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Experimental and Computational Chemistry Investigations of Tartaric acid as a Green Corrosion Inhibitor for API 5L X 52 Carbon Steel in 0.5 M HCl

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Abstract: *Investigation of suitable corrosion inhibitor for API 5L X 52 carbon steel in 0.5 M HCl, is of significant industrial importance because of the role of the metal in several sectors. Tartaric acid was tested as a corrosion inhibitor for the metals using weight loss, potentiodynaic polarization and electrochemical impedance methods. The tested compound displayed maximum inhibition efficiency of 85%, which showed a strong dependency on concentration, temperature and time. Spontaneous and exothermic physical adsorption of the inhibitor on the metal surface was ascertained as the mechanism of inhibition. Isotherms established by the Langmuir and Freundlich assumptions fitted the adsorption process Information from computational chemistry calculations indicated significant roles of the frontier molecular orbitals towards the inhibition of the metal corrosion. Also, the sites for electrophilic, nucleophilic and radical attacks were observed to be within the carboxyl functional groups.*

Keywords: *API 5L X 52 carbon steel, corrosion, inhibition, tartaric acid, experimental and computational chemistry investigations*

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1.0 Introduction

Despite several published and unpublished researches on measures towards the control of corrosion, the corrosion industry is still experiencing some setbacks especially in the development of eco-friendly and efficient corrosion inhibitors (Awe *et al*., 2019; Odoemelam *et al*., 2019; Anand and Chitira, 2020). However, a consensus on the best option has ended on the utilization of green corrosion inhibitors, most of which are the product of plant and animal (Rosaline *et al*., 2011; Zeferani *et al*., 2013). . The search for green corrosion inhibitors has provoked several materials of plants and animal origin to be tested for their effectiveness as corrosion inhibitors (El-Haddad *et al*.,m 2019). Some of the tested materials include plant extracts, extracts of plant wastes, plant exudates, etc. (Ameh and Eddy, 2014; Ukpe *et al*., 2014; Ukpe, 2019ab).

Advance investigations have also been extended to some organic acids such as amino acids and their derivatives (Awe and Eddy, 2012; Eddy, 2010, 2011; Ekwumemgbo *et al*., 2013). However, much more interesting is the employment of fruits acids as corrosion inhibitors because of their nontoxicity, eco-friendliness, accessibility and unique corrosion inhibition properties. Therefore, the present study is aimed at utilizing tartaric acid as a corrosion inhibitor for API5L X 52 carbon steel in a solution of HCl.

2.0 Materials and Methods

Analar grades chemicals and reagents were purchased from Finlab stores in Abuja, Nigeria. This included tartaric acid, HCl, distilled water, zinc dust and acetone.

2.1 Experimental

2.1.1 Gravimetric experiment

Gravimetric experiments were carried out as reported elsewhere (Wan *et al*., 2021; Zhu *et al*., 2022). Based on the values of the estimated weight loss of the metal in the blank solution (1 M HCl) and in the presence of different concentrations of the tartaric acid (0.5, 1, 2, 3 and 4 M) in the acid solution respectively, the corrosion rate (CR) and the inhibition efficiency (%IE) of the tartaric acid for the meatal were evaluated using equations 1 and 2 respectively (Khattabi *et al*., 2014; Nwosu and Amusat, 2021)

$$CR\ (mg.cm^2) = \frac{m_i - m_f}{At} \qquad (1)$$

$$\%IE = \frac{CR_b - CR_{inh}}{CR_b} \times \frac{100}{1} \qquad (2)$$

where m_i and m_f are the masses of the metal before and after immersion in the test solution, CR_b and CR_{inh} are the corrosion rates of the metal in the test solution without and in the presence of the tartaric acid (TRA)

2.1.2 Electrochemical impedance spectroscopy (EIS)

EIS test was performed using a Gamry EIS 300 potentiostat as shown in appendix 5 at 303 K in the three-electrode cell system with the frequency range of (10000Hz – 0.05Hz), with a signal amplitude of 10 mV rms, DC voltage of 0.05 v, area of 1cm^^{2} and estimated z (ohms) of 100. A platinum electrode was used as a counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The working electrode used in this study was prepared from cylindrical API 5L X -52 pipeline carbon steel with 1cm^2 of the area exposed to the test solution. Measurements were performed in aerated solutions after 30 minutes of immersion in the test solution.

All potentials were reported vs. SCE. The charge transfer resistance values were obtained from the diameter of the semi-circles of the Nyquist plots. The inhibition efficiency of the inhibitor and the surface coverage were calculated from the charge transfer resistance values using equations 3 and 4 (Berisha *et al*., 2021),

$$\%IE = \frac{R_{ct(inh)} - R_{ct(blank)}}{R_{ct(inh)}} \times \frac{100}{1} \qquad (3)$$

$$\theta = \frac{R_{ct(inh)} - R_{ct(blank)}}{R_{ct(inh)}} \qquad (4)$$

where Rct-inh is the charge transfer resistance of the inhibited solution and Rct-blank is the charge transfer resistance of the uninhibited solution.

2.1.3 Potentiodynamic polarization

Potentiodynamic polarization studies were carried out at a potential range of 0.25 – 0.6 mV for API 5L X -52 steel at open current potential with a scan rate of 0.5m V/s at 303 K.The sample period of 1 (s), sample area of 1 cm^^{2}, the density of 7.87 (g/cm^^{3}) and an equivalent weight of 27.92 gms were also employed. The linear Tafel segments of the cathodic and anodic curves were extrapolated to obtain the corrosion current densities (Icorr). The inhibition efficiency was evaluated by using (Icorr) values as given in equation 5 below (Verma *et* al., 2021),

$$\%IE = \frac{i_{cor(blank)} - i_{cor(inh)}}{i_{cor(blank)}} \times \frac{100}{1} \qquad (5)$$

where $i_{cor(blank)}$ is the corrosion current without and I$i_{cor(inh)}$ is the corrosion current with inhibitor.

3.0 Results and Discussion

3.1 Inhibition efficiency

Fig. 1 shows plots, indicating the variation of weight loss with time for the corrosion of API 5L X 52 carbon steel in 0.5 M HCl. The plot reveals a linear pattern for the increase of weight loss (of the metal in 0.5 M HCl) with time. However, the addition of various concentrations of tartaric acid led to an observable decrease in weight loss with time, which translated to a decrease in the corrosion rate of the metal with the concentration of the tartaric acid and with time. Such a trend gives evidence of the inhibition capacity of the tartaric acid for the corrosion of API 5L X 52 carbon steel in 0.5 M HCl. In Table 1 average corrosion rate of the metal and evaluated inhibition efficiencies in the presence of various concentrations of the tartaric acid are presented. The tartaric acid (TRA) acid is evidently behaving as an adsorption inhibitor because its inhibition efficiency for the metal increases with concentration, even as the corrosion rate decreases with an increase in the concentration of the TRA (Eddy *et al*., 2008, 2009, 2010a, 2011, 2012). The data in Table 1 also reveal that the acid forms a protective coverage on the surface of the metal through adsorption, which also increased with increasing TRA concentration. (Haldhar *et al*., 2021; Mohd *et al*., 2021).

Table 1: The corrosion rate, surface coverage and inhibition efficiency of tartaric acid for the corrosion of API 5L X 52 carbon steel in 0.5 M HCl at 303 and 333 K.

C (M)	CR Mg/cm^2		θ		%IE	
	303 K	**333 K**	**303 K**	**333 K**	**303 K**	**333 K**
0.5 M HCl	3.114	20.873	=	-		
1	0.976	17.338	0.6866	0.2173	68.66	21.73
2	0.826	15.955	0.7347	0.2356	73.47	23.56
3	0.720	13.965	0.7688	0.3310	76.88	33.10
4	0.628	12.896	0.7983	0.3822	79.83	38.22
5	0.512	12.029	0.8356	0.4237	83.56	42.37

The characteristics of APl 5L X-52 carbon steel corrosion in 2 M HCl solution in the presence of the studied inhibitors were also studied by electrochemical impedance spectroscopy (EIS) at 303 K. The Nyquist plots of API 5L X-52 carbon steel in 2 M HCl in the 2 M acid concentration and in the presence of different concentrations of the inhibitor at 303 K is shown in Fig. 2 while information evaluated from the plots are in Table 2. The Nyquist plots display a depressed semicircle in a high frequency region with centre under the real axis. The size of the semicircle increases with an increase in the concentration of the TRA, indicating that the corrosion of API 5L X – 52 carbon steel is controlled by a charge transfer process, (Momoh-Yahaya *et al*., 2012). The Nyquist plots were appropriately analyzed by fitting the data into the electrical equivalent circuit model. The model considered the solution resistance (Rs), charge transfer resistance of the interfacial corrosion (Rct) and constant phase element representing the double-layer capacitance (Cdl) (equation 6). (Beniken *et al*., 2018).

$$C_{dl} = (Q \times R_{ct}^{1-\alpha})^{\frac{1}{\alpha}} \qquad (6)$$

where Q defines a proportionality factor, α is a phase shift factor that varies between -1 and +1 and is also an index for defining heterogeneity and roughness of the surface. The results indicated (Table 2) reveal that the solution resistance increases with an increase in the concentration of the inhibitor which indicates that the tendency towards corrosion was retarded by the TRA inhibitor. However, the charge transfer resistance and the f_{max} (f_{max} is the frequency at which the imaginary component of the impedance (Z_{max}) is maximum.) decreased with a decrease in the concentration of the inhibitor. Based on equation 4, an increase in the double layer capacitance should correspond to a decrease in charge transfer resistance and hence an increase in inhibition efficiency as shown in Table 2. Evaluated values of the inhibition efficiency of TRA also increased with an increase in the TRA concentration and ranged from 50.70 to 63.10 % and is in excellent agreement with results gotten for the weight loss experiment ($R^2 = 0.9163$).

Experimental information obtained from potentiodynamic polarization study is presented in Fig. 3 and Table 3. The plots (Fig. 3) reveal shifts in the position of the anodic and cathodic arms as the concentration of TRA increases which can be remarked as equivalent to a reduction in the potential current as the concentration of TRA increases. The observed decrease in corrosion current manifested in a corresponding increase in the inhibition efficiency of TRA as shown in Table 3.

The presented inhibition efficiency, which ranged (from 46 to 81%), also shows an increase in the inhibition efficiency with concentration (as shown in Table 3) and correlated excellently with gravimetric data (R^2 = 0.9859). The shifts in the corrosion potential between that of the blank and the inhibited systems ranged from 3.2 to 9.2 mV for the various concentrations of the tested inhibitor. Since these values are significantly less than 82 mV, therefore, the mechanism of adsorption of TRA on the surface of the metal is physisorption (Ikpi and Abeng, 2020). Also, the shift in the anodic lobe is more prominent than that of the cathode, which suggests that TRA is acting as an anodic inhibitor and operates by suppressing the oxidation reaction that releases electrons for the facilitation of corrosion through an increase in current (Ikpi *et al.*, 2012; Ikpi and Abeng, 2018)

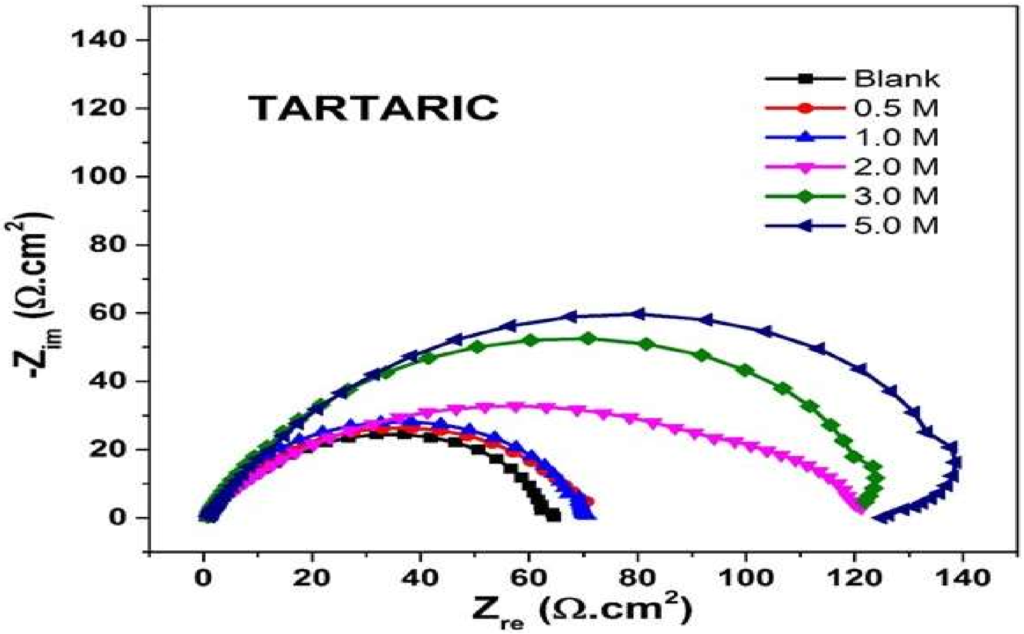

FIG. 29: Impedance spectra of the corrosion of API 5LX-52 carbon steel in 2 M HCl solution in the absence and presence of tartaric at 303

Table 2: Electrochemical and kinetic parameters from EIS technique for the corrosion of API 5L X - 52 carbon steel in 2 M HCl for different concentrations of TRA at 303 K

	C (g/L)	$R_s(\Omega)$	$R_{ct}(\Omega)$	f_{max}	Cdl	θ	IE (%)
Tartaric Acid	Blank	5.38E-01	64.55	1.56E+01	1.58E+03		
	0.5	7.61E-01	130.9	3.16E+02	6.50E+04	0.507	50.70
	1	8.30E-01	144.9	9.93E+00	2.26E+03	0.555	55.50
	2	9.36E-01	159.4	6.32E+00	1.58E+03	0.595	59.50
	3	7.99E-01	166.7	6.32E+00	1.66E+03	0.613	61.30
	5	1.01E+00	175	5.01E+00	1.38E+03	0.631	63.10

3.2 Activation energy and heat of adsorption

The activation energy for the adsorption of the TRA inhibitor on the metal surface was evaluated through the application of the Arrhenius equation (equation 5)(Essien and Ogoko, 2019)

$$log\left(\frac{CR_{(blank)}}{CR_{(inh)}}\right) = \frac{E_a}{2.303}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (7)$$

The corrosion rates for the blank ($CR_{(blank)}$) and for the inhibited ($CR_{(inh)}$) systems at 303 (T_1) and 333 K (T_2) were evaluated and the results obtained were presented in Table 1. The activation energies based on equation 5 are presented in Table 4.

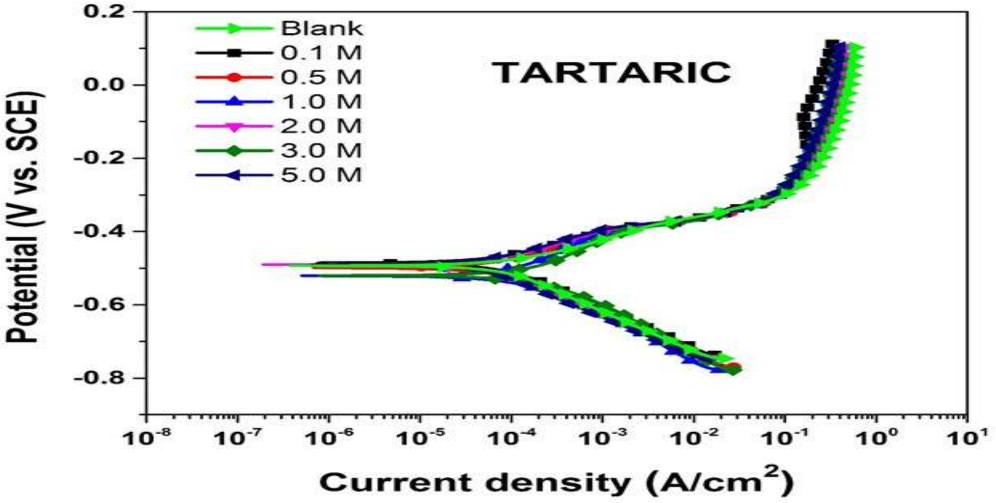

Fig. 3: Potentiodynamic polarization plot for corrosion of API-5L-X-52 Carbon steel inhabited by TRA

Table 3:Tafel Polarization Parameters for API-5L-X-52 Carbon in the absence and presence of different concentrations of inhibitors at 303K

C (M)	β_a(V/dec)	β_c (V/dec)	E_{corr} (Mv)	I_{corr} (μA)	CR (mpy)	R_p(Ω/cm²)	IE%
Blank	7.00E-02	1.30E-01	-493.2	97.76	44.67	7.73E-02	
0.1	7.32E-02	1.06E-01	-485	52.8	33.27	3.20E-02	46.00
0.5	7.84E-02	1.06E-01	-499	46.2	30.25	3.07E-02	52.70
1.0	7.43E-02	1.16E-01	-490	34.6	24.95	2.46E-02	64.60
2.0	6.41E-02	9.79E-02	-490	29	22.4	1.28E-02	70.30
3.0	6.46E-02	9.98E-02	-490	24.3	20.23	1.12E-02	75.10
5.0	6.43E-02	1.02E-01	-490	19.1	19.67	8.99E-03	81.00

Table 4: Activation energy and thermodynamic parameters for the inhibition of the corrosion of API-5L-X-52 Carbon steel by different concentrations of TRA

C (g/L)	$E_a\ (J/mol)$	$Q_a(J/mol)$
0.5 M HCl	53.27	-6.43
0.1	80.56	-8.28
0.2	82.90	-9.52
0.3	83.02	-11.23
0.4	84.61	-14.62
0.5	88.38	-6.43

The results for the activation energy (Table 4) indicated the lowest E_a value for the blank (0.5 M HCl) solution and a progressive increase in the activation energy with the increasing concentration of the TRA inhibitor. Therefore, the ease of corrosion decreases with an increase in TRA concentration, hence there is a gradual increase in the resistance toward corrosion as TRA concentration increases.

The heat of adsorption of TRA on the metal surface can be evaluated from the degree of surface (θ) and temperature (T) data using equation 8 (Ikpi *et al.*, 2012)

$$Q_{ads} = 2.30R\left(\frac{\theta_2}{1-\theta_2} - \frac{\theta_1}{1-\theta_1}\right) \times \left(\frac{T_1T_2}{T_2-T_1}\right) \quad (8)$$

Estimated values of Q_{ads} are also presented in Table 4. Since the Q_{ads} values are negative, the adsorption of TRA on the metal surface is exothermic. (Eddy *et al*., 2010b)

3.3 Application of adsorption isotherms

The adsorption of TRA inhibitor fitted some adsorption isotherms (after some tests of fitness) including the Langmuir (equation 9) and the Temkin (equation 8) adsorption models (Akinbulumo *wt al.,* 2020; Ogunleye *et* al., 2020; Sanaei *et al*., 2019; Stango and Vijayalakshmi, 2018)

$$\frac{C}{\theta} = \frac{1}{k_{ads}} + C \quad (9)$$

$$\theta = \frac{-lnk_T}{2a} - \frac{-lnC}{2a} \quad (10)$$

k_{ads} in equation 9 is the Langmuir adsorption-desorption constant, while 'a' and k_T in equation 8 are the interaction parameter and the Temkin adsorption constant respectively. The standard free energy of adsorption (ΔG^0_{ads}) can be evaluated from these constants using the following equations ((Eddy, 2010; Eddy and Odoemelam, 2008; Odoemelam *et al*., 2009; Ouknin *et al*., 2020)

$$\Delta G^0_{ads} = -RTlnk_{ads} \quad (11)$$

Figs. 4 and 5 show the adsorption isotherm for TRA inhibitor according to Langmuir and Temkin models. The linearity of the plots was established by the high values of R^2 recorded in the chat. The slopes evaluated from the plots were significantly less than the unity value expected for an ideal Langmuir isotherm, which predicts monolayer adsorption with no interaction between the adsorbed species. Consequently, interaction parameters were deduced from the Temkin isotherms (Fig. 5) and the values were positive (0.24 and 0.15) at both temperatures and signify the attractive behaviour of the adsorbed species

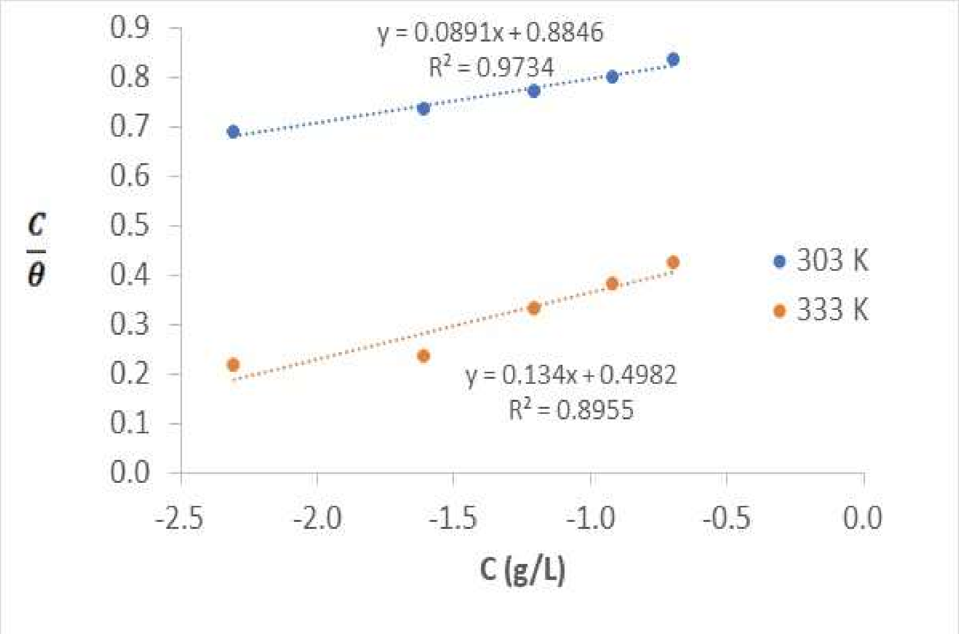

Fig. 4: Langmuir isotherm for the adsorption of TRA on the surface of API-5L-X-52 carbon steel

The estimated values of the free energy change, estimated from the Langmuir parameter at 303 and 333 K were -12.35 and -13.57 kJ/mol. Those evaluated from the Temkin constant were -12.17 and -12.87 kJ/mol respectively. These values are in agreement with each other and generally align with the fact that the adsorption of TRA is through the mechanism of physical adsorption since the ΔG^0_{ads} are below -20 kJ/mol (Akinbulumo *et al*., 2020; Fouda *et al*., 2021; Prabhu *et al*., 2021; Wang *et al*., 2019).

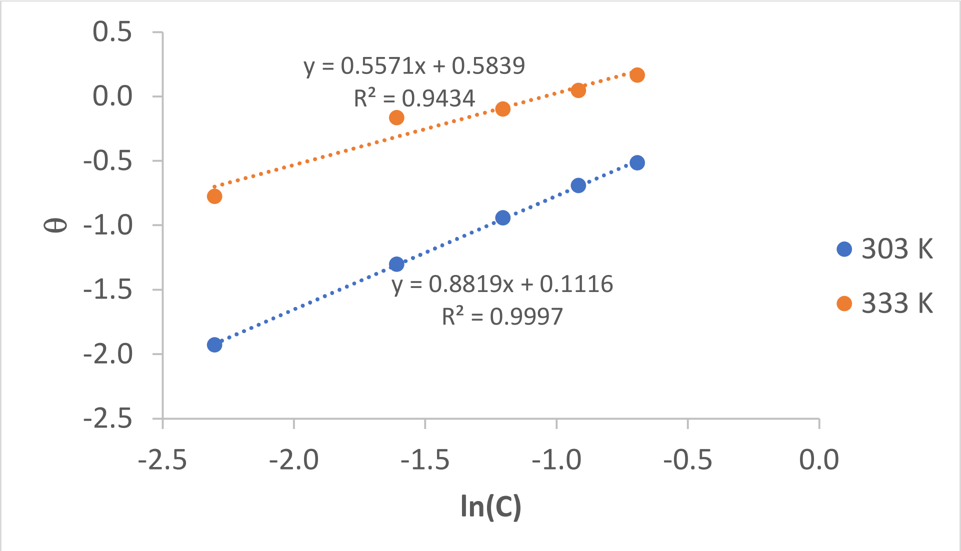

Fig. 5: Temkin isotherm for the adsorption of TRA on the surface of API-5L-X-52 carbon steel

3.4 Computational chemistry study

The optimized structure of tartaric acid is shown below. The compound contains S four carboxylic oxygen atoms and two alcohol oxygen atoms. It has two double bonds, hence it has some properties that are typical for most organic corrosion inhibitors (Ikpi *et al.*, 2017). The frontier molecular orbital energies have widely been used as reactivity indices because the energy of the highest occupied molecular orbital (E_{HOM}) is an index for the donation of the electron, even as that of the lowest molecular orbital (E_{LUMO}) signifies the tendency towards acceptance of electron and the difference (between the later and the former), signifies the tendency towards softness or hardness and thus electronic transition (Eddy, 2020; Eddy and Awe, 2018). The calculated values of the E_{HOMO} and E_{LUMO} for the TRA are -7.06 and -0.590 eV respectively. These values are not out of the range of values reported for some effective corrosion inhibitors (Eddyand Ameh, 2021). The dipole moment and the total molecular energy were 5.47 Debye and -607.53 a.u respectively. The HOMO, LUMO and electrostatic molecular surfaces for the TRA molecular are also shown in Fig. 6

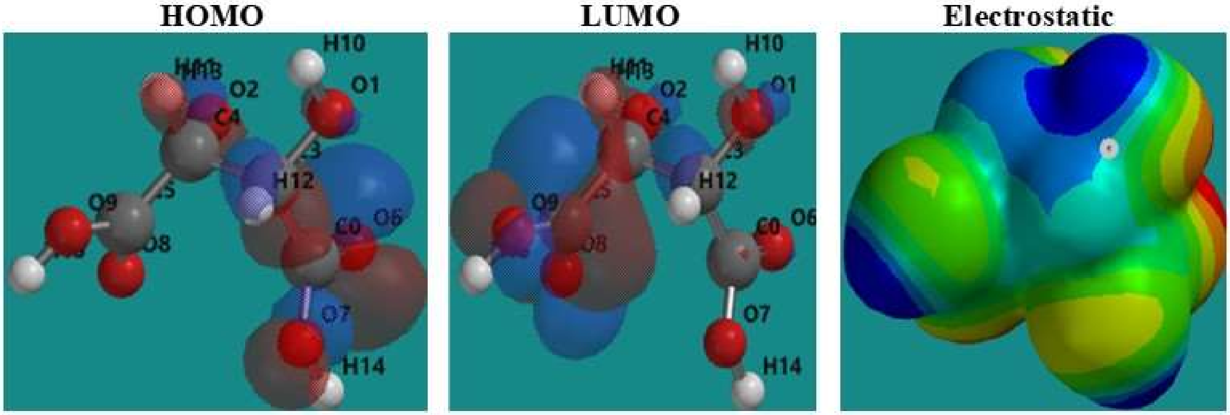

Fig. 6: Molecular surfaces for TRA inhibitor

The HOMO and the LUMO orbitals of TRA seem to exchange themselves between the two carboxylic groups in the molecules while the electrostatic potential map reveals that the molecule has different zones of charge distribution that may affect the adsorption of the inhibitor unto the metal surface.

The sites for electrophilic, nucleophilic and radical attacks in TRA molecule were identified using the condensed Fukui functions which are represented by equations 12 to 14 respectively (Ameh and Eddy, 2018a-b, Eddy and Ameh, 2011; Eddy *et al*., 2018)

$$,f_x^- = q_N - q_{N-1} \quad (12)$$

$$f_x^+ = q_{N+1} - q_N \quad (13)$$

$$f_x^0 = \frac{q_{N+1} - q_{N-1}}{2} \quad (14)$$

where q is the Hirsfeld or Mullike charge.

Table 4: Fukui Indices of TRA for electrophilic, nucleophilic and radical attacks

Atom label	Mulliken	Hirshfeld	Mulliken	Hirshfeld	Mulliken	Hirshfeld
C(1)	0.083	0.076	0.027	0.022	0.055	0.049
O(2)	0.031	0.044	0.031	0.039	0.031	0.041
O(3)	0.022	0.026	0.033	0.067	0.028	0.046
C(4)	-0.016	0.022	-0.017	0.009	-0.016	0.016
C(5)	-0.015	0.015	-0.011	0.041	-0.013	0.028
C(6)	0.023	0.028	0.187	0.188	0.105	0.108
O(7)	**0.281**	**0.277**	0.083	0.074	**0.182**	**0.176**
O(8)	0.096	0.120	-0.019	0.013	0.039	0.067
O(9)	0.130	0.121	**0.205**	**0.198**	0.168	0.159
O(10)	0.023	0.051	0.100	0.110	0.062	0.081

Based on the Mulliken and Hirsfeld Fukui functions, the possible sites for electrophilic attacks is the one with the highest positive value of the electrophilic Fukui function, which is the carboxyl oxygen atom, O(7),. This site is also the preferred site for the radical attack and the HOMO centre. On the other hand, the site for the nucleophilic attack is also the carboxyl carbon that forms a mirror image with the one for the electrophilic attack, i.e O(9). Also, this site is the centre for the concentration of the LUMO.

4.0 Conclusion

TRA is an efficient corrosion inhibitor for API-5L-X-52 carbon steel and tends to inhibit better with an increment in concentration but its efficiency tends to be reduced as the temperature and period of contact increase. The mechanism of adsorption of the inhibitor is physical adsorption. The adsorption obeys the Langmuir and Temkin isotherms and was spontaneous and stabilized by the release of energy. Computational chemistry calculations provided information on the preference of the two carboxylic ends to serve as the centres for electrophilic and nucleophilic attacks.

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Conflict of interest

The authors declared no conflict of interest