

Surface Characterization Studies of 2-Amino 4, 6-Dimethyl Pyrimidine (ADMP) in Neutral Chloride Medium

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ABSTRACT: The inhibition efficiency of 2-amino-4, 6-dimethyl pyrimidine (ADMP) on mild steel in aqueous solution containing 60 ppm Cl⁻ ions, and its amalgamation with Zn²⁺ ion as synergist are studied by surface morphological analysis like FT-IR, UV, SEM and AFM. FT-IR is efficiently employed to determine the functional groups in the molecular configuration of the inhibitor and in the complex with additional inhibitors. UV-Visible spectroscopy shows the development of (Fe²⁺ - ADMP) complex on the surface of the metal. This may be accountable for the surveyed variation in the absorbance, its intensity value and anticorrosion action. It is also prominent that there is a momentous variation in the shape of the spectra before and after the immersion of specimen showing the option of forming thin inhibitor layer over the mild steel surface indicating the adsorption as physical adsorption. SEM analysis illustrates the addition of 150 ppm of ADMP and 80ppm of Zn²⁺ to the metal surface curbed the corrosion and the surface damage has lessened significantly. This is due to the formation of skinny layer of inhibitor on the metal surface which controls the dissolution of mild steel. AFM studies presents straight insight into the variations in surface morphology that takes place at numerous hundred nanometers when topographical changes takes place due to corrosion and formation of protective coating on the metal surface in the presence and absence of inhibitors respectively.

KEYWORDS: Absorbance, anticorrosion; surface morphology; adsorption, molecular configuration.

I. INTRODUCTION

Corrosion can be viewed as a worldwide observable fact, ubiquitous and unstoppable. It is there everywhere, air, water, soil and in every background, we come across. The word corrosion¹ is as ripened as the globe which destroys the shimmer and magnificence of objects and curtails their life. Corrosion is a normal process² that weakens the binding energy in metals with the outcome concerning a metal being oxidized as the bulk metal loses one or more electrons. The lost electrons are conducted throughout the bulk metal to another location where they are reduced. Corrosion since prehistoric times has affected not only the excellence of everyday lives of people, but also their technical development. Corrosion is an extractive metallurgy in reverse. Corrosion can be prevented or at least controlled. Corrosion inhibitors are chemicals that react with the metal's surface or the environmental gases causing corrosion, thereby, interrupting the chemical reaction that causes corrosion. The use of chemical inhibitors is to decrease the rate of corrosion processes. A great number of scientific studies have been devoted to the subject of corrosion inhibitors. However, most of what is known has grown from trial and error experiments, both in the laboratories and in the field. The most useful technique to analyze the effectiveness of an inhibitor is weight loss measurements and electrochemical measurements like polarization curve method and the impedance measurements. In addition, microscopy techniques are used to characterize the corrosion process. For all types of inhibitors some environmental factors should be considered

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Vol. 6, Issue 6, June 2017

since some factors like metals, pH, composition, impurities, agitation, temperature, geometry of the system, the concentration of inhibitor and the mixture of one or more inhibitors may change the anti-corrosive mechanism³⁻⁵. Heterocyclic compounds are cyclic compounds in which one or more ring atoms are not carbon. Hetero atom can be N, O, S, B, Al, Si, P, Sn, As, Cu. But the common is N, O or S. Heterocyclic compounds are grouped into non-aromatic and aromatic. Heterocyclic compounds play a big role in organic chemistry and because they have different electron configurations from carbon, they react differently from carbon rings and differently from each other. Fully unsaturated six-membered nitrogen heterocycles, such as pyridine, pyrazine, pyrimidine and pyridazine have stable aromatic rings. Pyrimidine is a heterocyclic aromatic organic compound similar to benzene. It is single-ringed crystalline organic base, C₄H₄N₂. The presence of the electron releasing two methyl groups in the molecules increase the electron density on the pyrimidine heterocyclic ring inhibition by pyrimidine derivatives depend on the number of adsorption sites in the molecule and their charge density, molecular size and stability of these derivatives in acidic solutions. The inhibition effect of these compounds is attributed to the adsorption of the inhibitor molecules on the metal surface. The adsorption is assumed to take place mainly through the nitrogen atom of amino group (active centers). Transfer of lone pairs of electrons on the nitrogen to the surface to form coordinate type linkage is favored by the presence of vacant orbital in iron atom of low energy. Polar character of substituent in the changing part of the inhibitor molecule seems to have a prominent effect on the electron charge density of the molecule.

II. MATERIALS AND METHODS

2.1 Selection of Mild Steel

Mild steel is low carbon steel utilized as a part of our everyday life. The price is cheap and its properties are satisfactory for many applications. Mild steel otherwise called low carbon steel is malleable and flexible. Mild steel is entirely reasonable and it can be utilized for various building purposes, car ventures, local machines and development purposes. Mild steel is effortlessly inclined to corrosion and consequently it must be protected or sealed.

2.2 Preparation of mild steel coupons

The mild steel coupons utilized as a part of the present study have the composition as shown in Table 1.

Table 1: Composition of mild steel coupon

Element	Composition (%)
Carbon	0.20
Manganese	0.35
Silicon	0.003
Phosphorus	0.02
Iron	99.42

The mild steel coupons of dimensions 1cm × 4 cm × 0.2 cm with a small hole near the upper edge were cleaned mechanically with different evaluations of emery papers from the coarser grade to the finer grade. The cleaned mild steel coupons were washed with distilled water, degreased with acetone, air dried and stored in a dessicator.

2.3 Chemicals used

The chemicals utilized as a part of the present study are of Analar grade. Sodium chloride (NaCl) solution is used as an aqueous media for the study. Zinc sulphate (ZnSO₄) is used as synergist. 2-amino- 4, 6-dimethyl pyrimidine (ADMP) is the chosen inhibitor for the present corrosion study.

2.4 Surface morphology studies

2.4.1 Surface characterization by Fourier Transform Infra red spectroscopy (FTIR) studies

Mild steel coupons of dimension 1 cm x 4 cm x 0.2 cm after polishing and degreasing with trichloroethylene were immersed in neutral chloride media with and without the inhibitor. After 12 hours of immersion in the corrosive medium, the coupons were removed, washed, dried and the FTIR spectra were recorded using FTIR spectrophotometer.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 6, Issue 6, June 2017

2.4.2 Surface analysis by UV-Visible spectrophotometer

Mild steel coupons of dimension 1 cm x 4 cm x 0.2 cm after polishing and degreasing with trichloroethylene were immersed in neutral aqueous media with and without the inhibitor. After 12 hours of immersion in the corrosive medium, the coupons were removed. The solutions were taken as samples and the UV spectra were recorded using Double Beam UV-Visible spectrophotometer.

2.4.3 Surface analysis by Scanning Electron Microscope (SEM)

Mild steel coupons of dimension 1 cm x 4 cm x 0.2 cm after polishing and degreasing were immersed in neutral aqueous media for 12 hours in the absence and presence of the inhibitor for various concentrations. The coupons were then removed, washed with distilled water and dried at ambient temperature. Then SEM micrographs were taken and analyzed.

2.4.4 Surface analysis by Atomic Force Microscope (AFM) studies

For AFM studies the mild steel coupons of dimension 1 cm x 4 cm x 0.2 cm after polishing and degreasing with trichloroethylene were immersed in the test solutions with and without the inhibitor for 12 hours at room temperature. Then the coupons were removed, cleaned with distilled water, dried and used for analysis. Surface topography of all the samples was mapped using scanning probe microscope in semi-contact mode. Tip resonance frequency and scan speed were 154 kHz and 0.5 Hz respectively. All the measurements were performed under room conditions.

II. RESULTS AND DISCUSSION

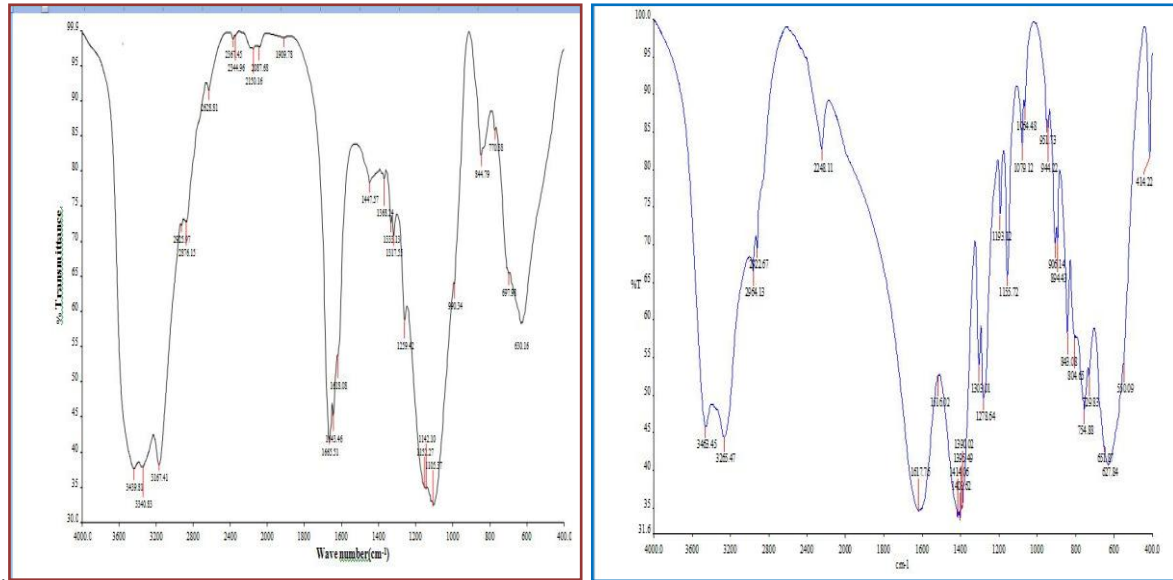
3.1 Surface Characterization Studies

3.1.1 FTIR Spectroscopy

FT-IR⁶ is effectively used to discover the functional groups in the molecular structure of the inhibitor and in the complex with other inhibitors.

The FT-IR Spectrum⁷ of pure ADMP is shown in Fig 1(a). The -NH₂ group frequency occurs at 3479 cm⁻¹. The -NH stretching frequency has shifted from 2876 cm⁻¹ to 2924 cm⁻¹. The C-H stretching vibrations occur at 2925 cm⁻¹. The C-C stretching vibrations appear at 1665, 1643 & 1618 cm⁻¹. The C-N vibrations appear at 1368, 1333 & 1317 cm⁻¹. The C-O vibrations appear at 1447 cm⁻¹. The FTIR Spectrum of the film created on the carbon steel surface after immersion in solution containing 80 ppm of Zn²⁺ and 150 ppm of ADMP in neutral chloride medium is revealed in Fig 1(b). The aromatic C=C ring stretching frequency shifted from 1665, 1643 & 1618 cm⁻¹ to 1617 cm⁻¹. The C-N stretching frequency shifted from 1368 cm⁻¹ to 1390 cm⁻¹. The -N=N- frequency shifted from 1447 cm⁻¹ to 1395 cm⁻¹.

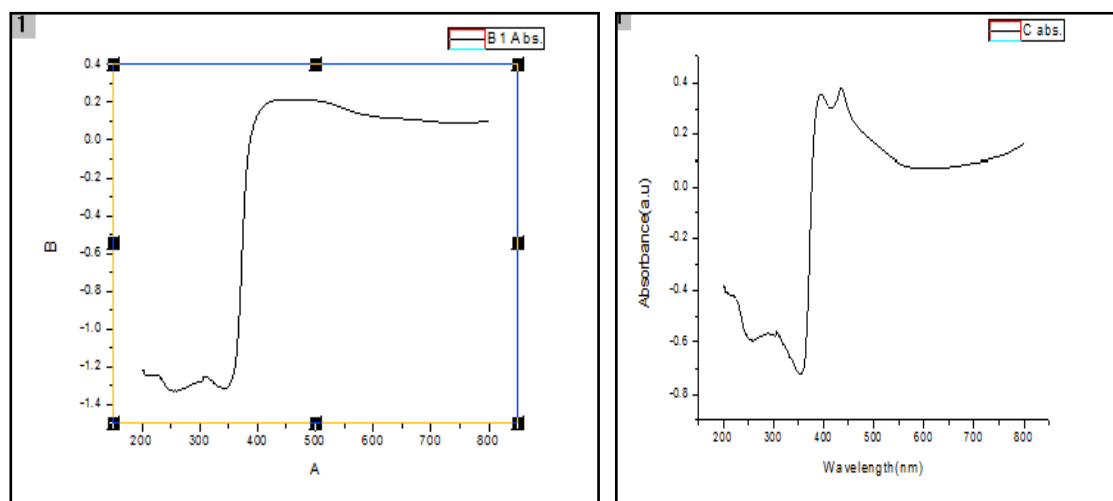
This examination recommends that ADMP has coordinated through nitrogen atom of the aromatic ring nitrogen atoms. The existence of stretch at 550.09 cm⁻¹ shows the presence of γ -Fe₂O₃ which verifies the interaction⁸ amid the inhibitor and the metal surface. The peak at 1303 cm⁻¹ corresponds to ZnO stretching frequency. The peak at 1395 cm⁻¹ is due to Zn(OH)₂⁹ formed on the cathodic surface¹⁰. As a result, the observation of shifting of functional group from their original position to the site shows the pattern of protective film on the mild surface consists of Fe²⁺-ADMP complex and Zn(OH)₂.



(a) (b)
Fig 1: FTIR spectrum of (a) pure ADMP (b) ADMP-Zn²⁺ system

3.1.2 UV-visible adsorption spectroscopy

In order to confirm the possibility of the formation of inhibitor-Fe complex, UV-Visible¹¹ absorption spectra obtained from aqueous solution containing 150 ppm ADMP before and after the immersion of mild steel are shown in Figure 2. The electronic absorption spectra of ADMP before immersion have absorption maximum at 252 nm and 356 nm, which can be attributed to π - π^* and n - π^* transitions¹². After 12hrs immersion of mild steel, the change in the position of absorption maximum at 261 nm and 372 nm indicates that the complex formation between two species (Fe²⁺ - ADMP) in solution. Formation of this complex may be responsible for the observed deviation in the absorbance and its intensity value and this may be responsible for anticorrosion activity¹³. It is also noted that there is a significant difference in the shape of the spectra before and after the immersion of specimen showing the possibility of forming thin inhibitor layer over the mild steel surface (Physisorption).



(a) (b)
Fig 2: UV-visible spectrum of (a) Blank (b) ADMP-Zn²⁺

3.2 Surface Morphology studies

3.2.1 Scanning Electron Microscopy (SEM) Analysis

The morphology of the corroded mild steel can be clearly analysed by SEM photographs. Fig 3(a) shows the SEM photographs of polished mild steel which shows the smooth surface of the metal. The SEM photograph of mild steel immersed in 60 ppm of chloride ion is shown in Fig 3(b). The surface is rough and damaged due to the metal dissolution and the formation of corrosion products on the metal surface. But Fig 3(c) shows the addition of 150 ppm of ADMP and 80ppm of Zn^{2+} to the metal surface. This formulation suppressed the corrosion and the surface damage has diminished considerably. This is due to the formation of thin layer of inhibitor on the metal surface which controls the dissolution of mild steel^{14, 15}.

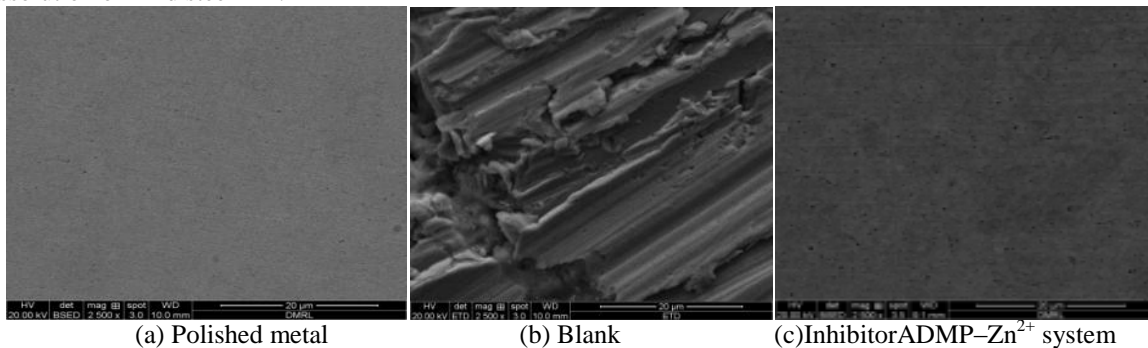
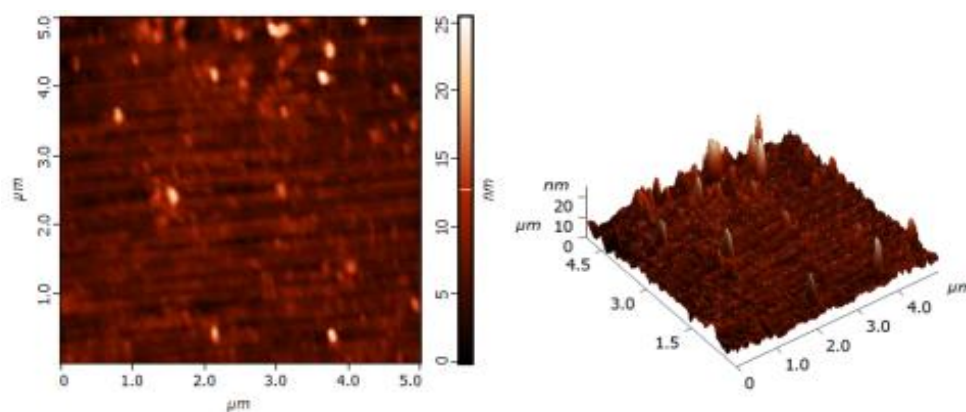


Fig 3: SEM photographs of ADMP – Zn^{2+} system along with polished metal and Blank

3.2.2 Atomic Force Microscope (AFM) studies

AFM is a dominant protocol for investigating the surface morphology^{16, 17} at nano to micro level and has turned out to be an innovative study to analyse the power of inhibitor on the originality and the development of the corrosion at the metal- solution interface. The inhibitive films fashioned on mild steel surface are inspected with AFM. The three dimensional (3D) images of topography in onward and reverse direction indicate the bumpiness of metal surface. The contact mode of operation used in this analysis enables a topographical height mode image which is three dimensional.

Atomic force microscopy presents straight insight¹⁸ into the modifications in surface morphology that takes place at numerous hundred nanometers, when topographical changes takes place due to corrosion and formation of defensive coating on the metal surface in the presence and absence of inhibitors respectively. The two dimensional (2D) and three dimensional (3D) AFM topographical images for the polished mild steel surface and the mild steel immersed in 60 ppm of chloride ions (blank) for 12 hours immersion period, are presented in Figs 4 (a) and (b).



2D image

(a) Polished mild steel surface

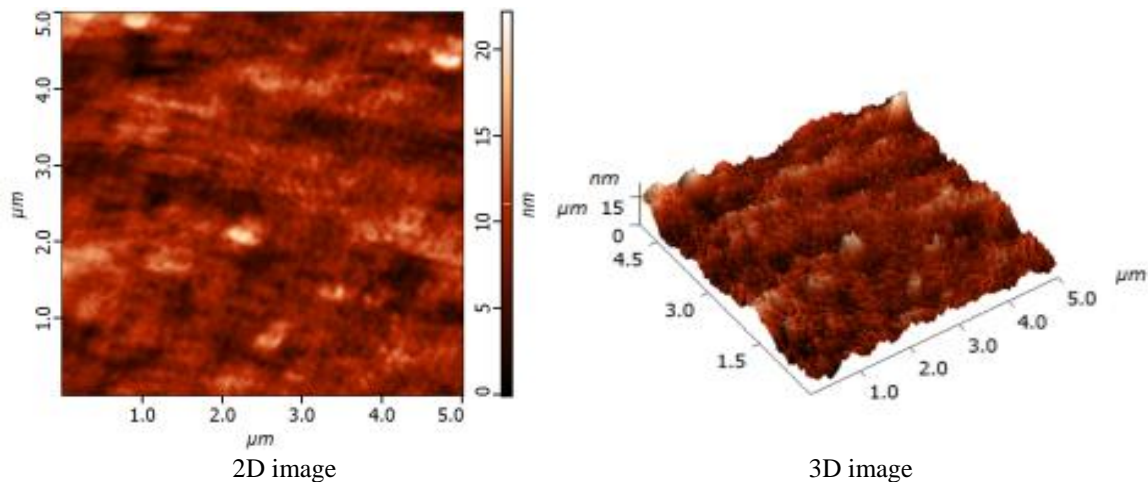
3D image

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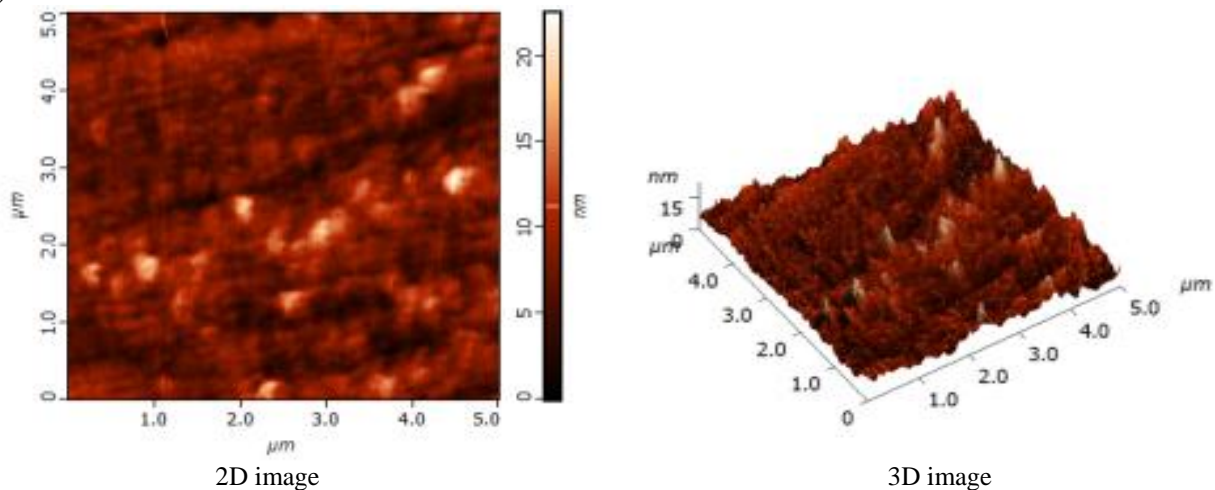
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Vol. 6, Issue 6, June 2017



(b) Blank solution

The bare metal surface shows a smooth and even surface but subsequent to immersion in the uninhibited brine solution for 12 hours, it is seen that mild steel surface instantly shows a jagged texture indicating metal dissolution due to stern corrosion in the blank solution. The shielded mild steel surface in the presence of the inhibitor ADMP is depicted in Fig 4(c).



(c) Inhibitor ADMP-Zn²⁺ system

Fig 4: Insitu AFM topographies of ADMP – Zn²⁺ system along with polished metal and blank solution

In the solution with the inhibitor ADMP, the surface of the electrode was even and almost no corrosion phenomenon happened. This is due to the fact that the inhibitor prevented the accumulation of the charge transfer, slowing down the corrosion of carbon steel effectively. The average roughness values are obtained from the AFM imaging studies. It is palpable from the data that the mild steel surface is secluded in the presence of the inhibitor. The average roughness values are lower than those for the blank solution.

International Journal of Innovative Research in Science, Engineering and Technology

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Website: www.ijirset.com

Vol. 6, Issue 6, June 2017

The roughness parameters are presented in Table 2. It is revealed by the quantitative AFM roughness parameter, the average roughness of untreated bare mild steel before and after immersion is found to be 1.92 nm and 10.51 nm respectively.

Table 2: Average roughness values for mild steel immersed in various solutions

Type of system	Average roughness(nm)
Polished metal	1.92
Blank	10.51
ADMP- Zn ²⁺ system	6.58

For mild steel immersed in 80ppm of Zn²⁺ and 150ppm of ADMP in neutral aqueous solution the roughness is found to be lowered to 6.58 nm which reveals the smooth¹⁹ run on the surface and confirms that ADMP-Zn²⁺ binary inhibitor formulation forms an inhibitive film on the mild steel surface and prevent corrosion more resourcefully.

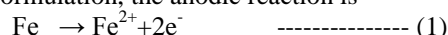
3.3 Mechanism of corrosion inhibition

The inhibition efficiency of an organic compound depends on factors like electronic structure, mode of interaction with metal surface, number of adsorption centres, molecular size and chemical properties of the inhibitor adsorbed .

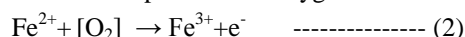
The adsorption of investigated compounds can be attributed to the presence of polar groups having Nitrogen and aromatic ring. Hence, the possible reaction centres are unshared electron pair of heteroatoms and electrons of aromatic ring²⁰.

In order to explicate all the observations in a holistic way, a reasonable mechanism is projected as follows.

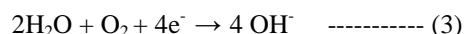
- When mild steel coupons are immersed in aqueous medium containing 60ppm of chloride ions and the inhibitor ADMP-Zn²⁺ binary formulation, the anodic reaction is



Fe²⁺ further undergoes oxidation in the presence of oxygen accessible in the aqueous solution.



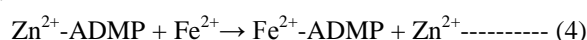
The corresponding reduction reaction at cathodic sites in neutral and alkaline media is,



Fe²⁺ ions produced at anodic areas and OH⁻ ions at cathodic areas combine to form Fe(OH)₃,

(Fe₂O₃.H₂O) which gets precipitated on the surface of the metal due to its very low solubility product.

- Addition of 80ppm of Zn²⁺ and 150ppm of ADMP to the aqueous solution forms Zn²⁺-ADMP complex in solution.
- When mild steel coupon is immersed in this solution, the Zn²⁺-ADMP complex disperses from the bulk of the solution to the metal surface and unites with Fe²⁺ ions on the metal surface and forms Fe²⁺-ADMP complex which is more stable than Zn²⁺-ADMP complex.
- Zn²⁺-ADMP complex is converted into Fe²⁺-ADMP on the anodic sites, (controls the anodic reaction corrosion process) and Zn²⁺ is released.



The released Zn²⁺ coalesces with OH⁻ ions to form Zn (OH)₂ on the cathodic sites.



The precipitated Zn (OH)₂ gets deposited on the cathodic sites and controls cathodic corrosion process.

- Therefore the protective film consists of Fe²⁺-ADMP complex and Zn (OH)₂.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 6, Issue 6, June 2017

- The inhibitive film formed on the mild steel surface consists of oxides/Hydroxides of iron and zinc, complexes of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and Zn^{2+} with ADMP.
- The FT-IR spectrum, SEM images and AFM micrographs of the surface film corroborates the formation of these complexes and the presence of $\text{Zn}(\text{OH})_2$ on the metal surface.

IV. CONCLUSION

The inhibition efficiency of 2-amino-4, 6-dimethyl pyrimidine (ADMP) on mild steel in aqueous solution containing 60 ppm Cl^- ions, and its combination with Zn^{2+} ion as synergist are studied by surface morphological analysis like FT-IR, UV, SEM and AFM. The rationale of this investigation is to build up a novel, environment friendly composite formulation for corrosion inhibition in aqueous medium and to use in industrial cooling water systems where the equipment parts are made of mild steel and the cooling water used usually consists of 60 ppm chloride ions. The corrosion inhibition in the industries using mild steel cooling water systems is attained by the addition of inhibitor to the system. The influence of the inhibitor upon metal corrosion is often associated with physical or chemical adsorption. This phenomenon is related to the presence of hetero atoms (N, O, P and S) as well as multiple bonds in the inhibitor. The inhibition efficiency of an organic compound depends on factors like electronic structure, mode of interaction with metal surface, number of adsorption centers, molecular size and chemical properties of the inhibitor adsorbed on metal surface. The adsorption of examined compound can be featured to the presence of polar groups having nitrogen and aromatic ring. Consequently, the probable reaction centers are unshared electron pair of hetero atoms and electrons of aromatic ring.

The most important findings are summed up as follows:

- FT-IR spectra reveals that the protective film consists of mainly Fe^{2+} -ADMP, Fe^{3+} -ADMP complex, $\text{Zn}(\text{OH})_2$ and small amounts of oxides/hydroxides of Fe^{2+} .
- The protective film outlined on the metal surface is characterized by UV-Visible absorption, SEM and AFM studies.

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Vol. 6, Issue 6, June 2017

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