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Original Research Article

Experimental and Theoretical Study on the Corrosion Inhibitive Potentials of Schiff Base of Aniline and Salicyaldehyde on mild steel in 0.5M HCl

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ABSTRACT

The need to control and ultimately eradicate the scourge of metal corrosion has become necessary given the high incidence of deaths and loss of property resulting from it. The choice of π-conjugated organic systems has been justified in that they are easier to produce and their modes and rates of adsorption are very superb, a consequence of the π-electrons. In this work, a Schiff base of the reaction of aniline and salicyaldehyde was applied as corrosion inhibitor on mild steel via weight loss techniques (at different inhibitor concentrations and at different temperatures) from which the corrosion rate (C_r), degree of surface coverage (θ) and the percentage inhibition efficiency (%IE) were calculated. The molecule was modelled and optimized using Density functional theory (DFT) with B3LYP correlation and 6-31G* and 6-31+G* basis sets to obtain the electronic properties like the frontier molecular orbitals energies (E_{HOMO} and E_{LUMO}), energy band gap (E_g), dipole moment (μ) and the reactivity descriptors like chemical hardness (η), softness (δ), global electrophilicity index (ω) and fraction of electrons transferred (ΔN). The C_r increased with increase in temperature and decreased as the inhibitor concentration increases while the %IE followed a reverse pattern. From the R^2 values, the molecule's adsorption obeyed the Freundlich adsorption isotherm. ΔG values which turned negative confirmed that the reactions are exothermic and spontaneous. The results obtained are consistent with available experimental data.

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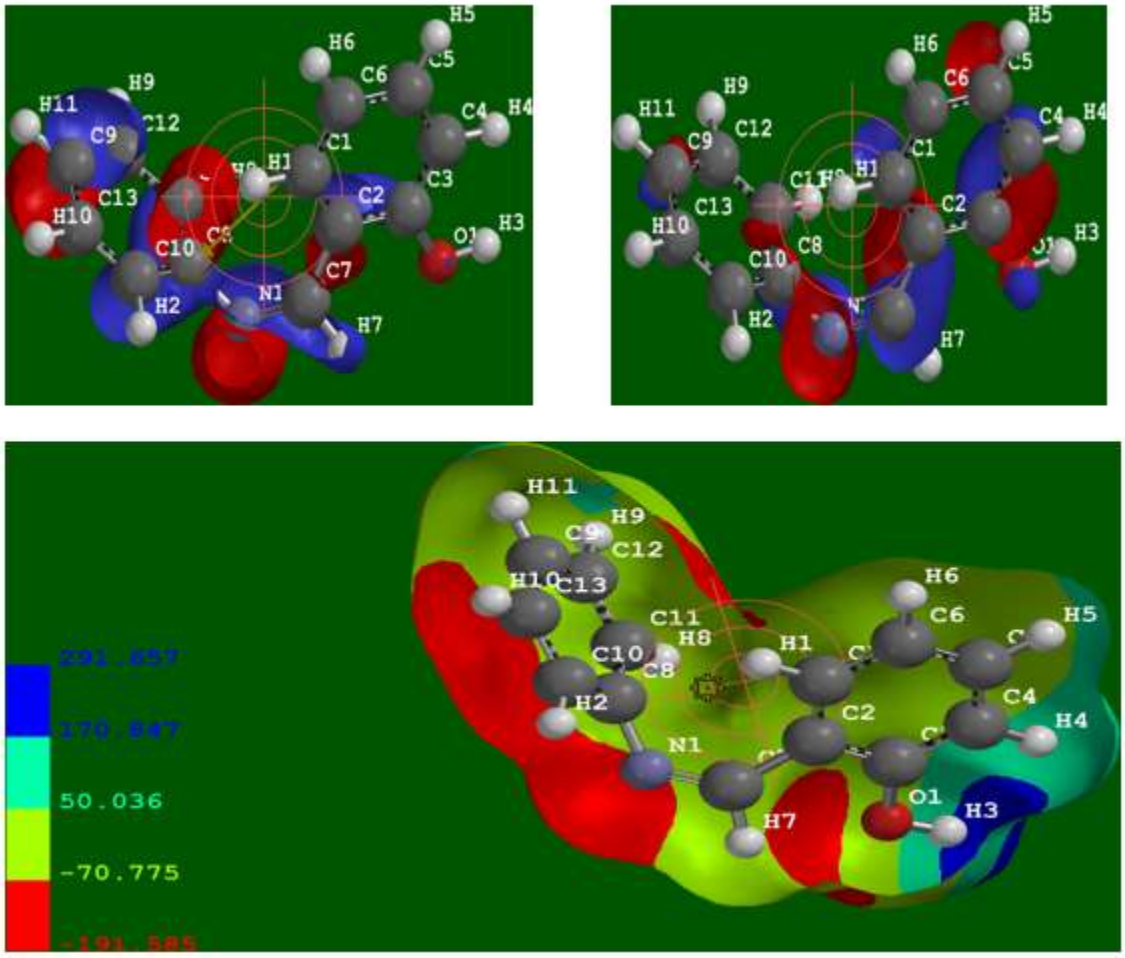

Introduction

Corrosion of mild steel used in industries during acid prickling, descaling and other industrial processes [1,2] has been a cause for concern among researchers. Loss of metal strengths and parts has caused deaths, loss of properties [3] and increased cost of production of goods [4]. To put an end to this menace, continuous search for materials that can inhibit corrosion has been ongoing [5]. Over the past decades, the use of corrosion inhibition has been a major breakthrough in this regard [6,7]. However, there is the need to design materials with optimal properties. Consequently, the properties of known materials have to be thoroughly investigated, analyzed and reported in order to have a sense of direction with regards to finding answers to the problem of metal corrosion. Organic corrosion inhibitors are massively reported to be highly potent in tackling this problem [7-9], because of their composition (they are mostly conjugated and can easily be tuned for optimal results). The presence of heteroatoms like O, N and S [9,10] is important for better adsorption

of the inhibitors on the metal surface. A lot of organic molecules have been reported to exhibit excellent anti-corrosion properties [7,9,10]. Organic Schiff bases have been reported for their medicinal and pharmaceutical applications [11,20,21,]. The molecule under investigation (N-Salicylideneaniline) has earlier been reported in our previous work as ligand in some transition metals for their antimicrobial properties [11], it is extensively π-conjugated, contains heteroatoms (O and N), hence our choice to investigate it as probable anti-corrosion agent. Some researchers have reported it in their work as an anti-corrosion agent [12], however, the adsorption process was not keenly investigated, and the theoretical investigation has not been reported on the anti-corrosion mechanism of the molecule. Corroborating theoretical results with those in experiments in past and recent times has helped in understanding molecular behaviours better. This work, therefore, seeks to investigate the corrosion inhibitive mechanism of N-Salicylideneaniline using experimental and theoretical approaches. The weight loss experiment was used to obtain the corrosion rate (C_r), degree of surface coverage (θ) and the percentage inhibition efficiency (%IE). The adsorption pattern was also determined. To understand better the mechanism of action of the inhibitor, quantum chemical calculations were carried out on the modelled molecule to determine its reactivity descriptors. The result obtained were compared to available experimental results.

Materials and Methods

Mild steels were mechanically machined into small sizes, polished, washed with distilled water and greased with acetone before drying overnight in desiccators [9]. 0.5M HCl was prepared and added (100 ml) to the weighed mild steels in the absence (blank) and presence of inhibitors of varying concentrations (0.0005, 0.001, 0.002, 0.003, 0.004 and 0.005 moldm^{-3}) in different test tubes at a temperature for 6 hours. The temperature was varied (25^{0}C, 35^{0}C, 45^{0}C, 55^{0}C and 65^{0}C) in a thermostated water bath. Samples were removed from the test solution after 6 hours, brushed, washed with distilled water, rinsed in acetone and dried before weighing it again. This experiment was repeated to get accurate and consistent result, with the mean of the final weights used. From the results C_r, θ and %IE were calculated using equations.

$$C_r = \frac{W_1 - W_2}{At} \quad (1)$$

$$\theta = 1 - \frac{C_r i}{C_r o} \quad (2)$$

$$\%IE = \theta \times 100 \quad (3)$$

W_o and W_1 being the weight losses (g) of mild steel in the absence and presence of the inhibitor respectively. A is the area of the mild steel (cm^2) while t is the immersion time (hrs). C_ri and C_ro are the corrosion rates (g cm^{-2} hr^{-1}) in the presence and absence of the inhibitor respectively.

Adsorption isotherms were used to explain the adsorption mode and mechanism of action of the inhibitor as it comes in contact with the mild steel. The Freundlich adsorption isotherm (Equation 4) was employed in this case [13].

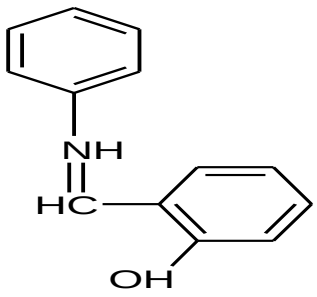

Fig. 1: *Structure of ANSB*

$$Log\ \theta = Log\ K_{ads} + nLogC \quad (4)$$

where *C* is the concentration of inhibitor, K*ads* the equilibrium adsorption constant and θ, the extent of surface coverage. The thermodynamic parameters like the standard Gibb's free energies of adsorption (ΔGoads) were calculated using equation 5.

$$K_{ads} = \frac{1}{55} e^{\frac{\Delta G^{o}_{ads}}{RT}} \quad 5$$

R being the universal gas constant, while ΔGads is the free energy of adsorption and 55.5 is water's molar concentration in the solution (isocratic contribution). The enthalpy, ΔHo and entropy ΔSo of adsorption were obtained from the intercept and slope, respectively of ΔGoads vs temperature (Equation 6) enthalpy, ΔHo and entropy ΔSo of adsorption [9].

$$\Delta G_{ads}{}^{o} = \Delta Ho - T\Delta So \quad 6$$

The kinetic model was used to calculate the activation energies, E_a by using the plot of lnCr against 1/T (equations 7 and 8) [9,13].

$$C_r = Ae^{\frac{E_a}{RT}} \quad 7$$

$$lnC_R = lnA - \frac{E_a}{RT} \quad 8$$

The molecule, ANSB was modeled and optimized after the global minimum was obtained from a conformational search using the Molecular Mechanical Force Field (MMFF). The optimization was completed without any constraint using the Density Functional Theory (DFT) method [17-19] with Becke Three Lee Yang Parr Correlation, B3LYP as seen in equation 9 [14] and 6-31G* and 6-31+G* basis sets. These methods were chosen because they have been used in past and recent times to successfully predict the properties of molecules [13,16-19].

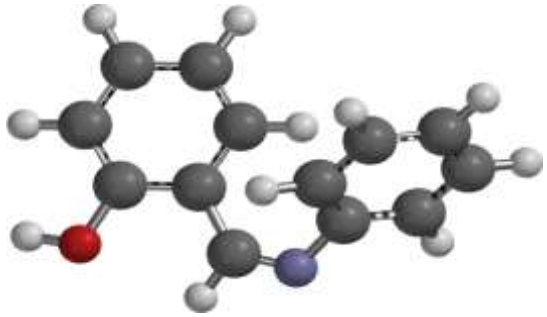

Figure 2: *Optimized structure of ANSB*

$$E_{XC}^{B3LYP} = aE_X^B + E_C^{LYP} + HF\ (20\%) \quad 9$$

The energies of the frontier molecular orbitals, E_{HOMO} and E_{LUMO} being the energies of the highest occupied molecular orbital and lowest unoccupied molecular orbital, the energy band gap, E_g (equation 10), dipole moment, μ (equation 11), chemical hardness, η (equation 12), softness, δ (equation 13), electronegativity, χ (equation 14), global electrophilicity index, ω (equation 15) and fraction of electrons transferred, ΔN (equation 16) were calculated.

$$E_g = E_{LUMO} - E_{HOMO} \quad 10$$

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad 11$$

$$\eta = \frac{E_g}{2} \quad 12$$

$$\delta = \frac{1}{\eta} \quad 13$$

$$\chi = \frac{I+A}{2} \quad 14$$

where $I = E_{HOMO}$ and $A = E_{LUMO}$

$$\omega = \frac{\chi^2}{E_g} \quad 15$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad 16$$

With χFe and χInh being the electronegativities of iron/bulk metal (7 eV) and the inhibitor respectively while ηFe (0 eV) and ηInh are the hardness of iron and the inhibitor respectively [9,10,13].

Results and discussions

Gravimetric experiment

The results from the gravimetric (weight loss) experiment (table 1) presented the C_r, %IE and θ. Generally, the C_r values decreased as the concentration of the inhibitor increases, this is in line with what was observed in previous works [9,13] while it increased as the temperature increases. This is because as the inhibitor concentration increases, more of the molecules are adsorbed on the metal surfaces and consequently decreases the rate of corrosion. However, molecules have been reported to desorb from the surface of metals as temperature increases, and as a consequence, increases corrosion rate (figure 3). The highest inhibition efficiency was observed at 298 K (25^0C), indicating the temperature that the inhibitor can perform optimally. This implies that the inhibition efficiency increases as the concentration of the inhibitor increases but decreases as temperature increases.

Adsorption isotherm and thermodynamic parameters

The adsorption of the molecule obeyed the Freundlich adsorption isotherm as seen from the R^2 values (table 4) from the plot of C/ɵ against C at different temperature. All ΔG values are around -9 to -12 $kJmol^{-1}$, indicating physical adsorption of the inhibitor at all concentrations.

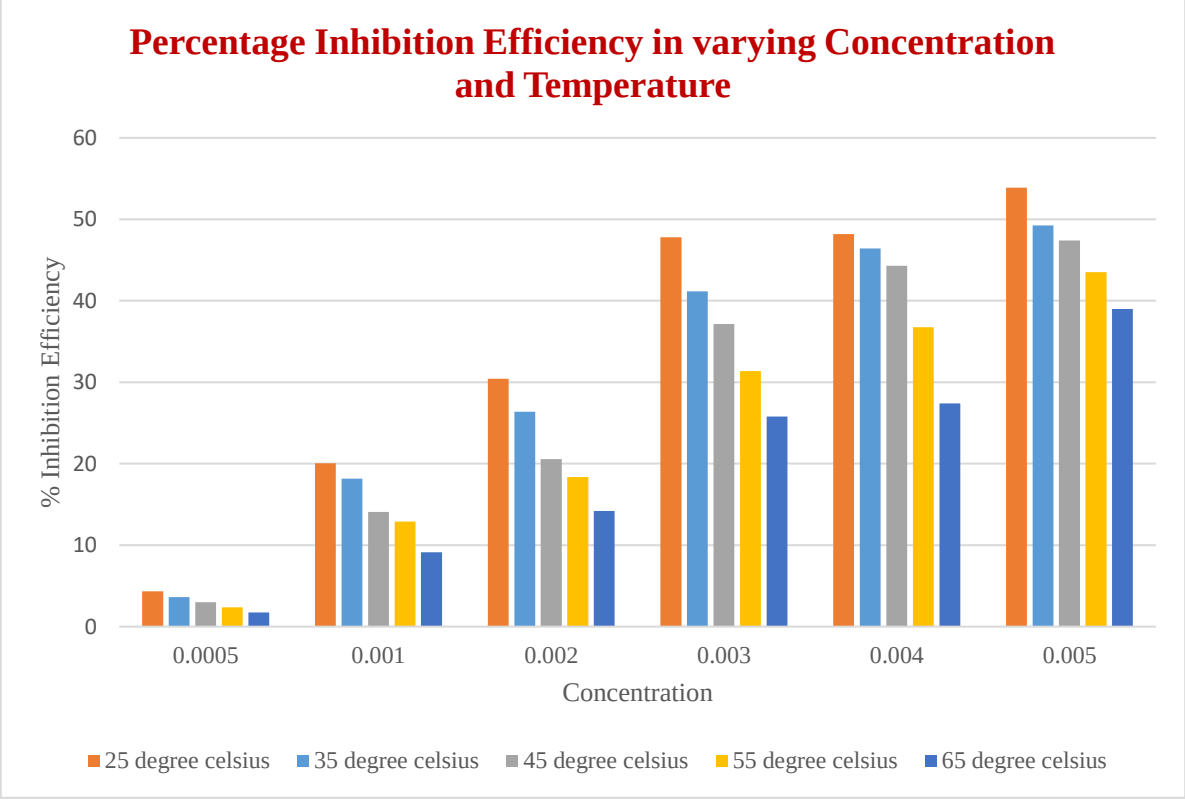

Fig. 3: *Variation of %IE in different inhibitor concentration and temperature*

Table 1: Results from the gravimetric analysis of ANSB on mild steel

Temperature (K)	Concentration (moldm^{-3})	C_r	%IE	~~Θ~~
298	Blank	0.000411	-	
	0.0005	0.000393	4.35	0.044
	0.001	0.000328	20.06	0.201
	0.002	0.000286	30.44	0.305
	0.003	0.000215	47.79	0.478
	0.004	0.000213	48.18	0.482
	0.005	0.000189	53.88	0.539
308	Blank	0.000496	-	
	0.0005	0.000478	3.627	0.037
	0.001	0.000406	18.16	0.182
	0.002	0.000365	26.36	0.264
	0.003	0.000292	41.15	0.412
	0.004	0.000266	46.40	0.464
	0.005	0.000252	49.27	0.493
318	Blank	0.000615	-	
	0.0005	0.000545	2.99	0.029
	0.001	0.000504	14.09	0.141
	0.002	0.000399	20.55	0.205
	0.003	0.000353	37.14	0.371
	0.004	0.000334	44.29	0.443
	0.005	0.000615	47.39	0.474
328	Blank	0.000789	-	
	0.0005	0.000770	2.36	0.024
	0.001	0.000687	12.89	0.129
	0.002	0.000644	18.36	0.14
	0.003	0.000541	31.38	0.314
	0.004	0.000499	36.76	0.368
	0.005	0.000446	43.49	0.435
338	Blank	0.000992	-	
	0.0005	0.000974	1.73	0.018
	0.001	0.000901	9.16	0.092
	0.002	0.000851	14.21	0.142
	0.003	0.000736	25.79	0.258
	0.004	0.000720	27.39	0.274
	0.005	0.000605	39.02	0.390

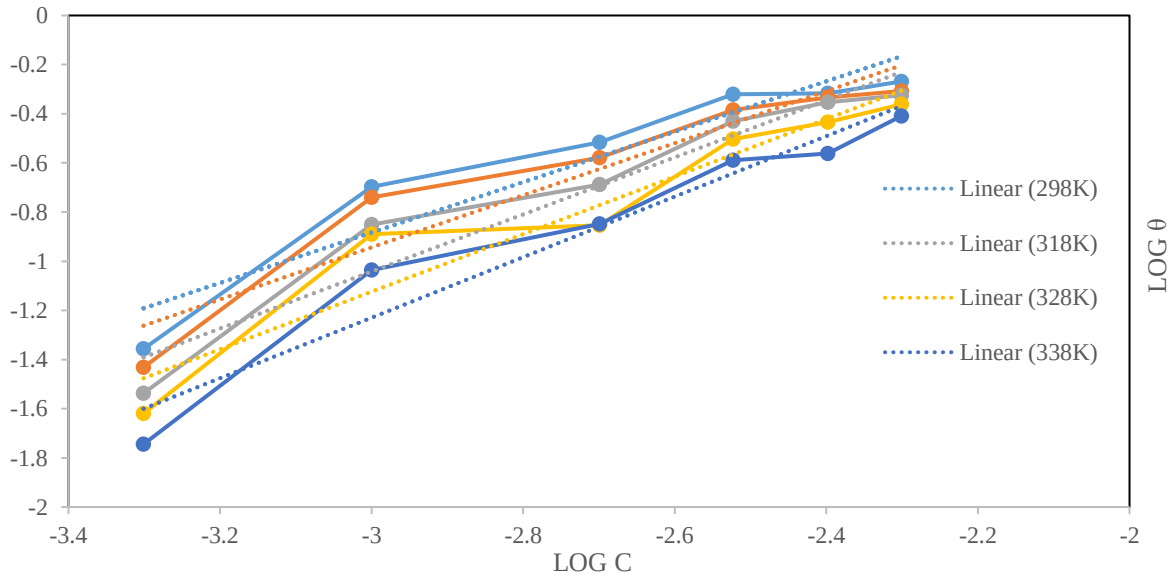

Fig. 4: *Freundlich adsorption isotherm for ANSB adsorption*

Table 2: *Thermodynamic Parameters of ANSB on mild steel*

Temp. (K)	R^2	Intercept	K	ΔG(J/mol)	ΔG(kJ/mol)
298	0.902	2.1932	156.03	-9755.44	-9.76
308	0.9047	2.2357	172.07	-10191.38	10.19
318	0.9337	2.4416	276.44	-11066.90	-11.07
328	0.9181	2.3881	244.40	-11269.02	-11.27
338	0.9421	2.4645	291.41	-11827.28	-11.83

Table 3: *Kinetic parameters of ANSB on mild steel*

Concentration ($moldm^{-3}$)	Ea (J)	Ea(KJ)
Blank	18458.95	18.46
0.0005	19012.37	19.01
0.001	21130.24	21.13
0.002	22837.91	22.84
0.003	25808.95	25.81
0.004	25511.60	25.51
0.005	24299.65	24.29

Table 4: *Electronic properties and global reactivity descriptors of ANSB*

E_{LUMO} (eV)	E_{HOMO} (eV)	I (eV)	A (eV)	E_g (eV)	η (eV)	S (eV^{-1})	χ (eV)	ω (eV)	ΔN	μ (D)
DFT/B3LYP/6-31G*										
-1.32	-5.58	5.58	1.32	4.26	2.13	0.47	3.45	2.79	0.83	4.00
DFT/B3LYP/6-31+G*										
-1.71	-5.90	5.90	1.71	4.19	2.09	0.48	3.81	3.45	0.76	4.15

Kinetic parameters

E_a for all concentrations fall below 80kJ/mol which is an indication of physical adsorption (physiosorption). E_a values of other concentrations are higher than that of blank, it is also an indication of physical adsorption. ΔG values are negative, indicating that the reactions are exothermic and spontaneous.

Quantum chemical calculations

The E_g value is 4.26 eV (6-31G*) and 4.19 eV (6-31+G*) respectively, indicating that there is electron movement from the molecule and the metal's vacant *d*-orbitals, this is evidenced by the E_{HOMO} value of -5.58 eV (6-31G*) and -5.90 eV (6-31+G*), indicating excellent donating ability of the inhibitor, the LUMO orbitals have low E_{LUMO} value of -1.32 eV (6-31G*) and -1.71 eV (6-31+G*), indicating that the inhibitor can readily accept electrons from metal's orbitals. The chemical hardness is a direct consequence of the E_g value (equation 12), that is, the molecules hardness must be relatively low in order to enhance adsorption of the inhibitor molecule and the metal, according to the hard and soft acids and bases principle HSAB. η is 2.13 eV (6-31G*) and 2.09 eV (6-31+G*) while δ is 0.47 eV^{-1} (6-31G*) and 0.48 eV^{-1} (6-31+G*). When the metal's hardness is assumed zero (very soft), it will react more readily with a soft base (the inhibitor molecule), thereby improving the adsorption and inhibition efficiency. To corroborate the fact that the molecule inhibited metal corrosion, the fraction of electron transferred (ΔN) tells us the extent to which the molecule binds to the metal surface. ΔN of an inhibitor must be < 3.6 for it to be considered effective [9,10,15]. ΔN for ANSB is 0.83 (6-31G*) and 0.76 (6-31+G*), an indication that it has donating ability and is effective as a corrosion inhibitor. The dipole moment is 4.00 D (6-31G*) and 4.15 D (6-31+G*), confirming that there is distribution of electron in the molecule and that there is strong dipole-dipole interaction between ANSB and the surface of the metal (that is, adsorption is enhanced through electronic force). The HOMO plot (figures 5 and 6) shows that the electron rich molecular orbital is localized majorly on the benzylidene moiety while the LUMO is delocalized almost entirely over the molecular system with major distribution over the phenol and azomethine moieties. This implies that there is possibility of intramolecular charge transfer in the system, as observed in our previous work on ANSB [11]. The electrostatic potential maps (figures 7a and 7b) show the electron rich benzylidene and hydroxyl moieties with different electron deficient phenyl ring. The unsymmetrical charge distribution suggests a possibility of charge transfer between benzylidene moiety and the phenol moiety.

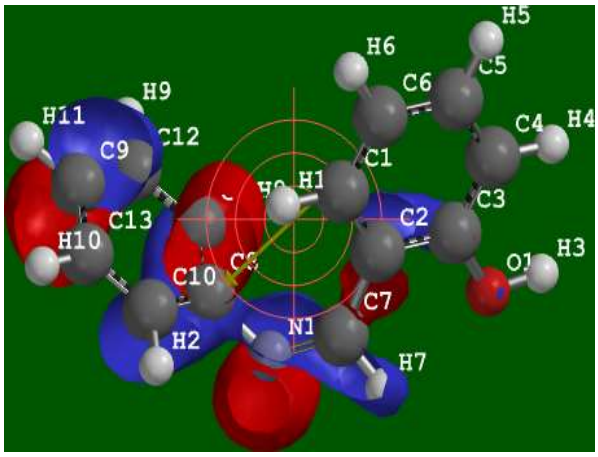

Fig. 5a: *HOMO plot 6-31G**

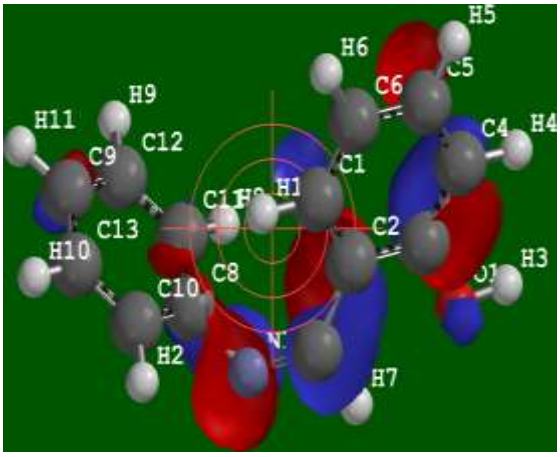

Fig. 5b: *LUMO plot 6-31G**

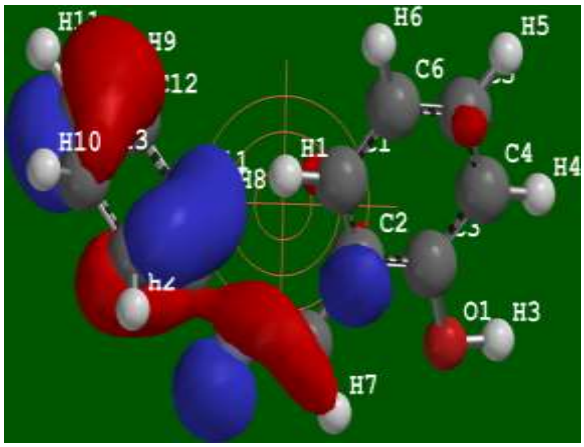

Fig. 6a: *HOMO plot 6-31+G**

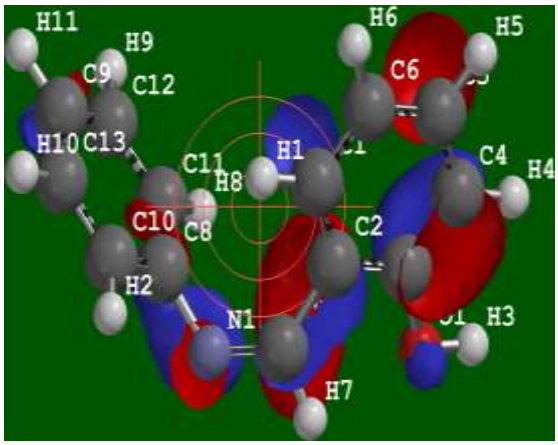

Fig. 6b: *LUMO plot 6-31+G**

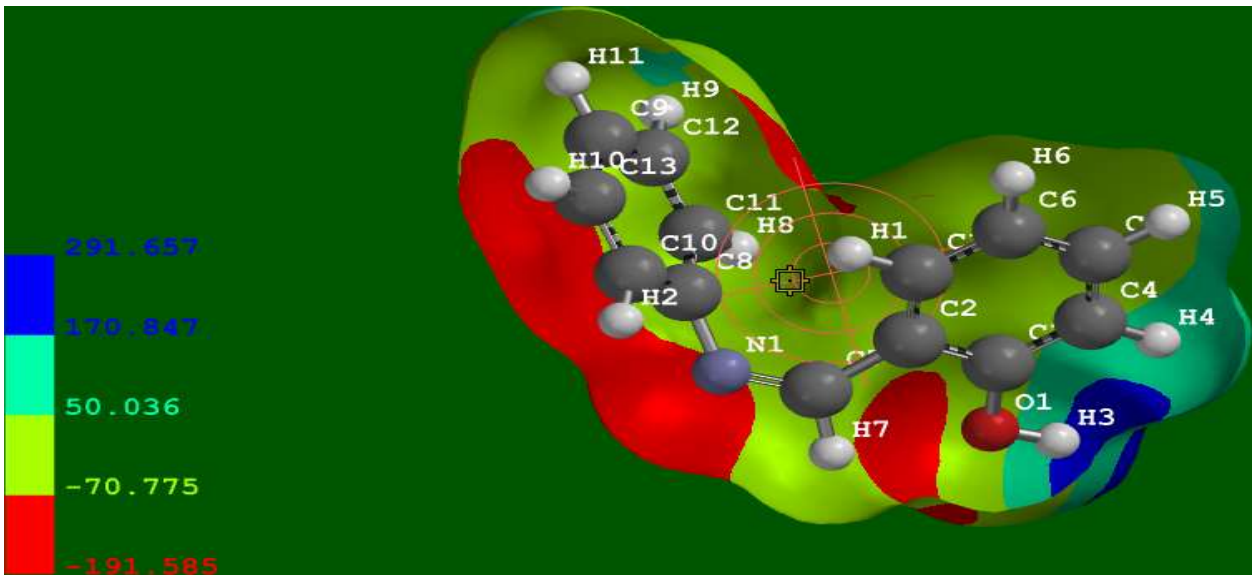

Fig. 7a: Electrostatic potential map of ANSB (6-31G*)

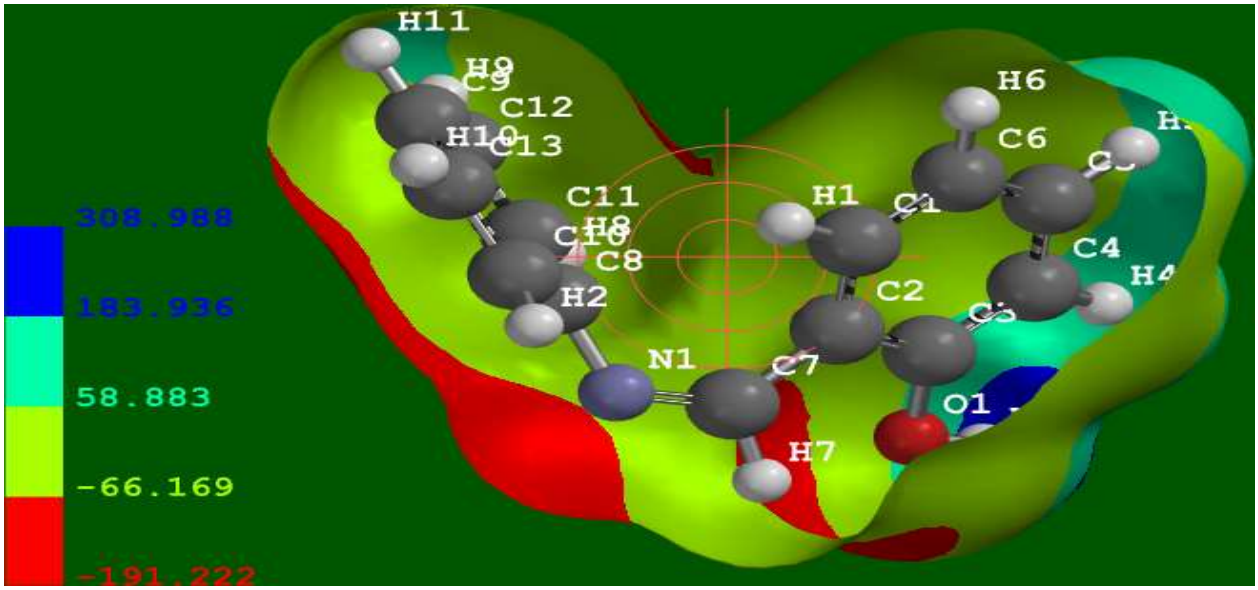

Fig. 7b: Electrostatic potential map of ANSB (6-31+G*)

CONCLUSION

The corrosion inhibitory performance of ANSB was evaluated using gravimetric methods. The inhibition efficiency increased with increase in concentration of the inhibitor molecule and decreased as the temperature is increased. The mode of adsorption obeyed the Freundlich adsorption isotherm. The ΔG values indicate that the adsorption is spontaneous, exothermic and a physiosorption process. The activation energies conformed a physiosorption process. The results obtained from theoretical quantum mechanical calculations is consistent with experimental results. The HOMO and LUMO plots together with the electrostatic potential map indicated that the molecule has parts that donate electrons and those that accept electrons from the mild steel.

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