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Corrosion Inhibition Ability of Caffeine on Low Carbon Steel in Corrosive Acid Media: An Experimental and Quantum Chemical Study.

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Abstract

In a 0.1 M hydrochloric acid medium, a study of the corrosion fatigue behavior of low carbon steel (LC-Steel) under the influence of caffeine is carried out. Mass loss (ML) studies, potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy (EIS) measurements were used in corrosion studies. A potentiodynamic polarization revealed that the inhibitor functions as a mixed inhibitor. Corrosion inhibition followed Langmuir's adsorption isotherm, which indicated at inhibitor adsorption on the LC-Steel surface. Decrease in double layer capacitance (C_{dl}) and increase in polarization resistance (R_p) along with the increment in Caffeine's concentration has resulted in appreciable inhibition efficiency. Which is well supported by reduced surface imperfections as, seen from SEM images. The geometrical quantum chemical parameters of inhibitor was explained by using theoretical PM6 semi-empirical method.

Key Words: Caffeine, Corrosion, Low Carbon Steel, Quantum calculation

1. Introduction

Carbon steel contains carbon from 0.04 to 1.70% by weight. It can be classified based on composition and characteristics. Carbon steel containing lower carbon content from 0.04 to 0.30% by weight is called as Low Carbon Steel (LC-Steel). It is one of the most commonly used form of steel. Because of their lower manufacturing cost, good mechanical strength and workability it is one of the most important structural materials finding extensive industrial applications [1,2]. The corrosion of carbon steel in aggressive media is a routine problem that attracts academic and industrial concerns over the years [3]. The use of corrosion inhibitor is one of the most consistent and efficient way to tackle this problem in aqueous acid media [4]. The performance of organic corrosion inhibitors is often related to the presence of π electrons and hetero-atoms such as

sulfur, oxygen and nitrogen in themolecule [5-7].

The organic compounds having following groups of molecules such as, azoles, amines, amino acids, triphenylmethane derivatives, thioles, and phosphates are used as efficient corrosion inhibitors. Chromate, molybdate and tetraborate have been cited as efficient inorganic corrosion inhibitors. But majority of such inhibitors are toxic in nature, hence there is a need to develop environmentally benign corrosion inhibitor. Caffeine is a naturally occurring molecule and it is a non-toxic and environmentally friendly substance found in several foods such as coffee, tea, cola, and chocolate, as well as in drug formulations for appetite regulation and for the treatment of flu-like illnesses [8]. The structure of caffeine is shown in Fig.

1. Caffeine has shown good adsorption ability onto Zn [9] and low-carbon steel [10] in ethanol solution. Caffeine has shown ability to inhibit the copper corrosion process in sulfuric acid medium [11] mild steel in acid chloride solution and aluminum in sodium sulfate aqueous solution [12, 13]. However, experimental, theoretical, and surface studies on LC-Steel when it interacted with caffeine molecule has not been investigated in detail. In the present work deterioration of

LC-Steel in 0.1 M hydrochloric acid media was discussed in detail. Mass loss, potentiodynamic polarization, and electrochemical impedance spectroscopy experimental methods were done to estimate the ability of the inhibitor molecule to check the corrosion reactions. Quantum chemical calculations were also carried out to know the mechanism of corrosion inhibition. Later adsorption of inhibitor molecules on the LC-Steel was verified by SEM images.

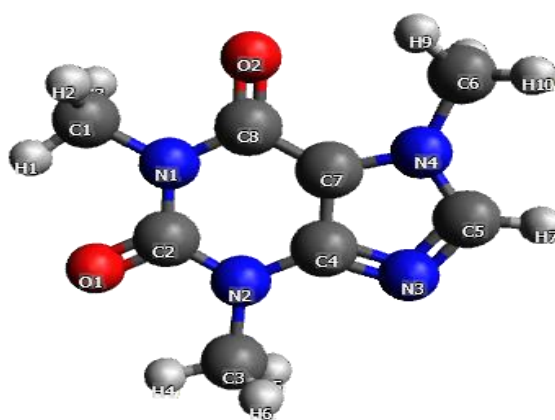


Figure 1: Structure of caffeine

2. Experimental Details

2.1 Metal Samples, Corrosive Media and Inhibitor Solution

For ML studies, LC-Steel specimens with widths of 4 cm x 2 cm x 0.1 cm were used. For the PDP and EIS techniques, a sample flap with an exposed widths of 1 cm x 1 cm were used. Strips of LC-Steel were abraded with silicon carbide paper ranging in grades from 220 to 2000. The LC-Steel strips were pre-treated with acetone and properly rinsed with deionized water prior to the test. The test media was made by diluting an AR grade concentrated hydrochloric acid solution with deionized water. Caffeine was added

$$\eta_w(\%) = \frac{C_{Ro} - C_R}{C_{Ro}} \times 100 \quad (1)$$

to 0.1 M hydrochloric acid solution to make different concentrations of inhibitor solution.

2.2 Mass Loss Measurements

The mass loss method is probably the most widely used method of initial inhibition assessment. At 298 K, various LC-Steel samples were immersed for 4 h in 0.1 M hydrochloric acid solutions containing varying inhibitor concentrations. An analytical balance was used to find the mass of every steel sample before and after immersion. Using Eqn. (1) inhibition efficiencies ($\eta_w\%$) were determined from mass loss measured.

Where CR_0 and C_R denote the corrosion rates of uninhibited and inhibited LC-Steel coupons, respectively.

2.3 Electrochemical Measurements

At 298 K, electrochemical measurements are made with a CHI608D electrochemical analyzer (made in the United States). The working electrode is LC-Steel with a 1 cm² exposed area, the counter electrode is platinum, and the reference electrode is a saturated calomel electrode. PDP curves were documented by auto changing the potential from -200 to +200 mV vs. the open-circuit potential (OCP) at a scan rate of 1 mV.s⁻¹.

$$\% \eta_p = \left(1 - \frac{i_{corr}}{i_{corr}^0} \right) \times 100 \quad (2)$$

Where, % η_p denotes corrosion inhibition efficiency, i_{corr}^0 , i_{corr} denotes corrosion current densities for blank and sample respectively.

EIS parameters were measured in the frequency range of 1 kHz to 0.1 Hz with an ac signal at OCP and an amplitude of 5 mV peak to peak. Eqn. (3) was used to calculate the EIS-based efficiency ($\eta_z\%$).

$$\eta_z \% = 100 \left(1 - \frac{R_{p,b}}{R_{p,i}} \right) \quad (3)$$

2.4 Scanning Electron Microscopic Studies (SEM)

The SEM was used to capture the morphology of the metal samples (model: VEGA3 TESCAN). The LC-steel samples were soaked for 4 h in 0.1 M hydrochloric acid without and with 50 mg/l inhibitor.

2.5 Quantum Chemical Calculations

The structure and electron distribution of caffeine, as well as its electron transfer to the LC-Steel surface, are predicted using quantum chemical calculations. Complete geometry optimizations of the molecule were conducted for the theoretical study

using the semi-empirical PM6 method in the MOPAC 2016 package.

3. RESULTS AND DISCUSSION

3.1 Mass Loss Method

ML studies were conducted to investigate the effect of caffeine addition at various concentrations on the rusting of LC-steel in 0.1 M hydrochloric acid solution. The results obtained from ML method are shown in Table 1.

ML results have shown decrease in corrosion rate from 0.0265 mmpy to 0.0052 mmpy for 50 mg/l of caffeine. The data from Table 1 indicates appreciable corrosion inhibition capacity of caffeine on LC-Steel surface. The inhibition efficiency was found to increase with the caffeine concentration and a highest of 80% was reported for 50 mg/l from ML method.

Table. 1 Mass loss data

Inhibitor concentration (mg/l)	Corrosion rate (mmpy)	η_m %	Θ
0	0.0265		
10	0.0105	60.58	0.61
20	0.0084	68.46	0.68
30	0.0077	71.09	0.71
40	0.0063	76.35	0.76
50	0.0052	80.29	0.80

3.2 Electrochemical Measurements

3.2.1 Potentiodynamic Polarization

Various corrosion parameters like corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel (β_a), and cathodic Tafel ($-\beta_c$) slopes were listed in Table 2. Fig. 2 shows Tafel plots for LC-Steel in the absence and presence of varied concentration of caffeine.

From the PDP data it is clear that LC-Steel corrosion has decreased with the rise in

inhibitor concentration. The addition of caffeine has brought both corrosion current and corrosion rate down. A maximum inhibition percentage of 81 is reported for

50 mg/l caffeine. If E_{corr} shifts beyond ± 85 mV then the inhibitor is said to be acting as either anodic or cathodic type[14].

Table 2: Potentiodynamic polarization data

C_{inh} (mg/l)	E_{corr} (V)	I_{corr} (mA cm ⁻²)	C_R (mpy)	$-\beta_c$ mV/decade	β_a mV/decade	$\% \eta_p$	Θ
0	-0.669	0.0002049	94.05	6.18	10.64		
10	-0.670	0.00009022	53.17	6.54	12.54	55.97	0.56
20	-0.663	0.00007105	41.87	6.36	12.44	65.32	0.65
30	-0.660	0.00005709	33.64	6.37	13.50	72.14	0.72
40	-0.670	0.00004035	23.78	6.80	15.41	80.31	0.80
50	-0.652	0.00003921	23.11	6.52	14.63	80.86	0.81

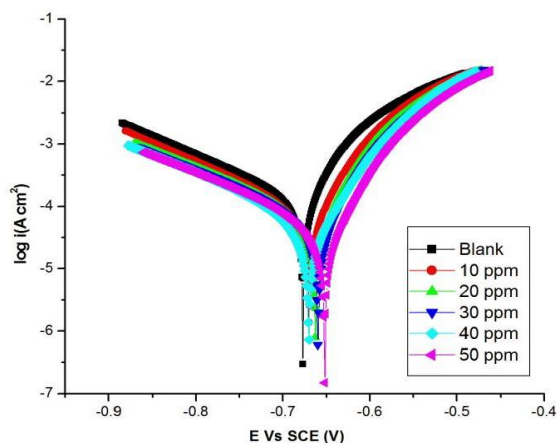


Figure 2: Tafel plots for LC-Steel

The shift in E_{corr} values for solution with caffeine compared to solution without caffeine are less than 20 mv. Hence the action of caffeine on LC-Steel suggests it to be a mixed type of inhibitor.

3.2.2 Electrochemical Impedance Spectroscopy

At 298 K, the EIS technique was used to examine the corrosion behaviour of LC-

Steel in 0.1 M hydrochloric acid solution in the absence and presence of various caffeine concentrations. Fig. 3 shows Nyquist plots for LC-Steel in the absence and presence of varied concentration of caffeine.

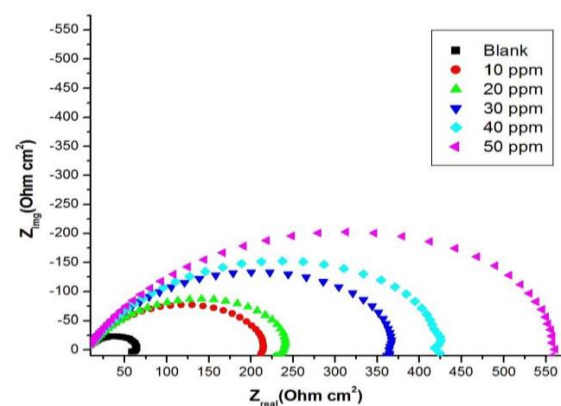


Figure 3: Nyquist plots for LC-Steel

The data obtained from EIS studies such as polarization resistance (R_p), double layer capacitance (C_{dl}), goodness of fit, inhibition efficiency ($\% \eta_z$), and surface coverage (Θ) values are listed in Table 3.

The diameter of semicircle loop is found to increase with the rise in caffeine concentrations, indicating improving corrosion resistance. From the data tabulated in Table 3, it is clear that C_{dl} values decreases, while R_p values

increases with increase in caffeine concentration. It indicates the increased thickness of the electrical double layer and also suggests adsorption of inhibitor on the metal surface.

Table 3: Electrochemical impedance spectroscopy data

Inhibitor concentration (mg/l)	R_p ($\Omega \text{ cm}^2$)	C_{dl} (10^{-6} F/cm^2)	Goodness of fit ($\times 10^{-3}$)	$\% \eta_z$	Θ
0	78.38	4.81	3.56		
10	228.27	3.49	0.78	65.83	0.66
20	257.74	3.09	3.20	69.74	0.70
30	395.11	2.77	1.62	80.26	0.80
40	457.49	2.61	1.29	82.95	0.83
50	601.01	2.63	1.37	87.02	0.87

3.3 Adsorption Isotherm

The interaction of caffeine with LC-Steel can be explained well using adsorption isotherm. Adsorption of inhibitor molecules on the metal surface is a substitution process where an exchange of adsorbed water molecules with organic molecules occurs [15]. Data were graphically validated by fitting to several isotherms. Langmuir, Temkin, and Freundlich and Kinetic-thermodynamic model of adsorption isotherms were all investigated. The Langmuir Isotherm, as stated in Eqn. 4, was found to graphically fit the experimental data satisfactorily. Langmuir Isotherm is as shown in Fig. 4.

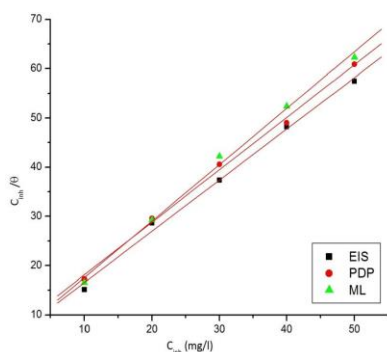


Figure 4: Langmuir adsorption isotherm

3.4 Scanning electron microscope (SEM)

Adsorption data in Table 4 showed high K_{ads} and negative ΔG°_{ads} , indicates that caffeine adsorbs spontaneously on the LC-Steel surface due to a strong inter molecular force of attraction [16]. It is largely acknowledged that for ΔG°_{ads} values in the order of 20 kJ/mol, the type of adsorption is physisorption, and for values over 40 kJ/mol chemisorption [17]. The calculated values of ΔG°_{ads} are in the order of -20 kJ/mol, suggests caffeine adsorb on LC-Steel through

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

physisorption.

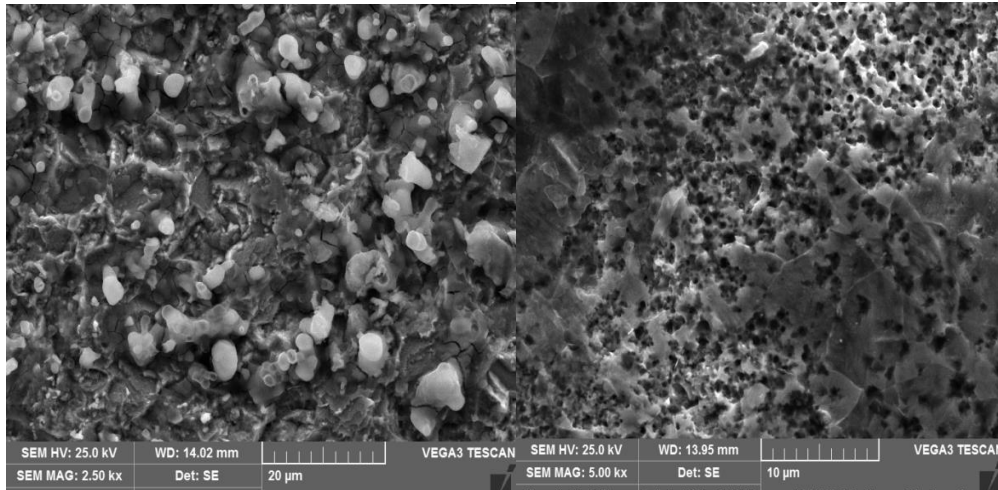
Experimental Methods	K_{ads}	$-\Delta G^{\circ}_{ads}$ (kJ/mol)
ML	163773.34	22.58
PDP	133886.73	22.08
EIS	162284.97	22.56

(4)

Table 4: Adsorption parameters for LC-Steel

SEM micrographs of LC-Steel specimens submerged in 0.1 M hydrochloric acid in the absence and presence of 50 mg/l caffeine are shown in Figs. 5 a and b,

respectively. In Fig. 5a, we can see a strong corrosion of the LC-Steel immersed in uninhibited solution. But the LC-Steel was less corroded.



(a)

(b)

Figure 5: SEM micrographs of LC-steel in (a) blank solution (b)50mg/l of caffeine

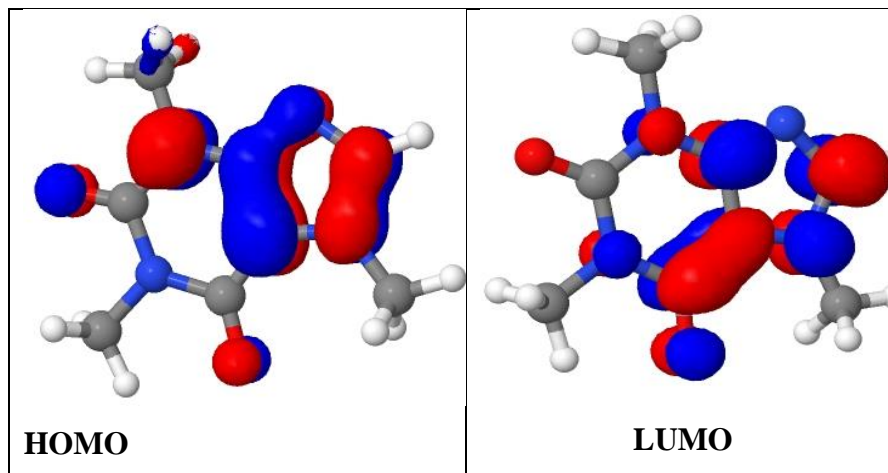


Figure 6: Highest occupied and lowest unoccupied molecular orbitals.

Table 4: Quantum chemical calculation data

E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Dipole moment (Debye)
-9.135	-0.566	8.569	3.91

Smaller the E_{LUMO} for an inhibitor compound easier will be electron donation to the metal. Hence corrosion inhibition ability of such inhibitors will be superior. The E_{HOMO} and E_{LUMO} values for caffeine was predicted to be -9.135 eV and -0.566, respectively. This indicates caffeine is a good corrosion inhibitor. The dipole moment of caffeine is higher (3.91 Debye) suggests it to be a better corrosion inhibitor.

3.5 Quantum Chemical Calculations

Quantum chemical simulations were done and verified with experimentally obtained data to gain precise information about the inhibitory mechanism. Fig. 6 shows the HOMO and LUMO orbitals of optimized caffeine molecule. The calculated quantum chemical parameters are given in Table 4. Electron transfer among molecules is caused by the interaction of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) [18]. The nature of a molecule to donate electrons is shown by E_{HOMO} , and the nature of a molecule to accept electrons is indicated by E_{LUMO} . Larger the E_{HOMO} .

4. Conclusions

In a 0.1 M HCl solution, caffeine was tested as a corrosion inhibitor for LC-Steel. The study suggested that caffeine protects the LC-Steel surface by forming a protective layer that is physically adsorbed via a Langmuir adsorption isotherm. Caffeine is a mixed type inhibitor with a preference for anodic reaction inhibition. The efficiency of inhibition has increased as caffeine content increases. The study revealed a maximum corrosion inhibition of 87%. The experimental findings produced by the ML, PDP, and EIS techniques were found to be in good agreement. The quantum calculations were discovered to agree with the experimental values.

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