO energy. Furthermore, with decreasing the energy gap (ΔE) between HOMO and LUMO, the interactions between the inhibitor molecule and metal atom become stronger, resulting in higher inhibition efficiency [23]. The quantum chemical parameters are presented in Table 4.

As can be seen from the quantum chemical parameters given in Table 5, clemastine has higher E_{HOMO} , lower E_{HOMO} , lower energy gap, and higher dipole moment than some inhibitors earlier reported as good corrosion inhibitors [24-27]. It has been reported that increasing the dipole moment facilitates adsorption, thus increasing the inhibition efficiency. However, there are some inconsistencies in the reported correlations between dipole moment and inhibition efficiency in the literature [23, 28].

Table 3: K_{ads} and ΔG_{ads} values corresponding to polarization and EIS data for carbon steel in 0.5 M H_2SO_4 solution containing clemastine.

Drug	Tafel		EIS	
	K_{ads} (M^{-1})	ΔG_{ads} (kJ.mol^{-1})	K_{ads} (M^{-1})	ΔG_{ads} (kJ.mol^{-1})
Cle	13699	-33.5	14347	-33.7

Table 4: The calculated quantum chemical parameters for clemastine.

Method	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (D)
DFT	-5.627	-0.806	4.821	3.555

Table 5: Comparison of quantum chemical parameters of clemastine inhibitor with some corrosion inhibitors reported earlier.

Inhibitor	E_{HOMO} (ev)	E_{LUMO} (ev)	ΔE (ev)	μ (D)	Ref.
Aminotriazole	-10.395	0.438	10.833	1.2	[34]
Triazole	-9.309	0.106	9.415	2.9	[34]
Benzotriazole	-8.433	-0.571	7.862	3.8	[34]
2,3-diaminonaphthalene	-8.16	0.14	8.02	2.9	[35]
C-1 ^a	-9.645	-0.165	9.480	0.803	[36]
C-2 ^b	-9.295	0.222	9.517	1.32	[36]
Ketoprofen	-10.86	-0.21	10.65	20.75	[37]
Clemastine	-5.627	-0.806	4.821	3.555	This work

[a] dibenzo-bis-imino crown ether

[b] dibenzo-diaza crown ether

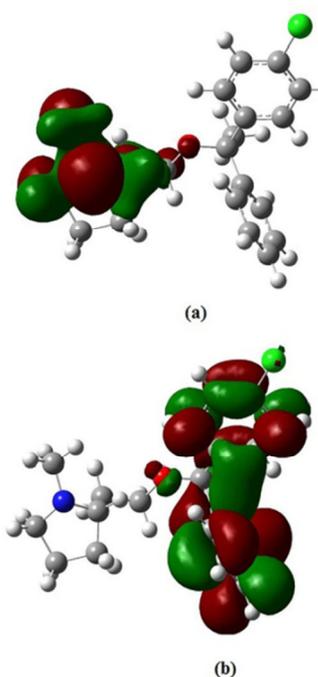


Figure 6: The frontier molecular orbitals; (a) HOMO and (b) LUMO for clemastine obtained using DFT method.

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Figure 6 shows the Frontier orbital energy distributions of the HOMO and LUMO for clemastine. The reactive ability of the inhibitor is closely related to the Frontier molecular orbitals (HOMO and LUMO). As can be seen in Figure 6(a), the HOMOs of clemastine are largely delocalized over the nitrogen atom. It can be seen from Figure 6(b) that the electronic distributions of LUMO are mostly located on the aromatic rings of clemastine. These results prove that the most active sites of clemastine are probably located around these regions.

4. Conclusion

The effect of corrosion inhibition of clemastine on carbon steel in 0.5 M H_2SO_4 solution was studied by polarization and EIS techniques. Polarization data showed that the Langmuir isotherm can describe the adsorption of clemastine on the carbon steel surface. The results extracted from the polarization data were in good agreement with those obtained from EIS data. The relationship between the inhibitive effect and molecular structure of clemastine was established using the electronic properties of clemastine calculated by the DFT approach.

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