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Corrosion inhibition performance of sulfamethazine for mild steel in Phosphoric acid solution: Gravimetric, electrochemical and DFT studies

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ABSTRACT

The inhibition effect of Sulfamethazine (SFMT) on the corrosion of mild steel in 2.0 M phosphoric acid has been investigated by weight loss, polarization potentiodynamic and electrochemical impedance spectroscopy (EIS). SFMT is able to reduce the corrosion of steel effectively in phosphoric acid. Results obtained revealed that these compounds are good mixed-type inhibitors without changing the mechanism of the corrosion process. The effect of temperature on the corrosion behavior of mild steel in phosphoric acid with addition of SFMT was studied in the temperature range 298–328 K. The studied compounds appeared to function through general adsorption following the thermodynamic–kinetic adsorption isotherm. The thermodynamic and activation parameters were determined and discussed. Quantum chemical calculations were applied to theoretically determine the relationship between molecular structure and inhibition efficiency.

Keywords: Mild steel; Corrosion inhibition; Phosphoric acid; DFT; EIS

INTRODUCTION

Acid solutions are commonly used for the removal of undesirable scale and rust in metal finishing industries, cleaning of boilers and heat exchangers[1]–[3]. To prevent unexpected metal dissolution and excess acid consumption in the process of cleaning, therefore, inhibitors will be inevitable to be put into use. Most of the well-known acid inhibitors are organic compounds especially those with N, O and S showed an effective corrosion inhibition. New inhibitors are discovered every day. In principle, inhibitors prevent the corrosion of metal by interacting with the metal surface via adsorption through the donor atoms, p-orbitals, electron density and the electronic structure of the molecule[4]–[9]. In particular, –NH2 and –SO groups in the structures of inhibitors often act as reaction centers during the adsorption of the inhibitor[10], [11]. In this way, the inhibitors form an adsorbed protective film on the metal surfaces, and protect the metals from the attacking acid solution.

Quantum chemical calculations are very effective methods for determining a correlation between molecular structure and inhibition efficiency. They can also be utilized to support the accuracy of experimental results. Thus, it is important to compute the quantum chemical parameters, such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the fraction of electrons transferred (ΔN) and the energies of the frontier molecular orbitals[12]–[15].

In this paper, SFMT is selected based on the consideration of their molecular structures. The inhibition effect of SFMT on the corrosion of mild steel in H_3PO_4 solution was studied using weight loss, potentiodynamic polarization curves, and electrochemical impedance spectroscopy (EIS). Effects of inhibitor concentration, temperature were fully investigated. The adsorption isotherm of inhibitor on steel surface, the standard adsorption free energy (ΔG°_{ads}) and apparent activation energy (E_a) are obtained. Quantum chemical calculation of DFT was applied to study the molecular parameters of **SFMT**. The molecular structure of Sulfamethazine is presented in Fig. 1:

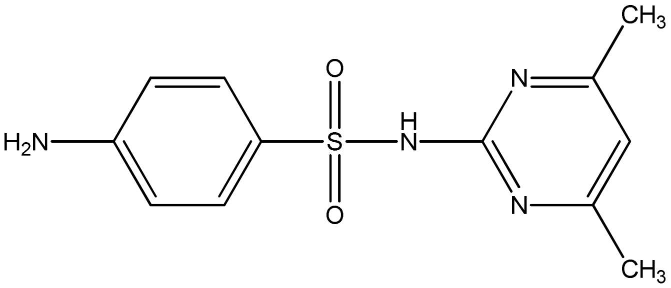

Figure 1: Chemical structure of Sulfamethazine

MATERIALS AND METHODS

Electrolytic solution and concentration range

The aggressive solutions of 2.0 M H_3PO_4 was prepared by dilution of analytical grade 85% H_3PO_4 with distilled water. The concentration range of **SFMT** used was 5×10^{-4}M to 1×10^{-5}M

Weight loss tests and electrochemical measurements

In this study, the effects of **SFMT** on the metal corrosion were performed by the electrochemical measurements (Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves measurements), and weight loss tests. The detail of experiments referenced from the published article of R. Salghi et al. [16]–[19]

Computational procedures

Complete geometrical optimizations of the investigated molecules are performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee-Yang-Parr nonlocal correlation functional (B_3LYP) with 6-31G* basis set is implemented in Gaussian 03 program package [20]–[22].This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations. The geometry structure was optimized under no constraint. The following quantum chemical parameters were calculated from the obtained optimized structure: The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electron affinity (A), ionization potential (I) and the fraction of electrons transferred (ΔN).

According to Koopman's theorem[23] the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations.

$IE = -E_{HOMO}$
$EA = -E_{LUMO}$

Thus, the values of the electronegativity (χ) and the chemical hardness (η) according to Pearson, operational and approximate definitions can be evaluated using the following relations[24]:

$$\chi = \frac{I + A}{2} \qquad (1)$$

$$\eta = \frac{I - A}{2} \qquad (2)$$

The number of transferred electrons (ΔN) was also calculated depending on the quantum chemical method[25], [26]by using the equation:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \qquad (3)$$

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of χ_{Fe} =7.0 eV and η_{Fe} = 0, for calculating the number of electron transferred.

RESULTS AND DISCUSSION

Effect of concentration

Polarization potentiodynamic

Fig. 2shows Tafel plots for mild steel in 2.0 M H_3PO_4 containing different concentrations of the **SFMT**. The presence of the inhibitor slowly shifts the cathodic and anodic lines to lower values. This indicates lower currents and hence lower corrosion rates of mild steel in presence of the **SFMT** compared to that in blank. It can be concluded that the inhibitor acts mainly as a mixte inhibitor in2.0 M H_3PO_4 solution[27], [28]. The electrochemical parameters of mild steel in presence of different inhibitor concentrations are listed in Table 1. These include the free corrosion potential, E_{cor}, corrosion current density, i_{cor}, cathodic Tafel slope, b_c and inhibition efficiency, %*IE*. The cathodic Tafel lines show similar slope either in presence or absence of **SFMT**. It indicates that the mechanism of the cathodic reaction does not change in presence of the inhibitor and the inhibition action is achieved by simple blocking of the steel surface[29], [30].

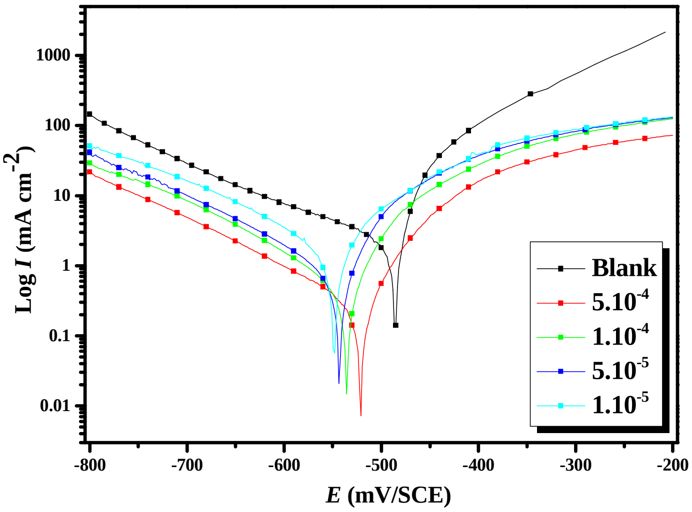

Figure2. Potentiodynamic polarization curves of carbon steel in 2.0 M H_3PO_4 in the presence of different concentrations of SFMT

It should be pointed out that the inhibition efficiency, %*IE* of the inhibitor was determined from the corrosion currents, i_{cor} in presence and absence of the inhibitor. It can be determined from i_{cor} values according to the following equation;

$$\eta_P\,(\%) = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100 \qquad (4)$$

Where, I^o_{corr} is corrosion current in the absence of inhibitor, I_{corr}iscorrosion current in the presence of inhibitor.

The decrease of the corresponding current densities with increasing inhibitor concentration is due to the formation of a protective films on the electrode surface.

Table1. Electrochemical parameters of carbon steel at various concentrations of SFMT in 2.0 M $H_3PO_4$and corresponding inhibition efficiency

Inhibitor	Concentration (M)	E_{corr} vs. SCE (mV)	$-\beta_c$ (mV dec^{-1})	I_{corr} (µA cm^{-2})	η_{Tafel} (%)
Blank	2.0	-488	135	2718	—
SFMT	5×10^{-4}	-525	134	271	90.0
	1×10^{-4}	-540	136	560	79.4
	5×10^{-5}	-547	145	901	66.8
	1×10^{-5}	-555	153	1332	51.0

Electrochemical impedance spectroscopy

Nyquist plots of MS in uninhibited and inhibited acid solutions containing various concentrations of **SFMT** at 298 K are shown in Fig. 3.Nyquist's plots consisting of one depressed semi-circular shape in inhibited, and uninhibited acid solutions are seen in Fig. 3. This indicates that the corrosion of the MS in the presence and absence of inhibitor and mainly controlled by a charge transfer process[31], [32]. By increasing concentration of **SFMT** in 2.0 M H_3PO_4 solution, it causes a change in both shape and size of the Nyquist plots. The one depressed semicircular shape appearing in the Nyquist plots is attributed to the charge transfer resistance and the diffuse layer resistance, at low frequencies related to the adsorption of inhibitor molecules on the metal surface and all other accumulated kinds at the metal/solution interface (inhibitor molecules, corrosion products, etc.). In the evaluation of Nyquist plots, the difference between real impedance at lower and higher frequencies is commonly accepted as a charge transfer resistance[33], [34]. As in Fig. 3, the increasing R_{ct} values with increasing concentration of the **SFMT** indicate the formation of a protective film at the metal surface.

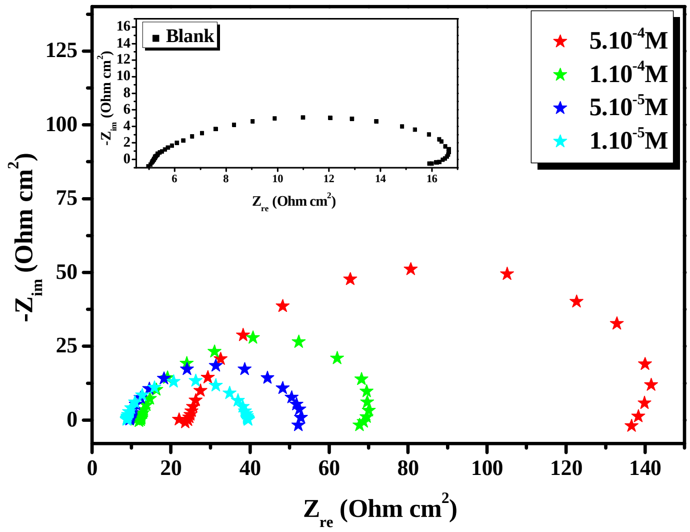

Figure3. Nyquist diagrams of carbon steel with different concentrations of SFMT at 298K

A suitable equivalent circuit diagram is given where R_s is solution resistance, and *CPE* is a constant phase element in Fig. 4fitting well with the experimental results by analyzing the EIS data. The Nyquist plots are not perfect semicircles as expected from the theory of EIS. Therefore, it is necessary to use the constant phase element, *CPE*, instead of double layer capacitance C_{dl} to give a more accurate fitting. On the other hand, the use of a *CPE* is required as a result of inhomogeneities like the surface roughness/porosity, adsorption, or diffusion. *n* is the phase shift expressed as a degree of surface inhomogeneities. The fitted data of impedance plots are given in Table 2. It can be seen from Table 2 that while R_{ct} values obtained from EIS measurements increase with the increasing concentration of **SFMT**, *CPE* values decrease. The decrease in the *CPE* could be the result in a decrease in local dielectric constant and/or an increase in the thickness of double layer due to the adsorption of **SFMT** molecules at the metal/solution interface. Furthermore, better protection provided by an inhibitor could be associated with a decrease in capacitance of the metal[10], [11]. The inhibition efficiency (η %) was calculated from the polarization resistance using the following equation:

$$\eta_Z\,(\%) = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \qquad (5)$$

WhereR_{ct}^{o} and R_{ct} were the polarization resistance of uninhibited and inhibited solutions, respectively. The double layer capacitance values (C_{dl}) is evaluated from constant phase element CPE (Q, n) and a charge transfer resistance value (R_{ct}), using the following relation:

$$C_{dl} = \sqrt[n]{Q.R_t^{1-n}} \qquad (6)$$

Where Q is the constant phase element (CPE) and n is a coefficient can be used as a measure of surface inhomogeneity.

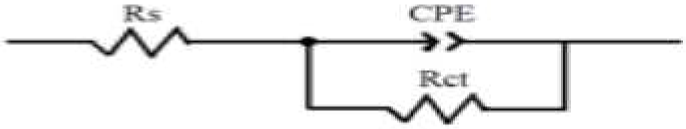

Figure4. Equivalent electrical circuit corresponding to the corrosion process on the carbon steel in phosphoric acid

Table2. Electrochemical Impedance parameters for corrosion of carbon steel in acid medium at various contents of SFMT

Inhibitor	Concentration (M)	R_t (Ω cm^2)	$Y_0\times10^{-5}$ (sn Ω^{-1}cm^{-2})	n	C_{dl} (μF/cm^2)	η_{EIS} (%)
Blank	2.0	14	21.024	0.88	94.96	—
	5×10^{-4}	136.6	1.5822	0.89	07.41	89.8
	1×10^{-4}	67.7	2.9733	0.90	14.92	79.3
SFMT	5×10^{-5}	44.0	5.0138	0.89	23.54	68.2
	1×10^{-5}	30.7	5.0484	0.91	26.62	54.4

Weight loss study

Corrosion parameters namely, corrosion rate (C_R), surface coverage (θ) and inhibition efficiency (η %) of mild steel in 2.0 M H_3PO_4 solution in the absence and presence of different concentrations of inhibitor at 298 K, obtained from weight loss measurements are shown in Table3. From Table 3,it is apparent that inhibition efficiency increased with increasing the concentration of the inhibitor. The inhibition efficiency of **SFMT** at 5.10^{-4} M was found to be 87.2%at 303 K (Table 3). The increase in inhibition efficiency and decrease in the corrosion rate with increasing concentration of inhibitor is due to increase in the surface coverage, resulting retardation of metal dissolution.

Table3. Effect of SFMT concentration on corrosion data of carbon steel in 2.0 M H_3PO_4

Inhibitor	**Conc. (M)**	**A (mg cm^{-2} h^{-1})**	**η_w (%)**	**θ**
Blank	2.0	1.972	-	-
	5×10^{-4}	0.2524	87.2	0.872
SFMT	1×10^{-4}	0.4871	75.3	0.753
	5×10^{-5}	0.5448	69.6	0.696
	1×10^{-5}	0.9111	53.8	0.538

Effect of temperature and activation parameters

Temperature effect was determined at various temperatures (298–328 K) in the absence and presence of optimum concentration of inhibitor in 2.0 M H_3PO_4. Fig. 5and 6 depicts the Tafel plots without and with optimum concentration of **SFMT.**

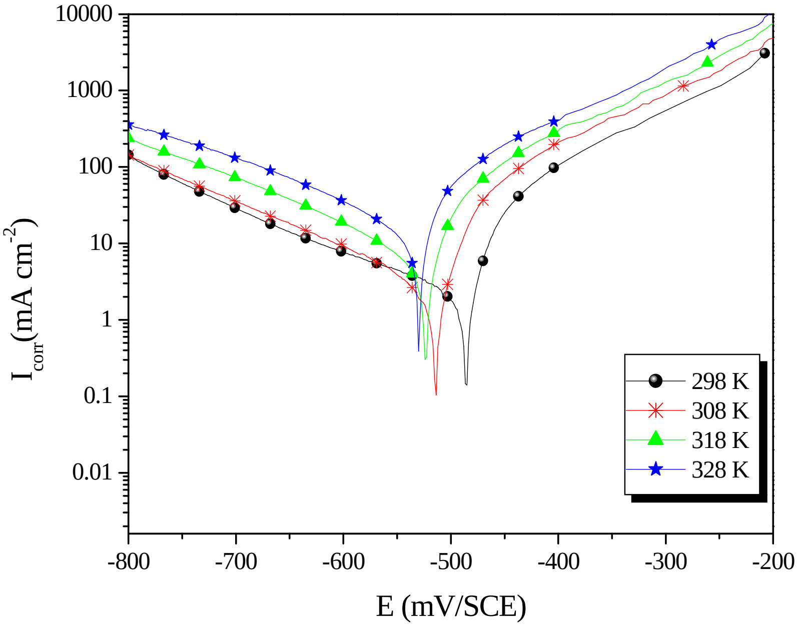

Figure5. Potentiodynamic polarization curves of carbon steel in 2.0M H_3PO_4 at different temperatures

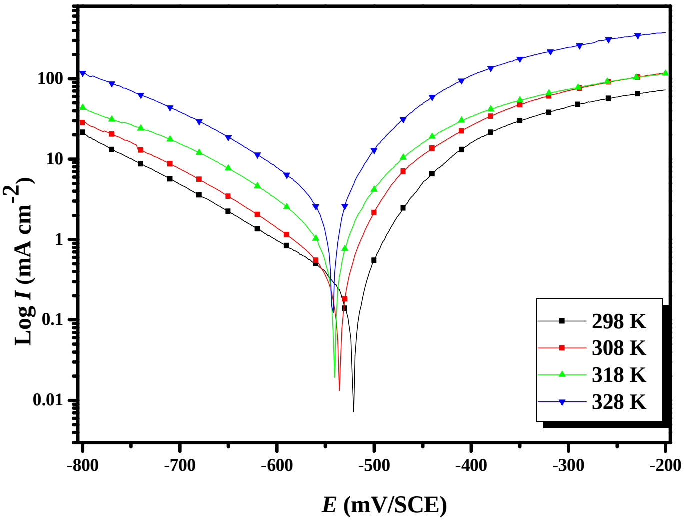

Figure 6. Potentiodynamic polarization curves of carbon steel in 2M H_3PO_4 in the presence of 5.10^{-4} M of SFMT at different temperatures

In acidic media, rise in temperature usually accelerates the corrosion reactions, resulting in higher dissolution of metal. It is clear from Table 4 thatη% decreases as the temperature increases from 298 to 328 K, this occurs due to an appreciable decrease in adsorption of inhibitor molecules on metal surface with rise in temperature and further cause desorption of inhibitor molecules because these two opposite processes are in equilibrium. Due to higher desorption rate greater surface area of MS comes in contact with corrosive environment, resulting in increased corrosion rates with rise in temperature[18].

Table4. Various corrosion parameters for carbon steel in 2M H_3PO_4 in absence and presence of optimum concentration of SFMT at different temperatures

Inhibitor	Temperature K	E_{corr} vs. SCE(mV)	$-\beta_c$ (mV dec^{-1})	i_{corr} (µA cm^{-2})	η_{Tafel} (%)
Blank	298	-488	135	2718	—
	308	-532	137	4220	—
	318	-523	132	6610	—
	328	-514	139	11890	—
5×10^{-4}M **SFMT**	298	-525	134	271	90.0
	308	-541	135	502	88.1
	318	-544	147	1363	79.4
	328	-547	142	3286	72.4

The energy of activation for the corrosion process were calculated from the Arrhenius equation:

$$C_R = A\exp\left(\frac{-E_a}{RT}\right) \qquad (7)$$

Where E_a represents apparent activation energy, R the gas constant, A is the pre-exponential factor. Arrhenius plots for the corrosion rate of MS are shown in Fig. 7. Values of E_a for MS in 2.0 M H_3PO_4 in absence and presence of inhibitor were calculated by linear regression between log (i_{corr}) and $1/T$. The value of E_a is higher for inhibited solution (68.79 kJ mol^{-1}) than that for uninhibited solution (39.50 kJ mol^{-1}). The higher values of E_a indicate that more energy barrier for the corrosion reaction in presence of the inhibitor is attained. Thus the adsorbed inhibitor molecules prevent charge or mass transfer from the mild steel surface[35].

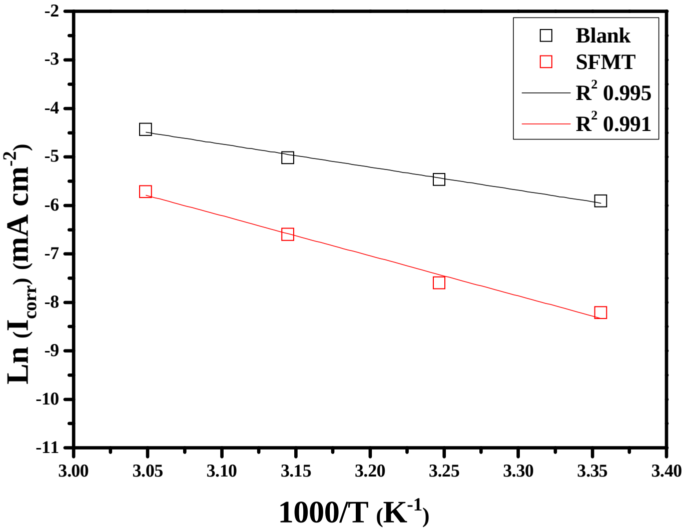

Figure7. Arrhenius plots of carbon steel in 2.0 M H_3PO_4 with and without 5.10^{-4} M of SFMT

Other activation parameters can be evaluated from the effect of temperature. Enthalpy and entropy of activation were calculated using the alternative form of Arrhenius:

$$C_R = \frac{RT}{Nh}\,exp\left(\frac{\Delta S_a}{R}\right) exp\left(-\frac{\Delta H_a}{RT}\right) \qquad (8)$$

Where, h is the Planck's constant, N is the Avogadro's number, R is the molar gas constant and T is the absolute temperature. Straight lines were obtained with a slope and an intercept (Fig. 8) from which the activation thermodynamic parameters ΔH_a and ΔS_a were calculated, as listed in Table 5. The values of E_a and ΔH_a are close to each other, as expected from the concept of transition-state theory, and follow the same pattern of variation with different concentrations of the inhibitor. The negative value of ΔS_a for inhibitor indicate that the formation of the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the course of the transition from reactants to activated complex[36], [37].

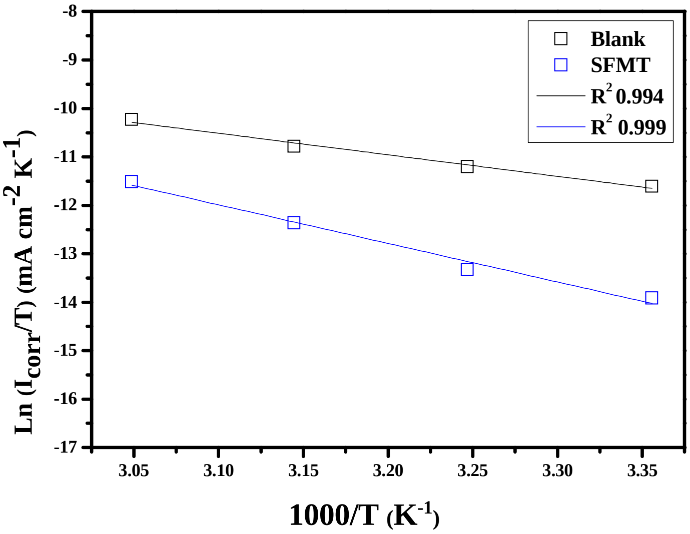

Figure8. Arrhenius plots of carbon steel in 2.0 M H_3PO_4 with and without 5.10^{-4} M of SFMT

Table5. The values of activation parameters E_a, ΔH_a and ΔS_a for carbon steel in 2.0 M H_3PO_4 in the absence and presence of 5.10^{-4} M of SFMT

Concentration (M)	E_a (kJ mol^{-1})	ΔH_a (kJ mol^{-1})	ΔS_a (J mol^{-1} K^{-1})	E_a-ΔH_a (kJ mol^{-1})
Blank	39.50	36.91	-112.98	2.59
5×10^{-4}M **SFMT**	68.79	66.19	-92.09	2.60

Adsorption isotherm

Studying adsorption isotherm is the best way to understand the interaction between inhibitor molecules and metal surface. The type of adsorption can be either physisorption or chemisorption. The studied inhibitor affect corrosion rate mainly through the variation of degree of surface coverage, so inhibition efficiency becomes the function of the electrode surface covered by the inhibitor molecules[38], [39]. The linear relation between degree of surface coverage θ ($\theta = IE\ (\%) / 100$) and concentration of the inhibitor is essential to obtain the adsorption isotherm. Attempts were made to fit the data to various isotherms like the Langmuir isotherm, the Temkin isotherm, the Frumkin isotherm, and the Freundlich isotherm. The best fit is found for the Langmuir adsorption isotherm. According to this isotherm, θ is related to C by

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (9)$$

Where, C is the concentration of the inhibitor, K_{ads} is the equilibrium constant of adsorption and θ is the surface coverage.

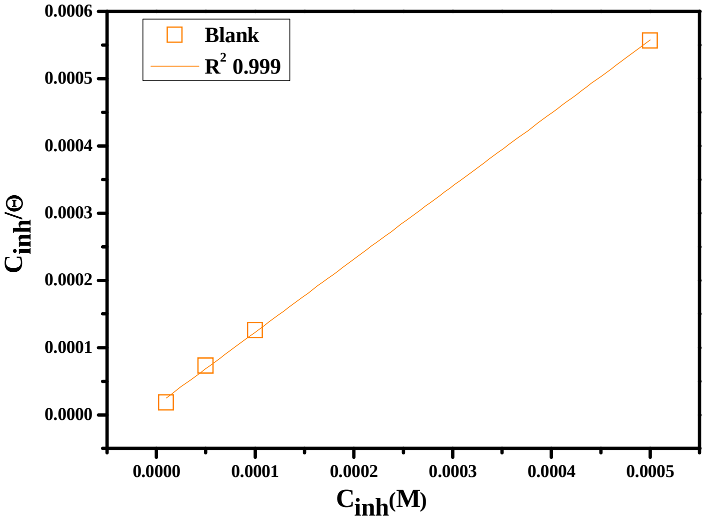

Figure9. Adsorption isotherm according to Langmuir's model derived from EIS measurement

A plot of C/θ versus C was drawn to get straight line (Fig. 9) with a slope around 1 and regression co-efficient close to1. This confirms the uniform monolayer Langmuir kind of adsorption of the inhibitor with no interaction with the neighboring sites.The value of K is related to the standard free energy of adsorption, $\Delta G°_{ads}$, by the following equation:

$$\Delta G^0_{ads} = -RTln(K * 55.5) \quad (10)$$

Where the value 55.5 is the water concentration in solution expressed in mol.L^{-1}.ΔG^o_{ads} value is calculated and presented in Table 6, which is negative and higher (-37.59kJ mol^{-1}). A negative value of free energy indicates spontaneity of adsorption of inhibitor on the metal surface. If the magnitude of ΔG^o_{ads} is around − 20 kJ mol^{-1} or less negative then the interaction is electrostatic or physical. Those around − 40 kJ mol^{-1} or more negative is chemisorption which occurs by a coordinate type of metal bond. The value obtained in the present study is -37.59 kJ mol^{-1}, so the type of interaction is a mixture of physisorption and chemisorption which is a complex kind of interaction[39], [40].

Table6. Thermodynamic parameters for the adsorption of SFMT in 2.0 M H_3PO_4on the carbon steel at 298K

Inhibitor	Slope	$K_{ads}(M^{-1})$	$\Delta G°_{ads}$(kJ/mol)
SFMT	1.08	69841.18	-37.59

Quantum chemical calculations

Computational methods have a strong impact toward the design and development of organic corrosion inhibitors. Recently, density function theory (DFT) has been used to analyze the characteristics of the inhibitor/surface mechanism and to describe the structural nature of the inhibitor on the corrosion process. Furthermore, DFT is considered to be a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data[41], [42]. Thus in our present investigation, DFT method was employed to give some insight into the inhibition action of **SFMT** molecule on the carbon steel surface. The quantum chemical parameters such as E_{HOMO}, E_{LUMO}, the energy gap ΔE (E_{LUMO} - E_{HOMO}), and dipole moment (μ) were obtained for the neutral **SFMT** molecule to predict their activity toward metal surface. These quantum chemical parameters were generated after geometric optimization with respect to all nuclear coordinates. Frontier orbital density distribution is useful in predicting adsorption centers of the **SFMT** molecule responsible for the interaction with metal surface atoms. Figure 1 shows the optimized structure and frontier orbital distribution of the molecule HOMO and the LUMO density distribution of **SFMT**. As can be seen from Fig.10 the HOMO is distributed over the entire **SFMT** molecule, but the density of LUMO is mainly localized on the Sulfamethazine. The presence of these adsorption centers can cause flat orientation of **SFMT** molecules on the surface of steel, thus high degree of surface coverage and inhibition efficiency is expected for **SFMT** from the theoretical point of view. These results suggest that the two O and four N atoms are the probable reactive sites for adsorption on **SFMT** on the metal surface. The calculated molecular parameters are listed in Table 7.

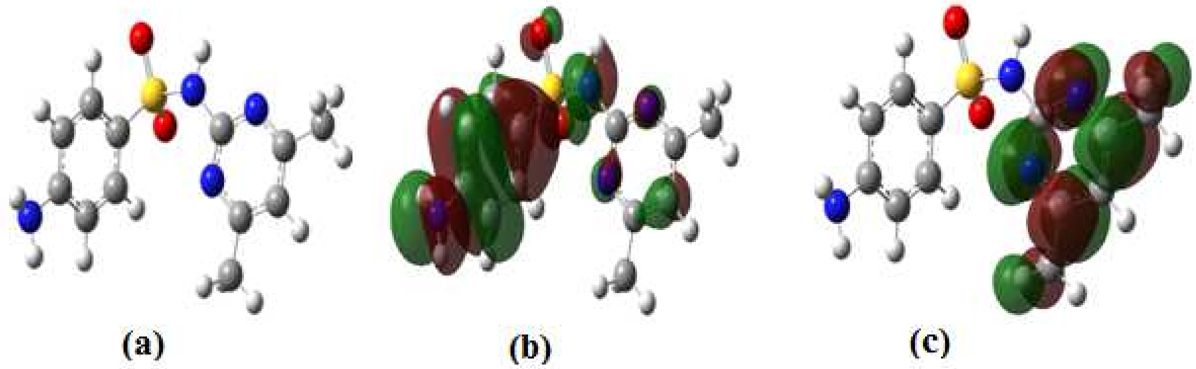

Figure10. (a) Optimized structure and frontier molecular orbital diagrams of SFMT by B3LYP/6-31G (d,p) HOMO (b) and LUMO (c).

Table7. Quantum chemical parameters for SFMT calculated using B3LYP/6-31G (d,p)

Molecular parameters	**SFMT**
E_{HOMO} (eV)	-5.91739
E_{LUMO} (eV)	-0.94015
ΔE_{gap} (eV)	4.97723
μ (debye)	7.3094
I (eV)	5.91739
A (eV)	0.94015
χ (eV)	3.429
η (eV)	2.489
ω	2.8808
ΔN	0.717
TE (eV)	-33551

E_{HOMO} is often associated with the electron-donating ability of a molecule and its high value (-5.91739eV) is likely to indicate a tendency to donate electrons to appropriate low-energy acceptor states. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. E_{LUMO} indicates the ability of the molecule to accept electrons; hence these are the acceptor states. The lower the value (-0.94015eV) of E_{LUMO}, the more probable it is that the molecule would accept electrons[43]. For the dipole moment (μ), higher value (7.3094D) of μ will favor a strong interaction of inhibitor molecules to the metal surface.
In addition, the electro negativity parameter (χ) is related to the chemical potential, and higher value of (χ)indicates better reactivity. Global electrophilicity index (ω) is the measure of the electrophilic tendency of a molecule. In our case, the inhibitor **SFMT** with high electrophilicity index value (2.8808eV) has the highest inhibition efficiency. Using Eq. (4), the value of electron-donating ability (ΔN) was calculated and its value is given in Table 7. If ΔN < 3.6 (electron), the inhibition efficiency increases with increasing value of ΔN, while it decreased if ΔN > 3.6 (electron)[43], [44]. In present contribution, **SFMT** is the donor of electrons, and the iron surface atom was the acceptor. The **SFMT** was bound to the mild steel surface, and thus formed inhibition adsorption layer against corrosion at carbon steel/hydrochloric acid solution interface.

CONCLUSION

The Sulfamethazine act as good corrosion inhibitor for mild steel in 2.0 M H_3PO_4 solution. Polarization studies showed that the tested inhibitor is mixed type in nature. EIS measurements show that charge transfer resistance (R_{ct}) increases and double layer capacitance (C_{dl}) decreases in the presence of inhibitor, which suggested the adsorption of the inhibitor molecules on the surface of mild steel. The results obtained from Langmuir adsorption isotherm suggested that the mechanism of corrosion inhibition is occurring mainly through adsorption process. The efficiency of **SFMT** is found to decrease proportionally with increasing temperature (298–328 K) and its addition to 2.0 M H_3PO_4leads to increase of apparent activation energy (E_a) of corrosion process. Quantum chemical results of **SFMT** indicating that the inhibitor is good corrosion inhibitor for mild steel in 2.0 M H_3PO_4solution.

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REFERENCES

[1] Solmaz R, Kardaş G, Yazici B, Erbil M, *Colloids Surf.* A,**2008**, 7, 312.
[2] Prajila M, Sam J, Bincy J, Abraham J, *J. Mater. Environ. Sci*,**2012**, 3, 1045.
[3] Naik U J, Panchal V A, Patel A S, Shah N K, *J. Mater. Environ. Sci*,**2012**, 3, 935.
[4] M Larouj, M Belayachi, H Zarrok, A Zarrouk, A Guenbour, M EbnTouhami, A Shaim, S Boukhriss, H Oudda, B Hammouti, *Der PharmaChemica*, **2014**, 6(3), 373-384.
[5] M Larouj, H Lgaz, HZarrok, H Serrar, H Zarrok, H Bourazmi, A Zarrouk, A Elmidaoui, A Guenbour, S Boukhris and H Oudda, *Journal of Material and Environmental Science*,**2015**, 6, 11, 3251-3267.
[6] M Larouj, M Belkhaouda, H Lgaz, R Salghi, S Jodeh, S Samhan, H Serrar, S Boukhris, M Zougagh and H Oudda, *Der PharmaChemica*, **2016**, 8(2), 114-133.
[7] H Lgaz, O Benali, R Salghi, S Jodeh, M Larouj, O Hamed, M Messali, S Samhan, M Zougagh and H Oudda, *Der PharmaChemica*, **2016**, 8(2), 172-190.
[8] Ben Hmamou D, Salghi R, Zarrouk A, Zarrok H, Hammouti B, Al-Deyab S S, Bouachrine M, Chakir A, Zougagh M, *Int. J. Electrochem. Sci*,**2012**, 7, 5716.
[9] L Afia, M Larouj, H Lgaz, R Salghi, S Jodeh, S Samhan and M Zougagh, *Der PharmaChemica*, **2016**, 8(2), 22-35.
[10] H Lgaz, Y ELaoufir, Y Ramli, M Larouj, H Zarrok, R Salghi, AZarrouk, A Elmidaoui, A Guenbour, EL M Essassi and H Oudda, *Der PharmaChemica*, **2015**, 7(6), 36-45.
[11] B El Makrini, M Larouj, H Lgaz, R Salghi, A Salman, M Belkhaouda, S Jodeh, M Zougagh and HOudda, *Der PharmaChemica*, **2016**, 8(2), 227-237.
[12] B El Makrini, H Lgaz, M Larouj, R Salghi, A RasemHasan, M Belkhaouda, S Jodeh, M Zougagh and H Oudda, *Der PharmaChemica*, **2016**, 8(2), 256-268.
[13] M Ozcan, R Solmaz, G Kardas, I Dehri, *Colloid Surf. A*,**2008**, 325, 57.
[14] C Verma, M A Quraishi, et A Singh, *J. Taiwan Inst. Chem. Eng*, **2016**, 58, 127‑140.
[15] G Gece, Corros. Sci,**2008**, 50, 2981.
[16] L Afia, R Salghi, L Bammou, E Bazzi, B Hammouti, L Bazzi, et ABouyanzer, *J. SaudiChem. Soc*, **2014,** 18, 19‑25.
[17] L Afia, R Salghi, A Zarrouk, H Zarrok, E H Bazzi, B Hammouti, et MZougagh, Trans. *IndianInst. Met*, **2013**, 66, 43‑49.
[18] A Anejjar, R Salghi, A Zarrouk, O Benali, H Zarrok, B Hammouti, et E EEbenso, *J. Assoc. ArabUniv. Basic Appl. Sci*, **2014**, 15, 21‑27.
[19] A Anejjar, RSalghi, A Zarrouk, H Zarrok, O Benali, B Hammouti, S S Al-Deyab, N-E Benchat, et R Saddik, *Res. Chem. Intermed*, **2015**, 41, 913‑925.
[20] C Lee, W Yang, R G Parr, Phy. Rev. B, **1988**, 37, 785.
[21] M J Frisch et al Gaussian 03, Revision C.02, Gaussian Inc, Pittsburgh, PA, **2003**.
[22] M J S Dewar, W Thiel, *J. Am. Chem. Soc*, **1977**, 99, 4899.
[23] R G Pearson, *Inorg. Chem*, **1988**, 27, 734.
[24] V S Sastri, J RPerumareddi, *Corrosion*, **1997**, 53, 671
[25] V S Sastri, J RPerumareddi, *Corrosion* (NACE) **1997**, 53, 617.
[26] I Lukovits, E Kalman, FZucchi, *Corrosion* (NACE) **2001**, 57, 3.
[27] W Chen, H Q Luo, N B Li, *Corros. Sc*,**2011**, 53, 3356.
[28] S K Shukla, M A Quraishi,*Corros. Sci*,**2010**, 52, 314.
[29] S K Shukla, M A Quraishi, *Corros. Sci*,**2009**, 51, 1990.
[30] F Bentiss, M Traisnel, M Lagrenee, *Corros. Sci*,**2000**, 42, 127.
[31] XingwenZheng, Shengtao Zhang, Wenpo Li, Linliang Yin, Jiahong He, JinfangWua. *Corros. Sci*,**2014**, 80, 383-392.
[32] I B Obot, N O Obi-Egbedi, *Curr. Appl. Phys*,**2011**, 11, 382.
[33] G Bereket, A Yurt, *Corros. Sci*,**2001**, 43, 1179.
[34] M Larif, A Elmidaoui, A Zarrouk, H Zarrok, R Salghi, B Hammouti, H Oudda, F Bentiss, *Res. Chem. Intermed*,**2012**, DOI: 10.1007/s11164-012-0788-2.
[35] IshtiaqueAhamad, Rajendra Prasad, M A Quraishi, *Corros. Sci*,**2010**, 52, 1472.
[36] M A Hegazy, H M Ahmed, A S El-Tabie, *Corros. Sci*,**2011**, 53, 671.
[37] S SAbd El-Rehim, M A M Ibrahim, K F Khaled,*J. Appl. Electrochem*,**1999**, 29, 593.
[38] S Martinez, I Stern, *Appl. Surf. Sci*,**2002**, 199, 83.
[39] H Zarrok, K Al Mamari, A Zarrouk, R Salghi, B Hammouti, S S Al-Deyab, E M Essassi, F Bentiss, H Oudda, *Int. J. Electrochem. Sci*,**2012**, 7, 10338.
[40] F Bentiss, M Lebrini, M Lagrenée, *Corros. Sc*,**2005**, 47, 2915.
[41] N A Odewunmi, S AUmoren, et Z MGasem, *J. Environ. Chem. Eng*,**2015**, 3, 1, 286‑296.

[42] N O Eddy, HMomoh-Yahaya, et E EOguzie, *J. Adv. Res,* **2015**, 6, 2, 203‑217.
[43] D Zhang, Y Tang, S Qi, D Dong, H Cang, et G Lu, *Corros. Sci*,**2016**, 102, 517‑522.
[44] M H Hussin, A A Rahim, M N Mohamad Ibrahim, et NBrosse, *Measurement*,**2016**, 78, 90‑103.