

Quantum Chemical Analysis of Inhibitive Effect of Pyrimidine Derivative on Mild Steel in Neutral Aqueous Media

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ABSTRACT: The inhibition of corrosion of mild steel in 2-amino 4, 6- dimethyl pyrimidine has been evaluated using mass loss techniques and quantum chemical studies using Density Functional Theory (DFT) methods. The analysis proved that the inhibition efficiency depend on the nature and concentration of the inhibitor. The inhibition efficiency increases with the increase of inhibitor concentration. The mechanism of bonding between the metallic surface and the inhibitor was studied by FTIR spectra. Various quantum chemical parameters like highest occupied molecular orbital energy (E_{HUMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), softness (σ) have been calculated. The temperature effect on the corrosion of steel in 60 ppm of chloride ion with and without the inhibitor was studied in the temperature range from 303-343 K. Surface morphology studies like the scanning electron microscopy (SEM) results showed the formation of a protective film on the metal surface. Surface morphology of inhibited mild steel was analyzed by SEM with dispersive X-ray spectroscopy (SEM-EDX) and atomic force microscopy (AFM). Surface studies were carried out to study the influence of inhibitor and the progress of corrosion at the metal solution interface.

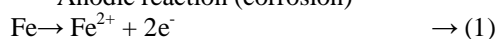
KEYWORDS: Mild steel, density functional theory, corrosion inhibition, mass loss, pyrimidine derivative, HOMO, LUMO, optimized structure.

I. INTRODUCTION

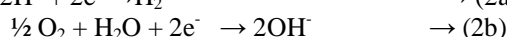
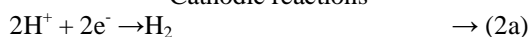
Corrosion is the result of interaction between a metal and environments which results in its gradual destruction. It is an undesirable event which destroys the lustre and beauty of the things and has many adverse effects on economic, health, safety and technology. Common structural metals are obtained from their ores or naturally-occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds and especially corrosion products have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose. Practically all corrosion reactions are electrochemical in nature. At anodic sites on the surface the iron goes into solution as ferrous ions which constitute the anodic reaction. As iron atoms undergo oxidation to ions they release electrons where negative charge would quickly build up in the metal and prevent further anodic reaction or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal.

The most common and important electrochemical reactions in the corrosion of iron are

Anodic reaction (corrosion)



Cathodic reactions



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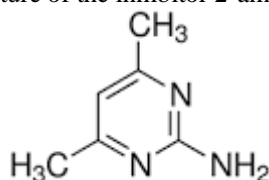
By retarding either the anodic or cathodic reactions the rate of corrosion can be reduced. This can be performed in many ways. One important method is by using corrosion inhibitors. A corrosion inhibitor is a chemical additive which when added to a corrosive aqueous environment reduces the rate of metal wastage. Among various organic inhibitors N-heterocyclic compounds are considered to be the most effective corrosion inhibitors [1]. Adsorption mainly depends on the nature of the metal surface, chemical structure of the inhibitor and the type of corrosive medium [2]. Previous investigations report that the adsorption of the organic inhibitors depend on the steric effects and electronic density of donor atoms, possible interaction of π -orbital of the inhibitor with d-orbital of the surface atoms leading to the formation of protective film[3,4].

The present work is aimed to investigate the inhibitive role of dimethyl pyrimidine in neutral aqueous media. The inhibitory action has been studied by weight loss measurements, temperature studies, SEM studies and AFM studies. Theoretical quantum chemical calculations were also employed to explain the inhibition efficiency of the inhibitor.

II. MATERIALS AND METHODS

2.1 Preparation of mild steel specimens

For mass loss experiments, mild steel specimens of size 1.0 cm x 4.0 cm x 0.2 cm and chemical composition 0.026% Sulphur, 0.06% Phosphorus, 0.4% manganese, 10.1% carbon and the rest iron were used. The length, breadth, thickness of mild steel and the radius of the hole was determined using a vernier caliper. The mild steel specimens were polished by using emery sheets of various grades, degreased with acetone [5] and finally dried with filter papers and weighed. The structure of the inhibitor 2-amino 4, 6-dimethyl pyrimidine [ADMP] is:



The molecular weight and the chemical formula are 123.16 and $C_6H_9N_3$ respectively.

2.2 Determination of Corrosion rate and Inhibition efficiency by weight loss methods

The weighed samples in triplicate were suspended by means of glass hooks in 100 ml of the corrosive medium for 1 hour, removed washed with double distilled water, dried and weighed again. The percentage inhibition efficiency (%IE) and the surface coverage (θ) were calculated from the following equation. The corrosion rate (CR), percentage inhibition efficiency (%IE) and the surface coverage (θ) were calculated from the following relation

$$\text{Corrosion Rate (mdd)} = \frac{\text{Loss in mass in milligrams}}{\text{Surface area of the specimen} \times \text{Period of Immersion in days}}$$

The inhibition efficiency was calculated using the relation

$$\% IE = \frac{WB - WI}{WB} * 100$$

Where: WB = Loss in mass of the specimen in the absence of inhibitor,

WI = Loss in mass of the specimen in the presence of inhibitor.

The surface area coverage (θ) is calculated by the formula

$$\theta = \frac{\% IE}{100}$$

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2.3 Computational chemistry

In computational chemistry Density functional theory (DFT) was used in this study. All calculations were done by Gaussian 03 W software. The geometry of all species was determined by optimizing all geometrical variables without any symmetry constraints. Frontier molecular orbitals (HOMO and LUMO) were used for predicting the adsorption centres of the inhibitor molecule. According to Koopman's theorem [5], the energies of the HOMO and LUMO orbitals of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A) by the following relations: $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$. Absolute electronegativity (χ) and absolute hardness (η) [6] of the inhibitor molecule is given by $\chi = \frac{I+A}{2}$ and $\eta = \frac{I-A}{2}$. The softness is the inverse of hardness: $\sigma = \frac{1}{\eta}$. The fraction of the electron transferred (ΔN) from the inhibitor to the metallic surface is calculated as $\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{Inh}}}{2(\eta_{\text{Fe}} - \eta_{\text{Inh}})}$ where χ_{Fe} and χ_{Inh} denote the absolute electronegativity of Fe and the Inhibitor molecule respectively.

2.4 Scanning Electron Microscopy Measurements (SEM)

The exterior of carbon steel was analyzed by Scanning Electron Microscope before and after immersion in the presence and absence of the inhibitor solution for a period of 12 hrs. The specimens were washed lightly with distilled water dried and examined without further treatments.

2.5 Surface analysis by AFM studies

The surface morphology of the mild steel surface was found by atomic force microscopy. The mild steel specimens were immersed in various test solutions in the absence and presence of inhibitor. Surface topography of the samples was mapped using scanning probe microscope (NTEGRA Aura, NTMDT, Russia) in semi-contact mode. The tip specifications are: model number, make company, made-of, length, height and radius. Tip resonance frequency and scan speed were 154 KHz and 0.5 Hz, respectively. All the measurements were performed under room conditions.

III. RESULTS AND DISCUSSION

3.1 Weight loss analysis

The results of weight loss of steel in 60 ppm of chloride ion with and without the addition of various concentrations of the inhibitor ADMP (2-amino 4, 6-dimethyl pyrimidine) are given in Table-1.

Table-1: Corrosion Rates of mild steel in neutral aqueous media containing 60 ppm of chloride ions in the presence and absence of inhibitor and the inhibition efficiencies by weight loss method.
Inhibitor System: ADMP + Zn²⁺

S.No	Concentration of ADMP (ppm)	Concentration of Zn ²⁺ (ppm)	CR (mdd)	IE %	Surface Coverage (θ)
1	0	0	26	-	-
2	50	80	22	15.38	0.1538
3	100	80	16	38.46	0.3846
4	125	80	9	65.38	0.6538
5	150	80	3	88.40	0.8840
6	175	80	6	76.92	0.7692
7	200	80	9	65.38	0.6538
8	300	80	10	61.53	0.6153

The inhibition efficiency attains a maximum of 88.4%. This shows that the protective properties depends upon the ability to reduce corrosion rate and are enhanced at higher electron densities around nitrogen atoms. Nitrogen atom is the adsorption centre for their interaction with the metal surface. The inhibitor shows good IE% because of the electron negative groups, heterocyclic compound and conjugation of π electrons. It is also known that the different

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substituent on the organic molecule polarize the functional group in a different position and the inhibition efficiency of organic inhibitor containing hetero atoms [7].

The effect of concentration on the inhibition efficiency is depicted in Fig-1 and the effect of concentration on the corrosion rate is shown in Fig-2.

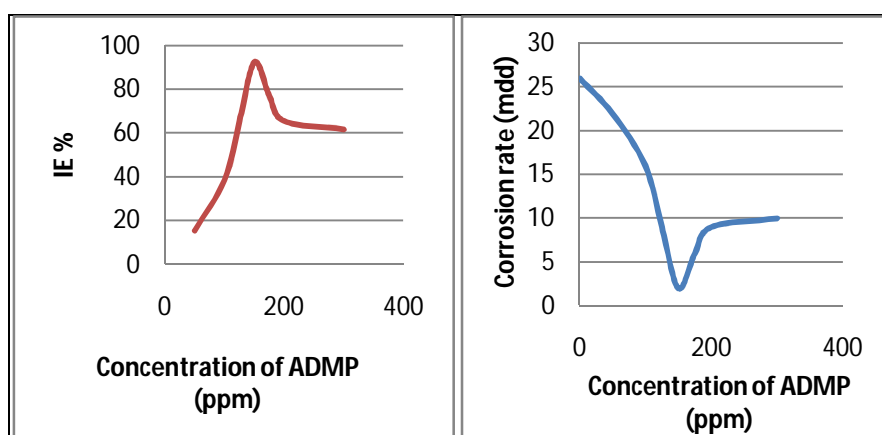


Fig-1: Effect of concentration on IE

Fig-2: Effect of concentration on corrosion rate

From the graph it is clear that as the concentration increases the inhibition efficiency also increases upto 150 ppm and then it decreases whereas the corrosion rate decreases and then after 150 ppm it increases. Thus the best concentration is 150 ppm ADMP and 80 ppm Zn^{2+} in neutral aqueous media.

3.2 Quantum chemical studies

Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/surface mechanism and to explain the structural nature of the inhibitor in the corrosion process. Furthermore DFT is considered as a useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data. This technique also provides insight into the chemical reactivity and selectivity in terms of global parameters like electro negativity, hardness, softness etc. Quantum chemical calculations were performed with complete geometry optimizations using Gaussian-03 package.

Theoretical assessment

Chemical calculations are used to determine the relationship between inhibitors and their corresponding inhibition efficiency. Optimized geometric structures of HOMO and LUMO for the inhibitors were studied which supported the corrosion inhibition efficiency obtained from experimental results [8].

The adsorption ability of the molecule over metal surface is related to their Frontier molecular orbital (FMO) i.e., HOMO and LUMO. Excellent corrosion inhibitors are usually the compounds which not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal.

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The 3D structures are shown in Fig- 3.

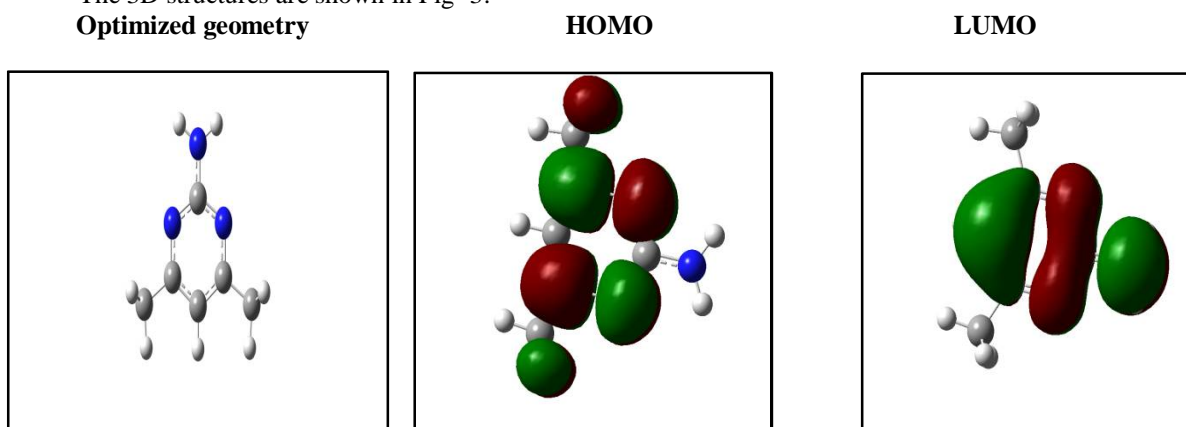


Fig 3: 3D structure of the inhibitor ADMP

Quantum chemical parameters obtained from the calculations which are responsible for the inhibition efficiency of inhibitors like highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), HOMO-LUMO energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), ionization potential (I), global hardness (η), softness (σ), global electrophilicity (ω), fraction of electrons absorbed from the inhibitor to iron surface (ΔN) and the total energy (TE) are presented in Table 3.

Table-3: Calculated Quantum Parameters for the optimized inhibitor

Quantum chemical parameters	Inhibitor ADMP
E_{HOMO} (eV)	5.9334
E_{LUMO} (eV)	0.6255
ΔE gap (eV)	5.3078
Dipole moment, μ (debye)	0.3643
Ionisation potential (eV)	-5.9334
Electron affinity, A (eV)	-0.6255
Global hardness (eV)	-4.5397
Global softness, σ (eV)	-0.2202
Global Electrophilicity, (ω)	0.014617
ΔN	1.13218
Electro negativity (λ)	-3.279541

E_{HOMO} , E_{LUMO} , ΔE and μ are the parameters which directly influence the electronic interaction of the inhibitor molecules with the metal surface. Higher E_{HOMO} of the molecule shows a higher electron donating ability to acceptor molecules with low energy empty molecular orbital explaining the adsorption on metallic surfaces by way of delocalized pair of π -electrons. E_{LUMO} signifies the electron receiving tendency of a molecule. The dipole moment describes the polarity of the inhibitor.

A molecule with a low energy gap is more polarisable and associated with the high chemical activity. High ionization energy indicates high stability and whereas small ionization energy indicates high reactivity of the atoms and molecules [9]. The molecular stability and reactivity are measured by the absolute hardness and softness. Large energy gap is

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shown by a hard molecule and a small energy gap indicates a soft molecule. High inhibition efficiency is shown by the inhibitor with the least value of global hardness i.e, a soft molecule [10]. The ability of a molecule to attract electron towards itself in a covalent bond is found from the electronegativity. According to Sanderson's equalization principle [11], high electronegativity molecule reaches equalization and the reactivity is low which indicates low inhibition efficiency. If the electronegativity value is low then it is a best indicator. The ability of the inhibitor molecule to accept electrons is identified by the electrophilicity index. It is a measure of the stabilization in energy after the system accepts the additional amount of electron charge from the environment. The fraction of electrons transferred describes the trend of donation of electrons. In literature it has been reported that the values of ΔN shows inhibition effect resulted from electron donation [12]. The inhibition efficiency increases with the increasing electron donating ability of the inhibitor at the metal surface and it can be concluded that the increasing value of ΔN shows high inhibition efficiency. According to Lukovit's study [13], if $\Delta N < 3.6$, the inhibition efficiency increases with increasing electron donating ability at the metal surface. Thus the inhibitor is a donor of electrons and the metal surface is an acceptor of electrons which favors chemisorption of the inhibitor on the metal surface. Thus the inhibitor binds to the metal surface and forms an adsorption layer against corrosion.

3.3 Scanning Electron Microscopy Measurements (SEM)

The classification of the inhibitive layer produced on the carbon steel surface was carried out by SEM analysis. Fig-4 shows a variety of high resolution SEM images in the presence and absence of the inhibitor ADMP solution. Fig 4(a) shows the smooth SEM image of the polished metal. Fig 4(b) shows that the whole metal surface is covered by a scale like black corrosion item for consumption due to the absence of the inhibitor and in Fig 4(c) a smooth surface is seen which indicates the development of an inhibitive film.

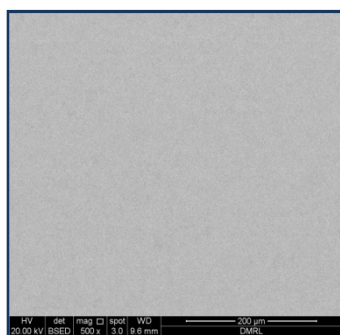


Fig 4(a) Polished Metal

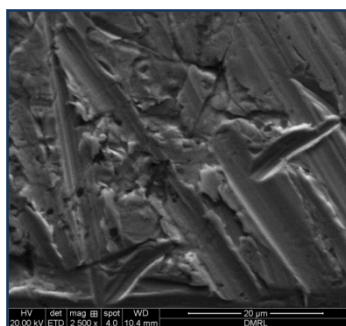


Fig 4(b) Metal in 60ppm

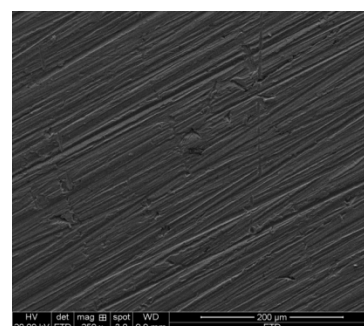


Fig 4(c) Metal in 60 ppm
NaCl, ZnSO₄ and ADMP

From the above figures it is clear that the aggressive Cl⁻ ions have not penetrated because of the good protective layer produced on the metal surface by the inhibitor ADMP and Zn²⁺ ions. Thus SEM analysis shows the protective coating. [14].

3.4 Atomic Force Microscopy studies

The influence of inhibitor on the generation and progress of corrosion at the metal/solution interface is investigated by a powerful technique named AFM. The surface morphology at nano to micro scale can be studied [15, 16]. The Root mean roughness and average roughness was performed. Table 2 shows the roughness values for steel inhibited in different environments.

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Table-2: AFM data for mild steel immersed in uninhibited and inhibited environment

S.No	Samples	RMS Roughness	Average Roughness
1	Polished mild steel	1.91589 nm	3.05699 nm
2	Polished mild steel in 60 ppm Cl ⁻ ion	6.63949 nm	9.73747 nm
3	Polished mild steel in 60 ppm Cl ⁻ ion + 80 ppm Zn ²⁺ 150 ppm ADMP	5.86156 nm	9.18032 nm

The value of RMS and average roughness for polished mild steel are 1.91589nm and 3.05699nm respectively. The RMS and average roughness values for mild steel dipped in 60 ppm of Cl⁻ ions are 6.63949nm and 9.73747nm respectively. The increase in the roughness values implies that the mild steel surface immersed in 60 ppm Cl⁻ ions has a greater surface roughness than the polished mild steel due to the corrosion effect. The RMS and average roughness value of mild steel in the presence of the inhibitor ADMP are 5.86156nm and 9.18032nm respectively. The values are less in the inhibited environment when compared to the uninhibited environment. The three dimensional (3D) and two dimensional (2D) AFM morphologies were shown in Figures 5-7.

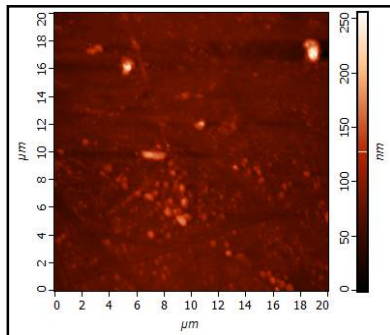


Fig 5a: AFM 2D image of polished mild steel

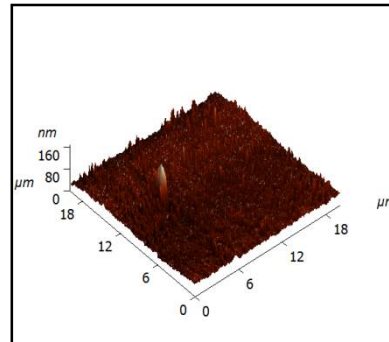


Fig 5b: AFM 3D image of polished mild steel

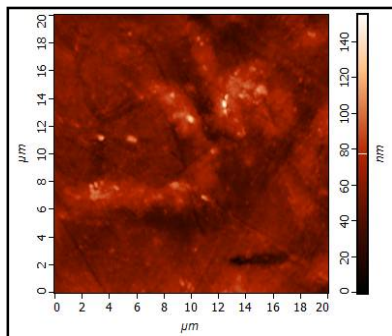


Fig 6a: AFM 2D image of mild steel in 60 ppm Cl⁻ ion

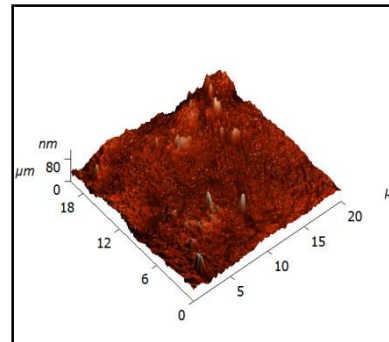


Fig 6b: AFM 3D image of mild steel in 60 ppm Cl⁻ ion

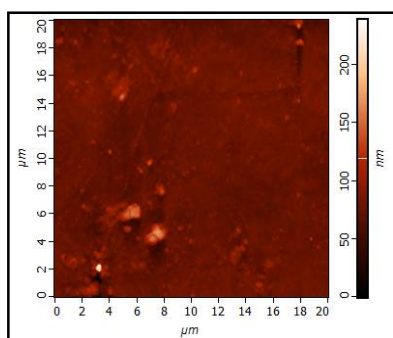


Fig 7a: AFM 2D image of mild steel in 60 ppm Cl⁻ ion ; Zn²⁺ + ADMP

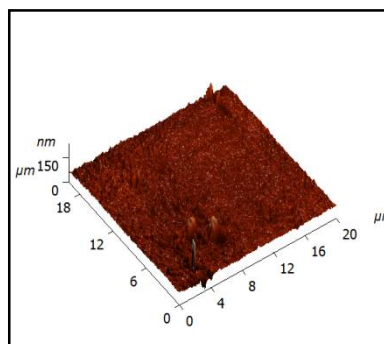


Fig 7b: AFM 2D image of mild steel in 60 ppm Cl⁻ + Zn²⁺ + ADMP

Fig 5a, 5b depicts the slight roughness observed on the polished metal is due to atmospheric corrosion. Fig 6a, 6b displays the corroded metal surface with a few pits in the absence of the inhibitor. Fig 7a, 7b shows the smoothness of the surface which is due to the formation of a compact protective film of Zn²⁺ - ADMP complex thereby inhibiting the corrosion of carbon steel.

3.5 Mechanism of Corrosion

- Polar groups having atoms of nitrogen, oxygen, sulphur and aromatic heterocyclics rings contribute towards the adsorption.
- The possible reaction centres are the unshared electron pairs of heteroatoms and electrons of aromatic rings.
- The protonated molecules adsorb on the metal. i.e donor acceptance takes place between the π-electrons of aromatic rings and vacant d-orbital of surface iron atoms.
- Interaction takes place between unshared electron pairs of hetero atoms and vacant d- orbital of iron surface atoms.
- There is a formation of Zn²⁺-ADMP complexes in solution containing of 60 ppm NaCl, 80 ppm ZnSO₄ and 150 ppm of ADMP solution.
- On the metal surface Zn²⁺-ADMP complexes are transformed into Fe²⁺ADMP complexes on the anodic sites, Zn²⁺ is released.

IV. CONCLUSIONS

- ✚ The corrosion inhibition of 2-amino 4-6 Dimethyl pyrimidine (ADMP) was studied in the absence and presence of inhibitor.
- ✚ The inhibitor has the ability of reducing the corrosion rate of carbon steel in aqueous solution containing 60 ppm of Cl⁻.
- ✚ The SEM image in the presence of the inhibitor shows the formulation of the inhibitor layer.
- ✚ The formulation consisting of 60 ppm of Cl⁻ ions, 80 ppm of Zn²⁺ ions and 150 ppm of inhibitor is the best formulation with an IE of 92.3 %.
- ✚ Quantum chemical parameters were calculated to provide further insight into the mechanism of inhibition of corrosion process.
- ✚ The fraction of electrons transferred is less as studied from quantum studies and hence the inhibitor binds well to the metal surface thus protecting from corrosion.

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