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Substituted 2-imidazoline derivative: New and efficient corrosion inhibitors for mild steel in sulphuric acid solution

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Abstract

The aim of this work is to obtain deeper insight into the mechanism of the protective action of the imidazole-based corrosion inhibitor, 2-(4'-N, N-Dimethylaminophenyl)-imidazoline (DMAP2I). Investigations were performed on mild steel in 0.5 M H_2SO_4 by electrochemical methods and non - electrochemical methods. Maximum protection efficiency reaches about 85% for DMAP2I at 200 ppm concentration level. The adsorption of the imidazoline derivative on mild steel surface follows Langmuir and Tempkin isotherm. The adsorption free energy on mild steel (20 – 30 kJ/mol) reveals a comprehensive (physical and chemical) adsorption of the inhibitors on the metal surface. Polarization curves reveal that DMAP2I act as a mixed-type inhibitor. Results obtained from potentiodynamic polarization and impedance measurements are in good agreement. Quantum chemical method is used to explore the relationship between the inhibitor molecular properties and its inhibition efficiency. The density function theory (DFT) is also used to study the structural properties of the inhibitor. It is found that when the imidazole derivative adsorbs on the mild steel surface, molecular structure influences their interaction mechanism. The inhibition efficiencies of the compound showed a certain relationship to highest occupied molecular orbital (HOMO) energy and Mulliken atomic charges.

Key words: mild steel corrosion, 2- imidazole derivative, Theoretical evidences

Introduction

The damage by corrosion generates not only high cost for inspection, repairing and replacement, but in addition these constituent a public risk. The protection of metal surfaces against corrosion is an important industrial and scientific topic. Thus there is always a necessity for developing novel substances that behaves like corrosion inhibitor. [1]. Inhibitors are one of the practical means of preventing corrosion, particularly in acidic media. The effectiveness of an inhibitor to provide corrosion protection depends to a large extent on the interaction between the inhibitor and the metal surface [2]. Usually, organic compounds that exert a significant influence on the extent of adsorption on the metal surface and therefore can be used as effective corrosion inhibitors. The efficiency of these organic corrosion inhibitors is related to the presence of polar function with N, O and S either in the aromatic or long chain carbon systems. These inhibitors have extended pi-electron systems and functional groups (such as -C=C-, -OR, -OH, -NR2, -NH2 and –SR) that provide electrons which facilitates the adsorption of the inhibitor on the metal surface [3]. The polar function is usually regarded as the reaction centre for the establishment of the adsorption process [4, 5]. Among them, nitrogen-containing heterocyclic compounds are considered to be effective corrosion inhibitors on mild steel in acid media. N-heterocyclic compound inhibitors act by adsorption on the metal surface and the adsorption of N-heterocyclic inhibitor takes place through nitrogen heteroatom, as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures [6].

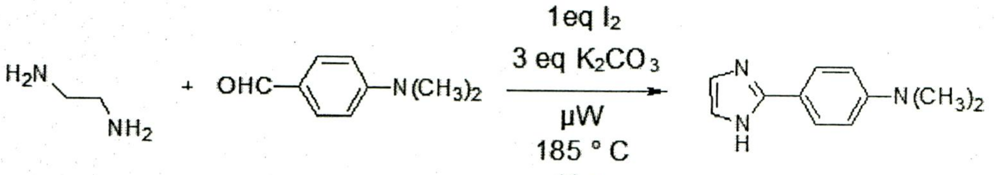
A perusal of literature revealed that imidazole and its derivatives were investigated as effective corrosion inhibitors. The encouraging results obtained with 3,4,5-trimethoxyphenyl-2-imidzoline [7] and o-chlorophenyl-2-imidazoline [8] have incited us, to extend the use of p-(N,N'-dimethylaminophenyl)-2-imidazoline and p-(N,N'-dimethylaminostyryl)-2-imidazoline as corrosion inhibitor for mild steel corrosion in acid media.

The aim of the present work, is to study the effect of synthesized 2-(4'-N, N-Dimethylaminophenyl)-imidazoline (DMAP2I) on the corrosion inhibition of mild steel in 0.5M H_2SO_4 using weight loss method, potentiodynamic and electrochemical impedance spectroscopy measurements. The second objective is to investigate the dependence of inhibition efficiency on theoretical chemical parameters calculated using DFT (density function theory) methods with B3LYP / 6-31G (d,p) basis set within the program package GAUSSIAN 09.

Experimental Section

Synthesis of the inhibitor

2-(4'-N,N-Dimethylaminophenyl)-imidazoline (DMAP2I) was easily synthesized in good yield (85%) from the reaction of dimethylaminobenzaldehyde with ethylenediamine in the presence of potassium carbonate and iodine under microwave (μW power) condition at 185 ° C for 10-15 sec as per the previously reported procedure [9]. The imidazole derivative was crystallised out with ethyl acetate.



Ethylene diamine   Dimethlaminobenzaldehyde

2-(4'-N,N-Dimethylaminophenyl)-imidazoline
(DMAP2I)

Solvent for Crystallization: Ethanol

Weight Loss Studies

Gravimetric experiments were carried out in the concentration range of 40-200 ppm of the inhibitor. Mild steel coupons of surface area 5 cm^2 were weighed and suspended in 100mL of 0.5M H_2SO_4 in triplicates for various time duration says ½h, 1h, 3h, 6h, 12h and 24h in the absence and presence of inhibitor at 303 ± 1K. At the end of the test, the coupons were taken out, washed with double distilled water, dried and weighed. The mean value of the weight loss has been reported from which the degree of coverage (θ), inhibition efficiency (v_W %), corrosion rate in mpy (δ) were calculated. The same procedure was carried out at different elevated temperatures (313K, 323K, 333K & 343K) for ½ h using thermostat to study the influence of temperature on the inhibitive effect of the inhibitor.

Electrochemical measurements

The experiments were performed in a classical three-electrode electrochemical cell. Mild steel specimen of 1 cm^2 area was used as the working electrode, platinum as a counter electrode and saturated calomel as a reference electrode. COMPACT STAT 10V; 30 Ma, IVIUM Model Parstat 2723, Advanced electrochemical system was used for data acquisition and analysis. The EIS measurements were made over a frequency range of 10 KHz to 0.01 MHz with signal amplitude of 25 mV. The Tafel polarization measurements were made after EIS for a potential range of -100 mV to +100 mV with respect to open circuit potential, at a scan rate of 1.66 mV/sec. The I_{corr} , E_{corr}, R_P, the Tafel slopes and R_{ct}, C_{dl} values were obtained from the data using the corresponding "Corr view" and "Z view" software from which the corresponding v % were calculated electrochemically.

Quantum Chemical Studies

The quantum chemical calculation for DMAP2I was performed with complete geometry optimization using DFT (density function theory) methods with B3LYP / 6-31G (d,p) basis set within the program package GAUSSIAN 09 [11]. The basis sets 6-31G (d,p) was utilized for the calculations. The quantum chemical quantities are often defined following Koopmans' theorem [12, 13]. Electronegativity (χ) is a measure of the power of an electron or group of atoms to attract electrons towards it [14] and Global hardness (η) measures the resistance of an atom to a charge transfer [15]. Global softness (σ) describes the capacity of an atom or group of atoms to receive electrons [15] whereas high value of electrophilicity describes a good electrophile while a small value of electrophilicity describes a good nucleophile [16, 17]. Fukui functions are often used to locate regions in the molecule that are susceptible to electrophilic or nucleophilic attack. When defined in terms of the charges on the atoms the electrophilic attack and the nucleophilic attack terms could be estimated utilizing the finite difference approximation approach as follows[18, 19]:

$$f+= q(N+1) - qN \quad \text{for nucleophilic attack} \qquad (1)$$

$$f- = qN - q(N-1) \quad \text{for electrophilic attack} \qquad (2)$$

where q_{N+1}, q_N and q_{N-1} are the charge of the atoms on the system with N+1, N and N-1 electrons respectively. The preferred site for nucleophilic attack is the atom or region in the molecule where the value of f^+ is the highest and the preferred site for an electrophilic attack is the atom/ region in the molecule where the value of f^- is the highest. All calculations are done at the ground state geometry.

Table 1 Effect of concentration of DMAP2I on mild steel at various time intervals in 0.5M H_2SO_4

Conc ppm	δ mpy	v_W %	δ mpy	v_W %	δ mpy	v_W %	δ mpy	v_W %	δ mpy	v_W %	δ mpy	v_W %
Blank	1290	-	1347	-	1508	-	5309	-	2331	-	1790	-
40	1047	18.8	1048	22.2	1167	22.6	3314	37.6	1628	30.1	1420	20.6
60	860	33.3	833	38.1	918	39.1	2300	56.7	1336	42.7	1075	39.9
80	716	44.4	693	48.5	755	49.9	1982	62.7	1101	52.7	894	50.0
140	577	55.3	566	57.9	566	62.5	973	81.7	708	69.6	712	60.2
200	564	56.3	547	59.3	517	65.7	666	85.5	633	72.8	552	69.1

Result and Discussion

Weight loss studies

Effect of Concentration and immersion time

The values of percentage inhibition efficiency (v_w %) and corrosion rate (δ in mpy) obtained from weight loss method, at different concentrations of DMAP2I for various time intervals are presented in Table 1. Analysis of the Table 1 revealed that, DMAP2I showed increased inhibition efficiency with increasing concentration reaching 85 % for 200 ppm concentration and further increase in concentration did not cause any appreciable change in the performance of the inhibitor. The efficiency of the imidazoline derivatives may be due to the lone pair of electrons on the nitrogen atom and π-electrons of the aromatic ring, resulting in the adsorption of the compound on the metal surface [20]. The inhibition efficiency varies from nearly 56% for 200 ppm concentration (at 1/2 h) to about 85% (at 6 h) and then to 69% (at 24 h) for DMAP2I. Immersion studies reveal that as the time of immersion increased from 1/2 h to 6 h, the inhibition efficiency also increased. After 6 hours there is a slight decline in the inhibition efficiency at 12h and 24h [21]. The decrease in inhibition efficiency at longer immersion time may be due to desorption of the protective layer on the mild steel surface.

Effect of Temperature

Temperature dependence of the inhibitor efficiency and the comparison of the obtained thermodynamic data of the corrosion product, both in absence and presence of inhibitor lead to some conclusion, concerning the mechanism of inhibiting action. The effect of temperature on inhibition efficiency from weight loss measurements taken at various temperatures ranging from 303 K to 343 K in the absence and presence of the investigated DMAP2I (½ h immersion) is summarized in Fig. 1.

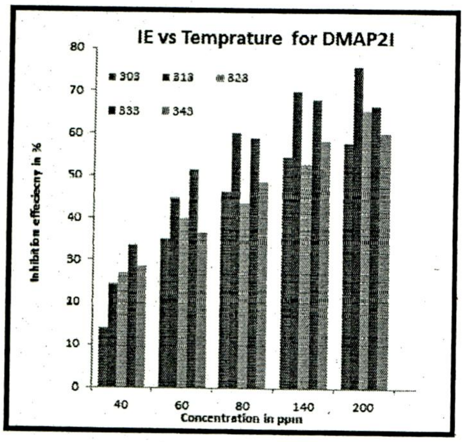


Fig. 1 Effect of temperature on inhibition efficiency at higher temperature for DMAP2I

The obtained data revealed that in acidic media, the inhibition efficiency increased with an increase in the inhibitor concentration, at all studied temperature. At the same time, IE was found to decrease with rise in temperature affording a maximum efficiency of 75% at 313 K for DMAP2I.This suggest that the inhibitor species are adsorbed on the mild steel/solution interface, where the adsorbed species mechanically screen the coated part of the metal surface from the action of the corrosive medium. The adsorption and desorption of inhibitive molecules continuously occur at the metal surface and an equilibrium exists between these molecule. With increase in temperature, the equilibrium between adsorption and desorption process are shifted leading to higher desorption. It explains the lower inhibition efficiency at higher temperature [22].

Adsorption isotherm

Corrosion inhibitor is found to protect steel corrosion in acid solutions, by adsorbing themselves on steel surface. Adsorption is a separation process involving two phases between which, certain components can become differentially distributed. Basic information on the interaction between the inhibitor of the mild steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the linear relation between degree of surface coverage (θ) and inhibitor concentration (C) must be found. Langmuir adsorption equation relates degree of surface coverage to concentration of inhibitor according to equation (3)

$$\text{Log}\ (C/\theta) = \log K + \log C \qquad (3)$$

Tempkin isotherm is formulated as in equation (4)

$$\text{Exp}\ (-2a\theta) = k\,C \qquad (4)$$

A plot of log (θ/1-θ) versus log C (Langmuir plot) and a plot of θ vs log C (Tempkin plot) from weight loss data obtained for imidazoline derivative, yielded straight lines as represented in Fig 2. For the studied compound, the linear regression coefficients (R^2) are almost equal to 1 indicating that the adsorption of DMAP2I obeys both Langmuir and Tempkin Adsorption. The fit of the experimental data to this isotherm provides evidence for the role of adsorption effect of DMAP2I [23].

Energy of activation and thermodynamic parameters

Values of Ea for mild steel with the absence and presence of DMAP2I was determined from the slope of log CR Vs 1/T. Ea for blank acid is 51 kJ/mol which increases to 90kJ/mol for 200pppm inhibited solution. The higher values of Ea in the inhibited solution can be correlated with the increased thickness of the double layers indicating physical adsorption (electrostatic interaction). Imidazoline molecule which contains nutrigen can be protonated in acid medium and the electrostatic cation adsorption is responsible for its good protective [24]. Standard free energy values of adsorption at different temperature were derived from Langmuir plots using the equation (12)

$$-\Delta G^{\circ}\text{ads} = 2.303\ \text{RT}\ (1.74 + \log \theta/(1-\theta) - \log C) \qquad (12)$$

Thermodynamically, $\Delta \mathbf{G}^{\circ}_{\mathbf{ads}}$ is related to the enthalpy and entropy of adsorption ΔH°_{ads} and $\Delta \mathbf{S}^{\circ}_{\mathbf{ads}}$ respectively by the famous Gibbs Helmholtz equation (13)

$$\Delta G^{\circ}\text{ads} = \Delta H^{\circ}\text{ads} - T\Delta S^{\circ}\text{ads} \qquad (13)$$

From the plots of -ΔG vs Temperature, change in enthalpy and change in entropy were calculated. The calculated values of ΔG°_{ads} are negative which indicate that, the spontaneous adsorption of inhibitor's molecules on the metal surface. As, observed, the studied inhibitor obey the general rule that, the effectiveness of corrosion inhibition increases with increasing negative value of ΔG°_{ads}. The calculated ΔG°_{ads} values range from -25 to -34 kJmol^{-1} indicating the comprehensive adsorption of DMAP2I on mild steel surface. The negative values of ΔH°_{ads} (-30 to -50 kJ/mol) suggest that the adsorption of inhibitor molecules is an exothermic process. The entropy of inhibitor adsorption, ΔS°_{ads} (-20 J/mol) was negative because inhibitor molecules, freely moving in the bulk solution were adsorbed in an orderly fashion onto the mild steel surface, resulting in a decrease in entropy.

Table 2 Electrochemical parameters of mild steel in 0.5M H_2SO_4 with DMAP2I

Conc ppm	- E_{corr} mV/sec	I_{corr} μA/cm^2	ba mV/dec	bc mV/dec	v_{PP} %	R_p ohm/cm^2	v_{LP} %	R_{ct} ohm/cm^2	C_{dl} μF/cm^2	v_{EIS} %
Blank	519	179.8	89	234	-	3.9	-	7.9	305	-
40	483	166.0	69	140	5.70	4.53	13.9	16.9	253	53.3
60	475	101.9	73	159	14.7	5.23	25.4	21.8	177	63.77
80	520	93.5	94	235	28.7	5.77	32.4	24.0	176	67.19
140	471	92.2	87	232	47.5	6.66	41.4	27.0	85	70.79
200	474	86.9	81	154	51.6	8.07	51.6	31.2	63	74.71

Electrochemical Measurements

Potentiodynamic Polarization Studies

The effect of DMAP2I polarization behaviour of mild steel in 0.5 M H_2SO_4 has been studied by polarisation measurements and the recorded Tafel plots are shown in Fig. 2. a. The respective kinetic parameters plots are given in Table 2. Inspection of the Table 2 reveals that, an increase in inhibitor concentration the I_{corr} values decrease considerably. Thus, inhibition efficiency increases with inhibitor concentration, reaching the maximum values of 51.6% at 200 ppm. The trend in variation in E_{corr} on addition of inhibitor is not regular. The potentiodynamic curves show that there is a clear reduction of both the anodic and cathodic currents in the presence of DMAP2I, compared with those for the blank solution. This indicates that DMAP2I could be classified as mixed type inhibitor [25].

Linear polarization resistance

There is a slight variation in the R_p values in H_2SO_4 ranging from 3.9 Ohm/cm^2 to 8.07 Ohm/cm^2 for DMAP2I resulting in a maximum efficiency of 51.6 %. The increase in R_p values suggests that, the inhibitor inhibit corrosion by blocking the active sites [26].

Electrochemical Impedance Spectroscopy

Nyquist plots of mild steel are shown in Fig. 2. b and the impedance data are given in Table 2. From the Table, it has been found that, the R_{ct} values increased from 7.9 Ohm/cm^2 for the blank H_2SO_4 solution to 31.2 Ohm/cm^2 at the maximum concentration of DMAP2I leading to an efficiency of 74.71%. It is attributed to the formation of protective film on the metal-solution interface. The semi-circular appearance of the Nyquist plot shows that the corrosion of mild steel in the examined inhibitor is controlled by charge transfer process [31]. The diameters of the capacitive loop increase in the presence of the inhibitor and were indicative of the degree of inhibition of the corrosion process. The interfacial double layer capacitance C_{dl} decreases from 305 μF/cm^2 for the blank to 95 μF/cm^2 for DMAP2I at 200 ppm. The decrease in double layer is attributed to increase in thickness of electronic double layer due to surface adsorption [27].

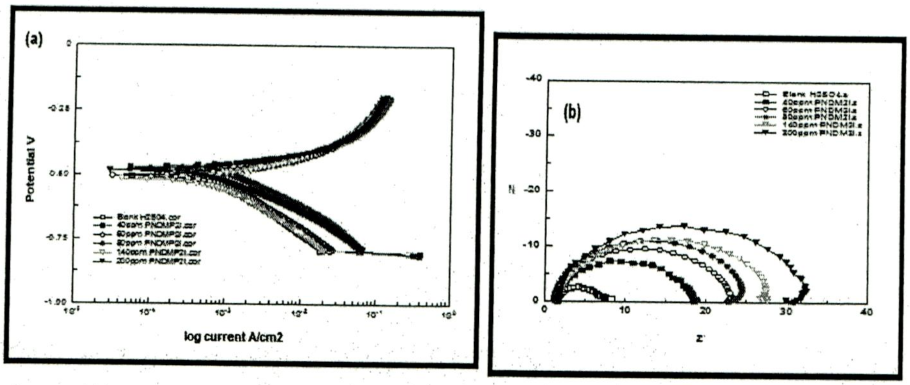


Fig 2 (a) Tafel curves (b) Nyquist plot for DMAP2I in 0.5M H_2SO_4

Computational Studies

The optimized geometry and the Frontier orbital structure of the molecule are presented in Fig. 3. The calculated quantum chemical parameters are reported in Table 3.

Frontier molecular orbital energies (E_{HOMO} and E_{LUMO})

E_{HOMO} represents the ability of the molecule to donate a lone pair of electrons while E_{LUMO} signifies the electron receiving tendency of a molecule [34]. The E_{HOMO} and E_{LUMO} values are - 4.7449 and -0.2228 eV for DMAP2I. The energy difference between E_{HOMO} and E_{LUMO} (i.e., ΔE) informs of the reactivity of the given compound; the smaller the ΔE value, the greater the reactivity of the molecule as the energy to remove an electron from the last occupied orbital will be low [28]. The low value of ΔE (3.7389ev) for DMAP2I account for its inhibition efficiency.

Dipole moment

The dipole moment gives information on the polarity (the hydrophobicity) of a molecule and therefore the electron distribution in the molecule. Higher the dipole moment, higher is the polarity of the molecule. The total dipole moment however reflects only the global polarity of a molecule [29, 30]. The dipole moment for DMAP2I is 4.42 Debye units. The high dipole moment for DMAP2I proves its better inhibition efficiency.

Ionization potential

Ionization potential is the amount of energy required to remove an electron from a molecule. The lower the ionization potential, easier it is to remove an electron from a molecule. Similarly, the electron flow will happen from the molecule with the low electronegativity towards that of a higher value [31].

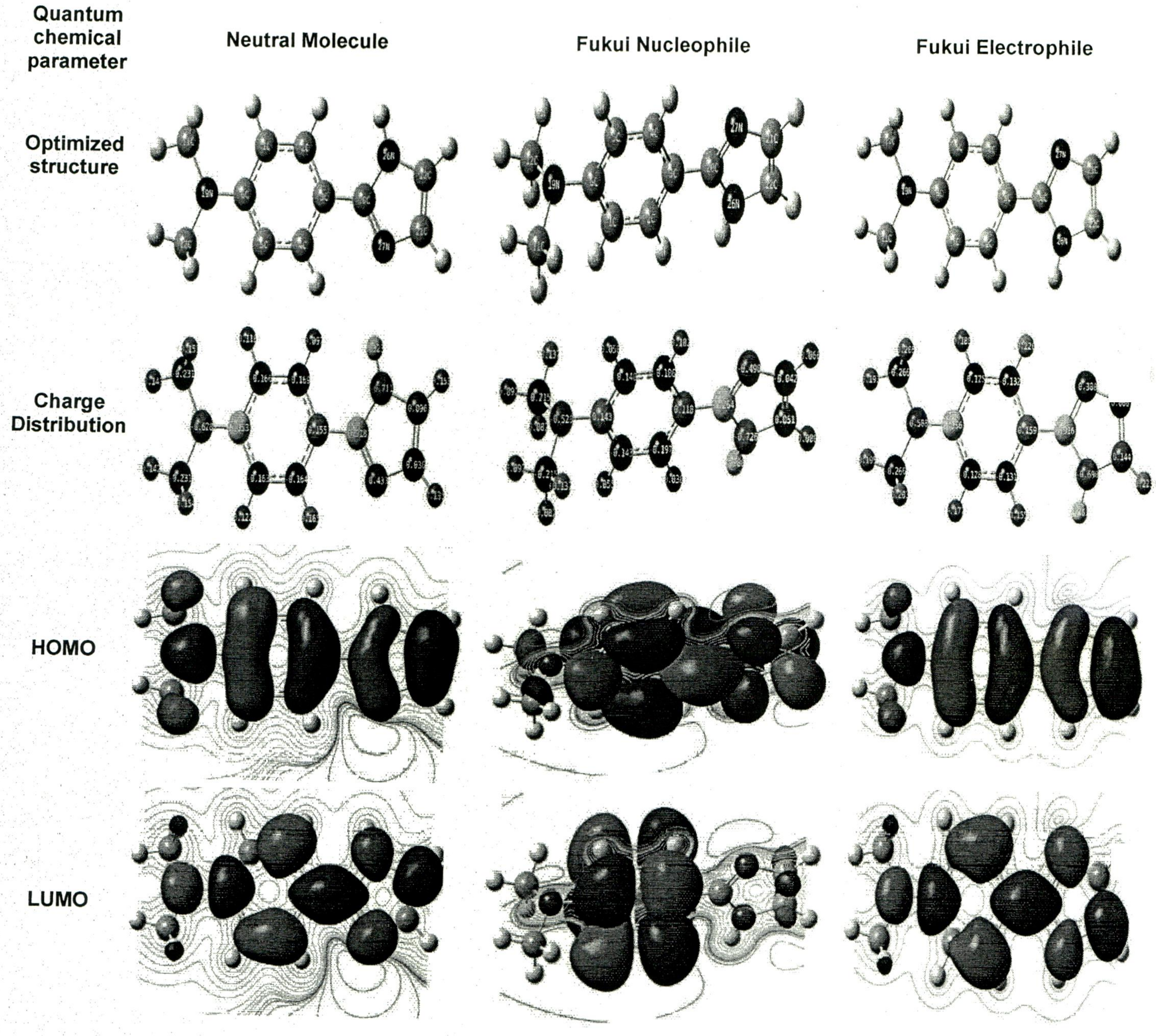


Fig. 3 Optimized structures, HOMO and LUMO of DMAP2I using DFT/6-31G (d,p)

Absolute Hardness and Global Softness

A hard molecule has the least tendency to react while a soft molecule has high tendency to react. The high value of global softness (σ) for DMAP2I suggests it to be a strong inhibitor for mild steel surface [32].

Table 3 Quantum chemical parameters

Quantum chemical parameters	DMAP2I
Total energy (eV)	-16084.5
Dipole moment (D)	4.42
E_{HOMO} (eV)	-4.74496
E_{LUMO} (eV)	-0.22287
ΔE (eV)	4.52209
Ionization potential (IP) (eV)	4.744956
Electron affinity (EA) (eV)	0.222866
Electronegativity (χ)	2.261045
Hardness (η)	0.442273
Softness (σ)	2.883911
Electrophilicity (ω)	2.121146
Fraction of electron transferred (ΔN)	0.998673

Electronegativity (χ)

Electronegativity (χ) is a chemical property that describes the ability of a molecule to attract electrons towards itself in a covalent bond [33]. The result deduced indicates that the electron flow will happen from the molecule with the low electronegativity towards that of a higher value (iron). The best inhibition of DMAP2I is attributed to its low electronegativity.

Fraction of electron transferred (ΔN)

According to Lukovits, if $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron donating ability at the metal surface [34]. Similarly, molecules with a high electrophilic value (low ΔN) have a high tendency to act as an electrophile [35]. Hence DMAP2I with low ionization potential, electronegativity, electrophilicity and softness has the best inhibitory effect. This observation is in consistent with the results obtained from the experimental results.

Table 4 Mulliken charge density on selected atoms of DMAP2I

Atom	q_N	q_{N+1}	q_{N-1}	f^+	f^-
Aromatic ring carbon atom					
3C	0.155	0.118	0.159	-0.037	-0.004
1C	-0.166	-0.148	-0.12	0.018	-0.046
2C	-0.166	-0.148	-0.12	0.018	-0.046
6C	0.353	0.143	0.356	-0.21	-0.003
4C	-0.166	-0.148	-0.12	0.018	-0.046
5C	-0.166	-0.148	-0.12	0.018	-0.046
Imidazole ring atoms					
20C	0.318	0.264	0.316	-0.054	0.002
26N	-0.711	-0.726	-0.769	-0.015	0.058
22C	0.096	0.051	0.144	-0.045	-0.048
21C	-0.036	-0.042	0.008	-0.006	-0.044
27N	-0.433	-0.49	-0.538	-0.057	0.105
Dimethyl amino substituent group					
19N	-0.588	-0.582	-0.628	0.006	0.04
11C	-0.231	-0.215	-0.266	0.016	0.035
12C	-0.231	-0.215	-0.266	0.016	0.035

Mulliken charge density and Fukui indices

The charge on the atoms also gives information on the electron distribution in the molecule and therefore the reactivity of a molecule. It also informs the specific centres on the molecule for which a certain type of reactions is likely to occur. Centres with the highest negative charge in the molecule are often susceptible to an electrophilic attack [36]. Table 4 reports the Mulliken atomic charges for the non-hydrogen atoms of the studied molecules. The results show that N atoms have the highest negative charge, followed by the ring carbon atoms. These atoms will readily donate electrons to the electrophilic species (metal surface). The donated electrons are accepted in the partially filled or vacant *d* orbitals of the metal, which allows the molecules to be adsorbed on the metal surface [37]. All C atoms directly attached to N atoms are electron deficient (i.e., they have positive charge) and therefore could be subject to nucleophilic attack. The calculated Fukui condensed functions are reported in Table 4. The preferred site for nucleophilic attack is the atom or region in the molecule where the value of f^+ is the highest and the preferred site for an electrophilic attack is the atom/ region in the molecule where the value of f^- is the highest. The highest value of f^- is on imidazole nitrogen atoms and the dimethyl amino substituent atom in the inhibitor. Comparing the Atomic charge over the atom with their Fukui functions, the number of atoms preferably for electrophilic attack where more for DMAP2I (5 atoms). Hence DMAP2I has more susceptible sites for adsorption on the mild steel surface [38].

Conclusion

1. Compounds 2-(4'-N, N-Dimethylaminophenyl)-imidazoline (DMAP2I) is an effective corrosion inhibitors for mild steel in 0.5M H_2SO_4 medium.
2. Polarization studies confirmed mixed type inhibition.
3. EIS showed that the charge transfer controls the corrosion.
4. Calculations of the HOMO, energy gap and fraction of electron transferred made using the DFT method demonstrated the inhibitive effectiveness of DMAP2I.
5. Reactivity sites for nucleophilic and electrophilic attacks were indicated using the Fukui function.
6. The electrophilic attacking sites for the inhibitor lie on the nitrogen backbone.

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