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## CAFFEINE AS A CORROSION INHIBITOR OF MILD STEEL IN HYDROCHLORIC ACID

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### Abstract

Corrosion inhibition of mild steel in 1 M HCl was investigated in the absence and presence of different concentrations of Caffeine. Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques were employed. Impedance measurements showed that the double-layer capacitance decreased and charge-transfer resistance increased with increase in the inhibitor concentration and hence increasing in inhibition efficiency. Potentiodynamic polarization study showed that the inhibitor act as cathodic-type inhibitor. The inhibitor was adsorbed on the steel surface according to the Langmuir adsorption isotherm model and quantum calculation parameters (dipole moment,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and  $\Delta E$ ). It was concluded that the high corrosion inhibition efficiency of Caffeine was associated with its strong adsorption as a barrier film on the mild steel surface. E (%) values obtained from various methods used are in good agreement.

**Keywords:** Mild steel; Caffeine; Inhibition; Corrosion; HCl; DFT.

### 1. Introduction

Corrosion of mild steel has been a major concern in industry because it resulted into huge economic losses and environmental pollution. The use of organic molecules as inhibitors to protect/prevent metal from corrosion in acidic media has attracted the interest of researchers [1-5]. The corrosion inhibition is a surface process which involves the adsorption of the organic compounds on metal surface [6]. Organic compounds containing polar groups by which the molecule can become strongly or specifically adsorbed on the metal surface constitute most organic inhibitors [7-10]. These inhibitors, which include the organic N, P, S, and OH groups, are known to be similar to catalytic poisons, as they decrease the reaction rate at the metal/solution interface without, in general, being involved in the reaction considered. It is generally accepted that most organic inhibitors act via adsorption at the metal/solution interface [11-15].

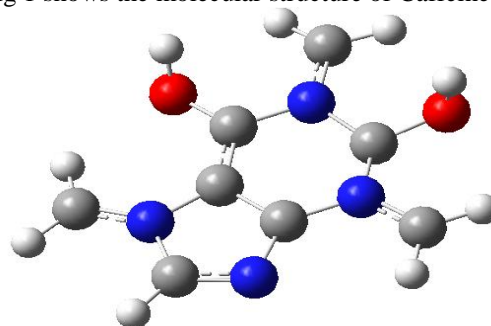
This present paper deals with the study of the inhibitory action of caffeine on mild steel 1.0 M HCl solution. The corrosion protection effect of Caffeine was investigated by means of weight loss measurement, potentiodynamic polarisation, and electrochemical impedance spectroscopy (EIS). Quantum chemical calculations are also employed

to provide additional insight into the mechanism of the inhibitory action.

### 2. Experimental

#### 2.1. Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of Caffeine inhibitor employed was  $10^{-6}$  –  $10^{-3}$  (M). Caffeine 98% were obtained from ACROS ORGANICS Reagent Company of USA. Fig 1 shows the molecular structure of Caffeine.



**Figure 1:** Chemical structure of Caffeine.

#### 2.2. Weight loss measurements

Coupons were cut into  $1.5 \times 1.5 \times 0.05 \text{ cm}^3$  dimensions having composition (0.09 % P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S

and Fe balance) used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 400, 800, 1000, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 100 cm<sup>3</sup>. The immersion time for the weight loss is 6 h at (308±1) K. In order to get good reproducibility, experiments were carried out in duplicate. The average weight loss was obtained. The corrosion rate (**V**) is calculated using the following equation:

$$V = \frac{W}{S \times t} \quad (1)$$

where W is the average weight loss, S the total area, and t is the immersion time. With the corrosion rate calculated, the inhibition efficiency (**E<sub>w</sub>**) is determined as follows:

$$E_w \% = \frac{V_o - V}{V_o} \times 100 \quad (2)$$

where **V<sub>0</sub>** and **V** are the values of corrosion rate without and with inhibitor, respectively.

### 2.3. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltmaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from -800 mV to -200 mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen. Inhibition efficiency (**E<sub>p</sub>**%) is defined as Eq. 3, where **i<sub>corr(0)</sub>** and **i<sub>corr(inh)</sub>** represent corrosion current density values without and with inhibitor, respectively.

$$E_p \% = \frac{i_{corr(0)} - i_{corr(inh)}}{i_{corr(0)}} \times 100 \quad (3)$$

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltlab PGZ100 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest

potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Inhibition efficiency (**E<sub>R</sub>**%) is estimated using the relation 4, where **R<sub>i(0)</sub>** and **R<sub>i(inh)</sub>** are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

$$E_R \% = \frac{R_i(inh) - R_i(0)}{R_i(inh)} \times 100 \quad (4)$$

### 2.4 Quantum chemical calculations

For the theoretical study, complete geometry optimizations of the molecules were performed using the Density Functional Theory (DFT) with the Beck's three parameter exchange functional and the Lee-Yang-Parr non-local correlation functional (B3LYP) with 6-311G(d,p) basis set of atomic orbital's as implemented in Gaussian 03 program package [15].

Some electronic properties such as energy of the highest occupied molecular orbital (**E<sub>HOMO</sub>**), energy of the lowest unoccupied molecular orbital (**E<sub>LUMO</sub>**), energy gap (**ΔE**) between LUMO and HOMO, dipole moment and Mulliken charges on the backbone atoms were determined. The optimized molecular structures and HOMO, LUMO surfaces were visualized using Gauss View [16].

## 3. Results and discussion

Mild steel corrosion behavior in 1 M HCl was investigated in the absence and presence of Caffeine derivatives with the help of weight loss and electrochemical techniques. It was seen that mild steel dissolution rate was very high in 1 M HCl alone but presence of inhibitor significantly decreased the corrosion rate of mild steel.

### 3.1. Weight loss measurements

The effect of addition of Caffeine at different concentrations on the corrosion of mild steel in 1.0 M HCl solution was studied by weight loss at 6 h. Table 1 gathers the values deduced of **W<sub>corr</sub>** and the inhibition efficiency (**E<sub>w</sub>**%).

Inhibitor	C (M)	C <sub>R</sub> (mg.cm <sup>-2</sup> .h <sup>-1</sup> )	E <sub>w</sub>
1M HCl	-	0.82	---
Caffeine	10 <sup>-6</sup>	0.22	73
	10 <sup>-5</sup>	0.18	78
	10 <sup>-4</sup>	0.15	82
	10 <sup>-3</sup>	0.07	91

**Table 1:** Corrosion rate and inhibition efficiency in the absence and presence of Caffeine in 1.0 M HCl solution at 35°C.

Table 1 indicates clearly a decrease in the corrosion rate in the presence of Caffeine. This effect is hugely marked at higher concentration of inhibitor. The inhibitive action is more explicit by  $E_w\%$  data which increases with inhibitor concentration to reach 91% at  $10^{-3}M$ . Then Caffeine inhibitor studied inhibit the corrosion of mild steel in 1.0 M HCl is found to exhibit the best inhibitory action.

### 3.2. Polarization results

Anodic and cathodic polarization curves for mild steel in 1.0 M HCl with and without various concentrations of used inhibitor are shown in Figures 2.

Various corrosion parameters such as corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ) and the inhibition efficiency ( $E\%$ ) were determined by Tafel extrapolation method[17] and are given in Table 2.

This result suggests that Caffeine addition reduces anodic dissolution and also retards the hydrogen evolution reaction. It is seen that Caffeine addition decreases  $I_{corr}$  significantly. Also a slight decrease of the corrosion potential to more negative values in the presence of the inhibitor is explained by the catalytic action of Caffeine on anodic branches. We may conclude that the Caffeine acts as a cathodic type inhibitor.

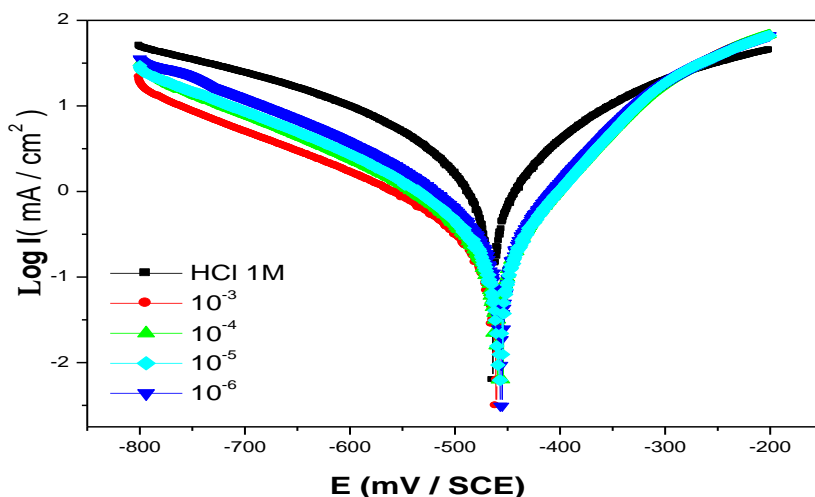


Figure 2: Tafel plot of mild steel with different concentrations of Caffeine in 1M HCl solution.

Inhibitor	C (M)	$E_{corr}$ (mV)	$I_{corr}$ ( $\mu A/cm^2$ )	$-\beta_c$	$\beta_a$	$E_p$ (%)
1M HCl	---	-464	1386	184	135	---
Caffeine	$10^{-6}$	-457	231	128	76	83
	$10^{-5}$	-458	170	128	73	88
	$10^{-4}$	-463	154	135	74	89
	$10^{-3}$	-460	138	152	71	90

Table 2: Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 1M HCl without and with addition of various concentrations of Caffeine at 35°C.

### 3.3. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is commonly used technique in corrosion researches to explain the mechanisms and adsorption phenomena [18,19]. Especially, in inhibition studies, a single semi-circular shape is observed for mild steel in acidic media. As in previous studies [20–21], the parallel results were detected in EIS data. The EIS results and equivalent circuit were presented in Figs. 3 and 4, respectively.

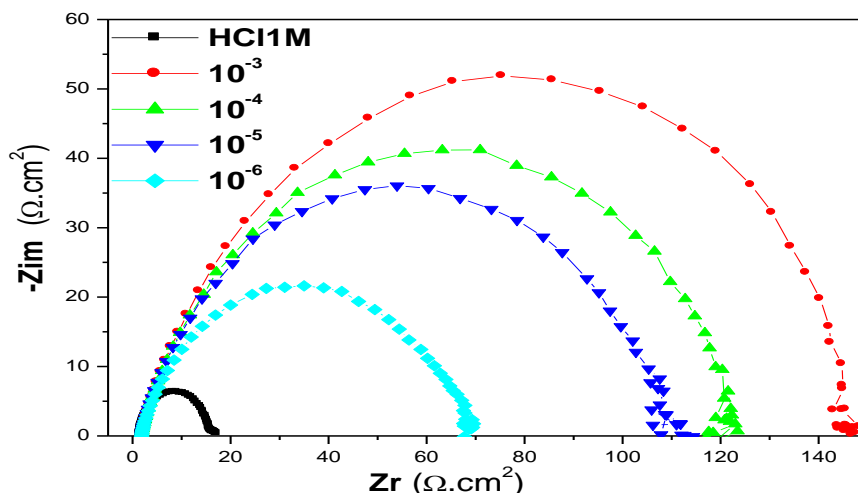


Figure 3: Nyquist plot at different concentrations of Caffeine in 1M HCl solution.

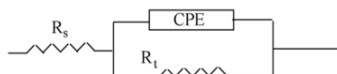


Figure 4: Electrical equivalent circuit model used for the modeling metal/solution.

The diameter of Nyquist plot shows the difference in real impedance at lower and higher

frequencies. The CPE is the constant phase element which is used in place of double layer capacitance ( $C_{dl}$ ) to give non-ideal capacitive behavior [22]. In Fig. 3, Nyquist plots for mild steel in 1 M HCl solution with, and without different concentrations of the Caffeine were seen. The Nyquist plots were detected as one part of a semicircle.

Inhibitor	C (M)	$R_t$ $\Omega$ cm <sup>2</sup>	$R_b$ $\Omega$ cm <sup>2</sup>	F Htz	C $\mu$ f/cm <sup>2</sup>	E (%)
Blank	-	14.57	1.37	54.64	200	--
Caffeine	$10^{-6}$	69	1.53	24.52	94.12	79
	$10^{-5}$	108	1.68	20.03	73.62	87
	$10^{-4}$	122	1.67	19.35	67.47	88
	$10^{-3}$	148	1.68	16.60	64.83	90

Table 3: Impedance parameter values for the corrosion of mild steel in 1M HCl.

Results obtained show that  $R_t$  increases and  $C_{dl}$  tends to decrease when the concentration of inhibitor increases. A decrease in the  $C_{dl}$  values, which can result from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the Caffeine functions by adsorption at the metal solution/interface [23-24].

### 3.4. Adsorption isotherm

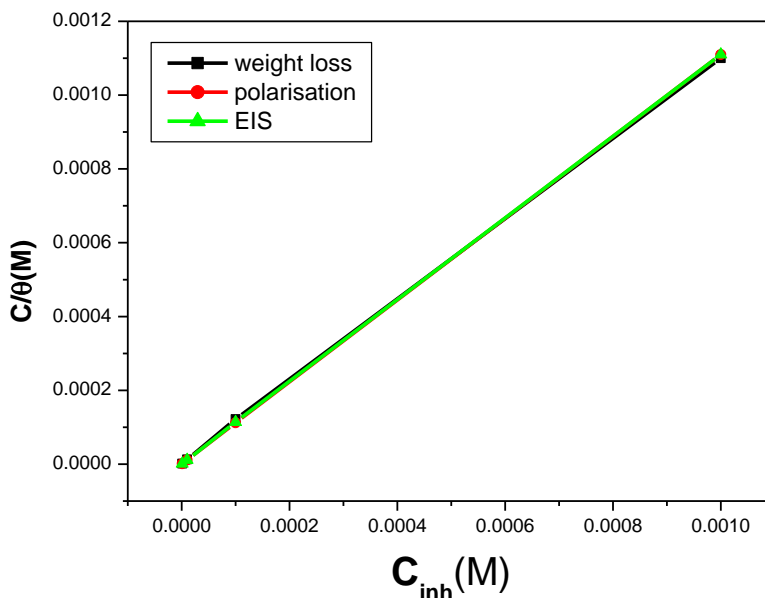
The interactions of Caffeine inhibitor and the mild steel surface can be examined by the adsorption isotherm. The degree of surface coverage values ( $\theta$ ) for various concentrations of the inhibitors in the solution have been estimated from the different techniques measurements

(Tables 1, 2 and 3). Suitable adsorption isotherm was obtained, using these calculated values. The linear relationships of  $C/\theta$  versus  $C$ , as shown in Fig 4, suggest that the adsorption of Caffeine on the mild steel obeyed the Langmuir adsorption isotherm. This isotherm can be represented as [25]:

$$C/\theta = 1/K_{ads} + C, \tag{5}$$

$$\theta = E/100. \tag{6}$$

The degree of surface coverage of each inhibitor at a given concentration can be calculated using the above equation (6). The strong correlation ( $R^2=0.99$ ) of the Langmuir adsorption isotherm for Caffeine was observed. Fig.5. depicts the graph of the Langmuir adsorption isotherm for the studied compound.

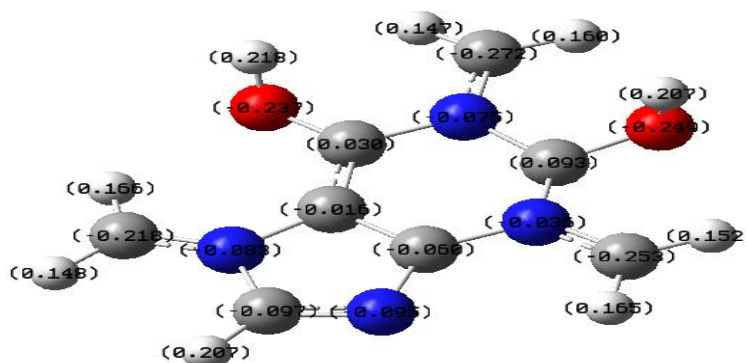


**Figure 4:** Experimental results at 308 K according to the Langmuir adsorption isotherm for Caffeine by various methods.

### 3.5. Theoretical calculations

To obtain detailed information about the inhibition mechanism, quantum theoretical calculations were performed and compared with the experimental results. We aimed to find good theoretical parameters to characterize the inhibition property of the Caffeine and realize the acidic medium. We optimized Caffeine at both

neutral forms. The Mulliken charges, HOMO and LUMO orbital's of optimized Caffeine are given in Fig. 5, respectively. The Mulliken charge of atoms in inhibitor molecule is defined the adsorption center. In this figure, the highest negative charge was located on (5) N atom. Adsorption may occur on N (-0.035) and O (-0.237) atoms.



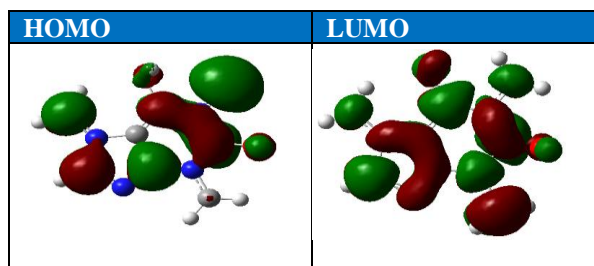
**Figure 5:** Optimized molecular structures of Caffeine with Mulliken charge.

According to frontier orbital theory, the reaction of reactants mainly occurred on the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). So it was imperative to investigate the distribution of HOMO and LUMO for exploration of inhibition mechanism. From Figs. 6 and 7, it could be seen that caffeine has similar HOMO and LUMO

distributions, which were all located on N and O atoms.

This kind of distribution favored the preferential adsorption of Caffeine ring on metal surface in two ways: one was the unoccupied d orbital's of Fe atom accepted electrons from inhibitor molecule to form coordinate bond. The other was the inhibitor molecule accepted

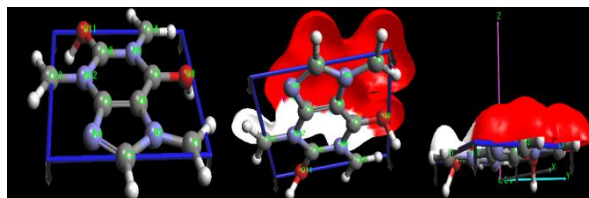
electrons from Fe atom with its anti-bonding orbital's to form back-donating bond [26].



**Figure 6:** The frontier molecular orbital density distribution of Caffeine.

Another important parameter to measure reactivity of the inhibitor molecule towards the adsorption on the metallic surface is the energy gap,  $\Delta E$  ( $\Delta E = E_{LUMO} - E_{HOMO}$ ); decreasing in  $\Delta E$  of the molecule leads to increasing in the %IE of the molecule because lesser/lower energy would be required to remove an electron from the last occupied orbital.

A molecule with a low energy gap is usually more polarisable with high chemical activity, low kinetic stability and high softness value [27]; thus Caffeine with low  $\Delta E$  value (0.073eV) and higher dipole moment (3.3858 Debye) (table 5) has better performance as a corrosion inhibitor.



**Figure 7:** Schematic interaction of on the metallic surface during corrosion inhibition process by Caffeine.

Quantum parameters	Caffeine
$E_{HOMO}$ (eV)	-0.223
$E_{LUMO}$ (eV)	-0.150
$\Delta E_{gap}$ (eV)	0.073
$\mu$ (debye)	3.3858
TE (u.a.)	0.14753481

**Table 5:** Calculated quantum chemical parameters of the studied compound.

#### 4. Conclusion

The inhibition behavior of Caffeine on mild steel in 1M HCl was investigated using different techniques. The following points can be highlighted;

1. The obtained results indicate that, Caffeine performs excellent inhibition activity against the corrosion of mild steel in 1M HCl. The determined high inhibition efficiency is attributed to the adherent adsorption of the Caffeine.
2. The potentiodynamic polarization curves show that Caffeine prevents metal dissolution and also hydrogen evolution reactions.
3. The adsorption of Caffeine molecules on the metal surface obeys Langmuir adsorption isotherm in 1 M HCl solution. The high adsorption equilibrium constant suggests strongly adsorbed Caffeine molecules on the mild steel surface.
4. The theoretical calculations show that there is a correlation between quantum and experimental parameters.

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