SYNTHESIS AND EVALUATION OF ANTI-CORROSIVE

BEHAVIOR OF SOME SCHIFF BASE DERIVATIVE

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ABSTRACT

Corrosion is derived from the Latin word "corrosus" meaning away. It can be defined as "the destruction or deterioration and consequent loss of metals through chemical or electrochemical attack by the environment". The process of corrosion is the transformation of pure metal into its undesired metallic compounds. The life time of metal gets shortened by the corrosion process. Most metals [except noble metals] occur in the form of their compounds such as **oxides, sulfides, carbonates, chlorides**, etc. The extraction or metals from their ores is an endothermic process, energy being supplied in the form of heat or electrical energy. Pure metals are relatively at higher energy state compared to their corresponding ores and they have a natural tendency to revert back to their combined state. Therefore, the metals combine with the environment and get converted into their compounds. Thus corrosion of metals can be considered as extractive metallurgy in reverse. Corrosion is breaking down of essential properties in a material due to reactions with its surroundings. Corrosion also includes the dissolution of ceramic materials and can refer to discoloration and weakening of polymers by the sun's ultraviolet light. To synthesis series of a Schiff bases from 4-amino antipyrine and different aromatic aldehyde ie, **furfuraldehyde, salicylaldehyde** and **anisaldehyde**. The 4-amino antipyrine as a effective inhibitors. it was found that the adsorbed inhibitors accounts for protecting the metal from corrosive medium and modifying electrode reactions resulting in the dissolution of the metals.the weight-loss measurements and electrochemical studies have the same tendency to explain about metal deterioration.

KEYWORDS: Corrosion Process, Sulfides, Carbonates, Chlorides, Furfuraldehyde, Salicylaldehyde, Anisaldehyde

INTRODUCTION

Corrosion is derived from the Latin word "corrosus" meaning away. It can be defined as "the destruction or deterioration and consequent loss of metals through chemical or electrochemical attack by the environment" [1]. Shrier describes the corrosion as the result of interaction of solid with the environment. The process of corrosion is the transformation of pure metal into its undesired metallic compounds. The life time of metal gets shortened by the corrosion process.Most metals [except noble metals] occur in the form of their compounds such as oxides, sulfides, carbonates, chlorides, etc. The extraction or metals from their ores is an endothermic process, energy being supplied in the form of heat or electrical energy. Pure metals are relatively at higher energy state compared to their corresponding ores and they have a

natural tendency to revert back to their combined state. Therefore, the metals combine with the environment and get converted into their compounds. Thus corrosion of metals can be considered as extractive metallurgy in reverse.Corrosion is breaking down of essential properties in a material due to reactions with its surroundings. In the most common use of the word, this means a loss of an electron of metals reacting with water and oxygen. Weakening of iron due to oxidation of the iron atoms is a well-known example of electrochemical corrosion. This is commonly known as rust. This type of damage usually affects metallic materials, and typically produces oxide(s) and/or salt(s) of the original metal. Corrosion also includes the dissolution of ceramic materials and can refer to discoloration and weakening of polymers by the sun's ultraviolet light. Most structural alloys corrode merely from exposure to moisture in the air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area to produce general deterioration. While some efforts to reduce corrosion merely redirect the damage into less visible, less predictable forms, controlled corrosion treatments such as passivation and chromate-conversion will increase a material's corrosion resistance. The cost of corrosion was estimated for each of the above categories. When summed, the total annual cost of corrosion for the industry sectors examined was $137.9 billion. The breakdown of these costs among the five sector categories is given in Figure 2. Not all industries were examined in this study; therefore, the total economic impact on the U.S. economy would naturally be greater than the $137.9 billion given here. Hydrochloric and hydrofluoric acid blends are used to clean ferritic, martensitic and austenitic steels. Iron oxide scale is soluble in hydrochloric acid, and therefore there is no acid attack on the metal surface. Hydrogen embrittlement is a major problem during the pickling of mild steel wire. The addition of inhibitor to the hydrochloric acid eliminates or reduces embrittlement. This embrittlement occurs when atomic hydrogen produced by the introduction of the acids, diffuses into the lattices of the metal and strains it. This results in brittleness at the molecular level, with no advanced indications such as visible pitting. Figure 3 shows the acid pickling of mild steel. In the figure right hand coupon prior to pickling, center coupon acid inhibited and left hand coupon no inhibitor used.
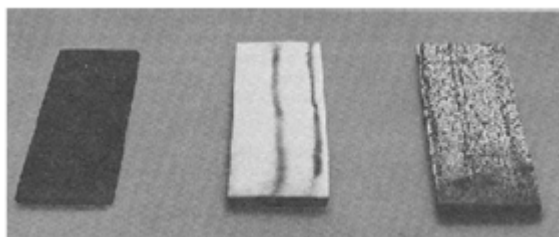

Figure 1

In the fracturing and acidizing of compact oil formations, dilute hydrochloric acid is used to dissolve the undesirable carbonate deposits or scales, which interfere with the passage of oil, in tubing or in the formation itself. The lines and tubing must be protected during this operation from corrosive attack by the acid, by the high temperatures and pressures, and by the potential for a "sour" environment resulting from the high hydrogen sulfide and carbon dioxide contents.
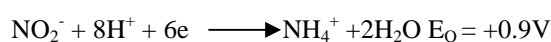
Adsorption Inhibitors

Adsorption inhibitors protect by adsorption on to the metal or metal oxide film exposed to electrolyte. Organic inhibitors are aliphatic and aromatic amines (N compounds), thiourea (S compounds) and aldehydes (O compounds). All

these have a charged state, for example aliphatic amines have ammonium cations present, R_3NH^+. The S and O compounds have a negative charge on them. Thiourea bonds strongly to a metal by sharing its electrons with the metal surface. This blocks solvating water molecules and also stops hydrogen gas molecule formation.N and O compounds are less adsorbed on the metal surface than the S type compounds. They tend to select active anodic sites. The larger the molecule the greater the inhibition as they displace solvating water molecules.

Film Form Inhibitors

The addition of specific ions with high redox reaction potentials will produce local reactions to form protective films. Two ions of this type are the chromate and nitrite ions.

They have redox reactions:-

$$NO_2^- + 8H^+ + 6e \longrightarrow NH_4^+ + 2H_2O \; E_O = +0.9V$$

$$2CrO_4^{2-} + 10H^+ + 6e \longrightarrow Cr_2O_3 + 5H_2O \; E_O = +1.31V$$

Both these reactions induce iron to dissolve in the ferric state with 3+ rather than in the ferrous state as 2+. The ferric oxides are stable on the surface and block further corrosion.

$$Fe^{3+} + 3H_2O \longrightarrow Fe_2O_3 + 6H^+$$

These tend to be nitrites, carbonate and benzoate filming inhibitors attached to parachutes of an organic cation. An example is dicyclohexyl ammonium nitrite. The inhibitor evaporates onto the metal surface.

Schiff Base

Schiff base compounds are the condensation product of an amine and a ketone/aldehyde. A Schiff base (or azomethine), named after Hugo Schiff, is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group but not hydrogen. Schiff bases are of the general formula $R_1R_2C=N-R_3$, where R_3 is an aryl or alkyl group that makes the Schiff base a stable imine. A Schiff base derived from aniline, where R3 is a phenyl or substituted phenyl, can be called an anil.
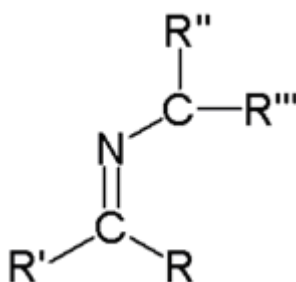
Schiff bases can be synthesized from an aromatic amine and a carbonyl compound by nucleophilic addition forming a hemiaminal, followed by a dehydration to generate an imine. In a typical reaction, 4,4'-diaminodiphenyl ether reacts with o-vanillin.The choice of the inhibitor is based on two considerations: first it could be synthesized conveniently from relatively cheap raw materials, secondly, it contains the electron cloud on the aromatic ring or, the electronegative atoms such as nitrogen and oxygen in the relatively long chain compounds [33]. Due to the presence of the –C=N group in

the Schiff base molecules, they should be good corrosion inhibitors. Schiff base inhibitors have been previously reported as effective corrosion inhibitors for steel, copper and aluminum.

Scope of the Present Investigation

The use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media. Acid solutions are generally used in several industrial processes. Hydrochloric acid is widely used in the pickling of steel and ferrous alloys. The most important areas of application are acid pickling, acid cleaning, acid rescaling and oil well cleaning, petrochemical industry, and other electrochemical systems. Corrosion inhibitors are needed to reduce the corrosion rates of metallic materials in these media. An inhibitor is therefore used to protect the cleaned surface, reduce acid wastage and metal loss and prevent pitting and discoloration of the metal. Some Schiff bases have been reported earlier as corrosion inhibitors for steel, copper, aluminum, and zinc. Some research work reveal that the inhibition efficiency of Schiff bases is much greater that of corresponding amines and aldehydes. This may be due to the presence of a C=N group in the molecule.Thus, a systematic study has been undertaken to understand the corrosion behaviour of mild steel and inhibitive action of 4-amino antipyrine and its Schiff base derivatives in 1M HCl environment. This compound is expected to show good inhibition efficiency for mild steel corrosion because it having a variety of donor atoms heteroatoms like oxygen, nitrogen and it would be the adsorbing center. Moreover the introduction of some functional group to the 4-amino antipyrine would expect as an effective inhibition. It was found that the adsorbed inhibitor accounts for protecting the metal from corrosive medium and modifying electrode reactions resulting in the dissolution of the metals.

## SYNTHESIS OF SCHIFF BASE

Synthesis of 4-Benzilidine Amino Antipyrine (FAAP)

0.0025 mole of 4-Amino antipyrine (AAP) dissolved in ethanol. To this, furfuraldehyde (0.0025 moles) was added. The resulting mixture was refluxed at 80°C – 90°C on the water bath for 4 hours. The hot solution was cooled. The solid was separated out and the resulting solid was filtered off. It was recrystallized from ethanol.
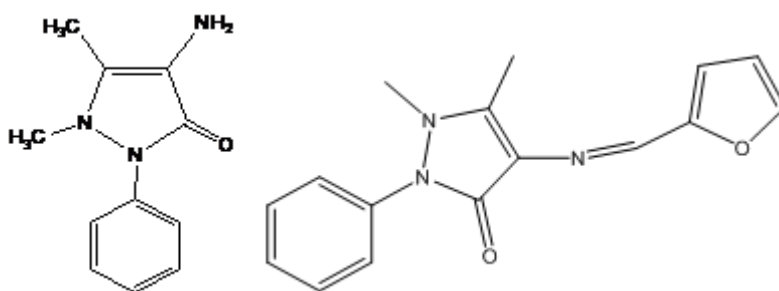
### Synthesis of 4-Salicylidine Amino Antipyrine (SAAP)

0.0025 mole of 4-Amino antipyrine dissolved in ethanol. To this, salicylaldehyde (0.0025 moles) was added. The resulting mixture was refluxed at 80°C – 90°C on the water bath for about 4 hours. The hot solution was cooled. The solid was separated out and the resulting solid was filtered off. It was recrystallized from ethanol.
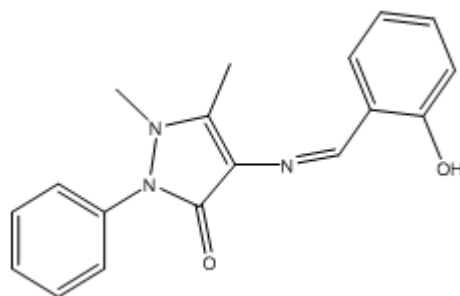
SAAP

Synthesis of 4-Anisalidine Amino Antipyrine (AAAP)

0.0025 mole 4-Amino antipyrine dissolved in ethanol. To this, Anisaldehyde (0.0025 mole) was added. The resulting mixture was refluxed at 80°C – 90°C on the water bath for about 4 hours. The hot solution was cooled. The solid was separated out and the resulting solid was filtered off. It was recrystallized from ethanol.
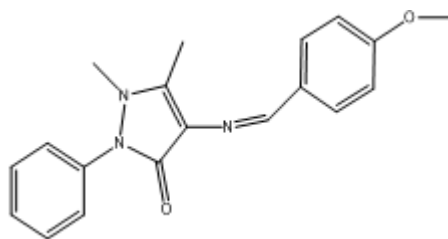
AAAP

Materials Used

In the present work, mild steel was used as material for the corrosion studies. The chemical composition of the mild steel was determined by analytical techniques and its composition is illustrated in the Composition of mild steel

Table 1

Sample	C	Mn	S	P	Si	Fe
Mild steel	0.12%	0.85%	0.055%	0.05%	0.09%	Balance

Electrolyte

1M HCl was used as an electrolyte which was prepared from 86.2 ml of HCl in 1000 ml of distilled water. All the test specimens of mild steel were cut into an overall apparent size of 1x1x0.3 cm, which were polished with different grids of emery papers namely 120, 320, 400, 600, 800 and 1000 and they were degreased with acetone and distilled water, this specimens were embedded by using epoxy resin with an electrical connection and exposed area of 1cm^2. 0.2 gm of ATA, VTA and FTA are dissolved separately in 100 ml of 0.1 M HCl (2000 ppm).Electrochemical experiments (Potentiodynamic polarization and Electrochemical Impedance) were carried out in a five–neck glass cell got provision for the working electrode, platinum electrode and luggin capillary. The potential of the working electrode has been measured with respect to calomel electrode (SCE). The lugging capillary and SCE has been connected through an agar – agar potassium chloride salt bridge.

Experimental Procedure

For weight loss measurement, the specimens were cut into the exposed area of 4x2x0.3 cm. They were polished to mirror finish using different grids namely 120, 220, 320, 400, 600, 800, 1000 and degreased with acetone, and distilled water. The specimens were separately weighed and immersed in solution containing 200 ml 1M HCl with different concentration like 20, 30, 40, 50, 60, 70 and 80 ppm, of ATA, VTA, and FTA solutions, for about 150 minutes. After 150 minutes the specimens were removed from the solution and cleaned. Dried the specimens and weighed. Then the weight–losses were measured.

The modern theory of acid metallic corrosion is now based firmly on electrode kinetics. 50 ml of 1M HCl was taken in a glass cell. The well-polished electrode has been introduced into the solution and the electrode has been allowed to attain a steady potential value for 15 minutes. Potentiodynamic polarization curves for mild steel specimen in the 1M HCl environment was recorded at a sweep rate of 1mV/s using Electrochemical Workstation Instrument (model CHI1760 (USA). Electrochemical impedance studies (EIS) is a powerful technique for the characterization of electrochemical system. The electrochemical impedance studies were carried out in the same setup used for potentiodynamic polarization studies described above. We applied the ac perturbation signal of 10 mV with in the frequency range of 100 KHz to 1Hz. All electrochemical impedance spectra were carried out using CHI760 (USA) instrument. The most common equivalent circuit used to corrosion of base metal in acid electrolyte is the Randles circuit.

Measurements of Corrosion Rate

The corrosion rates of mild steel in 1M HCl environment were calculated in miles per year (mpy) from the potentiodynamic polarization parameter by using the relation.

Corrosion rate (mpy) = $(0.129 \times i_{corr} \times EW) / (D \times A)$

Where,

i_{corr} – corrosion current density (A / cm^2)

EW – equivalent weight (g)

D – Density of mild steel specimen, A – Area of mild steel.

Determination of Inhibition Efficiency

Inhibition efficiencies of the inhibitors were calculated from the potentiodynamic polarization curve by using the following relation.

IE (%) = $[(i_{corr} – i_{corr}') / i_{corr}] \times 100$

Where,

i_{corr} - with inhibitor

i_{corr}' - without inhibitor.

Inhibition efficiencies were also calculated from the weight loss measurement using the following relation.

IE (%) = (Wo – Wi)∕Wo

Where,

Wo – weight loss without inhibitor

Wi – weight loss with inhibitor

RESULTS AND DISCUSSIONS

The corrosion of mild steel in 1 M HCl medium containing various concentrations of AAP and its Schiff bases FAAP, SAAP and AAAP (20, 30, 40, 50, 60, 70 80 ppm) were studied by weight loss measurements. In this case, inhibition efficiencies (IE %) were calculated by applying the following equation

IE (%) = (Wo – Wi)∕Wo

Where, Wo and Wi are the weight loss of mild steel in the absence and presence of inhibitor molecule, respectively. Figure 4-7 summarizes the inhibition efficiency (IE %) for the AAP and its Schiff bases studied at different concentrations. It is obvious from figures that all of these compounds inhibit the corrosion of mild steel in 1 M HCl solution at all concentrations used in this study and the inhibition efficiency was seen to increases with increasing additive concentration. At 50 ppm IE (%) attains maximum for all of the studied AAP and its Schiff bases. Thus, we deduce that these inhibitors are the better inhibitor for the mild steel and IE (%) was found to be in the following order: AAAP > SAAP > FAAP > AAP. The difference in their inhibitive action can be explained on the basis of the type of functional group present in the benzene ring which contributes to the adsorption strength through the donor acceptor bond between the non-bonding electron pairs and the vacant orbitals of the metal surface. As a result of this classification and in order to better understand the inhibition mechanism of Schiff bases, a detailed study using potentiodynamic polarization and electrochemical impedance spectroscopy were carried out
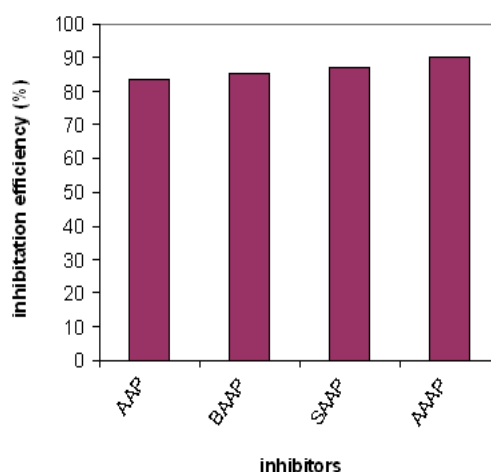

Figure 2

Potentiodynamic Polarization Studies

In order to better define the action of different additives and concentrations on the corrosion process a series of representative examples of Tafel polarization curves were recorded. Evaluation of inhibitor efficiencies (IE %) can also be

performed through electrochemical experiments, which consist of determination of Tafel curves. Figure 9 shows the potentiodynamic polarization curves for mild steel in 1M HCl absence and presence of various concentration of AAP. Correction for IR drop was performed prior to the experiments although, due to the high conductivity of the acidic solution and proper positioning of the Luggin capillary, it was found to be unnecessary. As it can be seen, both cathodic and anodic reactions of mild steel electrode corrosion were inhibited with the increase of AAP concentration in 1M HCl acid. This inhibitor suppressed the anodic reaction to greater extents than the cathodic one, in the case of 1M HCl, especially at 50 ppm concentration. This result suggests that the addition of AAP reduce anodic dissolution and also retard the hydrogen evolution reaction. Values of all potentiodynamic polarization parameters such as Tafel slopes b_c and b_a corrosion current density (i_{corr}), corrosion potential (E_{corr}) and corrosion rate obtained in uninhibited and inhibited acidic solutions are listed in Table 2. The rate is calculated by i_{corr} as described elsewhere [57]. It is seen that the addition of AAP decreases i_{corr} significantly for all the studied concentration, due to increase in the blocked fraction of the electrode surface by adsorption. AAP can be classified as inhibitor of relatively mixed effect (anodic/cathodic inhibition) in 1M HCl. Inhibition efficiency (IE %) increased with inhibitor concentrations and maximum inhibition efficiency was obtained at a concentration of 50 ppm and a further increase in the concentration did not cause any appreciable increase in performance. We can conclude that the ability of the molecule to adsorb on the iron surface is dependent on the position of the nitrogen atom on the pyrine ring. The excellent behaviour of AAP previously evidenced in the weight loss measurements and impedance study was again confirmed. shows the potentiodynamic polarization curves for mild steel in 1M HCl without and with various concentrations of Schiff bases FAAP, SAAP and AAAP, and the corresponding Tafel parameters are summarized in Tables 3-5. Figure 10 shows the influence of various concentrations of FAAP on the polarization behavior of mild steel in 1M HCl. It should be noted that with the addition of the FAAP both the anodic and cathodic current densities decrease, the anodic domain being more significant. The influence of SAAP on the polarization behavior of steel in 1 M HCl at various concentrations. Similar to FAAP both the anodic and cathodic current densities decrease, the anodic domain being more profound. shows the influence of AAAP on the polarization behavior of mild steel in 1 M HCl at various concentrations. Both the anodic and cathodic current densities are seen to decrease. Addition of whichever compound produces a positive shift in the E_{corr}, and as the concentration is increased the corrosion potential shifts to more noble values (Tables 3-5). Both the marked positive shift in the corrosion potential and decrease in the anodic current density and the decrease in the cathodic current density, suggests these compounds to act as mixed type inhibitors. The inhibition efficiency follows the order AAAP > SAAP > FAAP > AAP. The inhibition efficiency depends on many factors including adsorption centers, mode of interaction, molecular size and structure [58,59]. The effect of molecular size and structure can easily viewed from the difference in the structure of AAAP with respect to SAAP and FAAP. Another factor effecting the inhibition capability are the coordination sites of the compounds where AAAP has the highest coordination sites then the other compound.
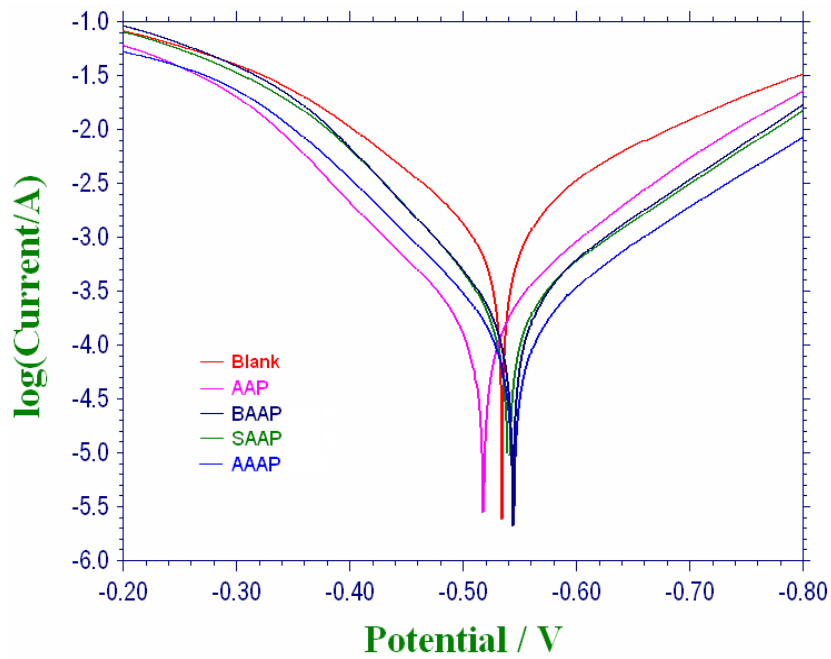
Figure 3

Table 2

S.No	System	b_c (V)	b_a (V)	E_{corr} (V)	i_{corr} x 10^{-4} (A)	Rate (mpy)	IE (%)
1	Blank	0.15	0.14	-0.5248	12.5863	5.753	--
2	AAP	0.12	0.10	-0.5100	2.0826	0.9613	83.52
3	FAAP	0.13	0.10	-0.5544	1.8200	0.864	85.53
4	SAAP	0.14	0.10	-0.5399	1.7482	0.799	86.11
5	AAAP	0.13	0.10	-0.5442	1.2880	0.5888	89.77

Potentiodynamic polarization curves of mild steel in 1M HCl in absence and presence of AAP, FAAP, SAAP and AAA
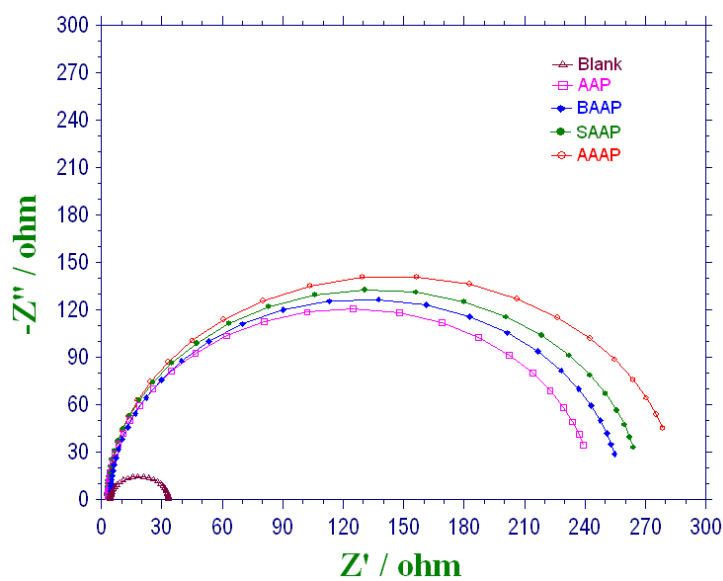

Figure 4

Nyquist plots of mild steel in 1M HCl in absence and presence of AAP, FAAP, SAAP and AAAP
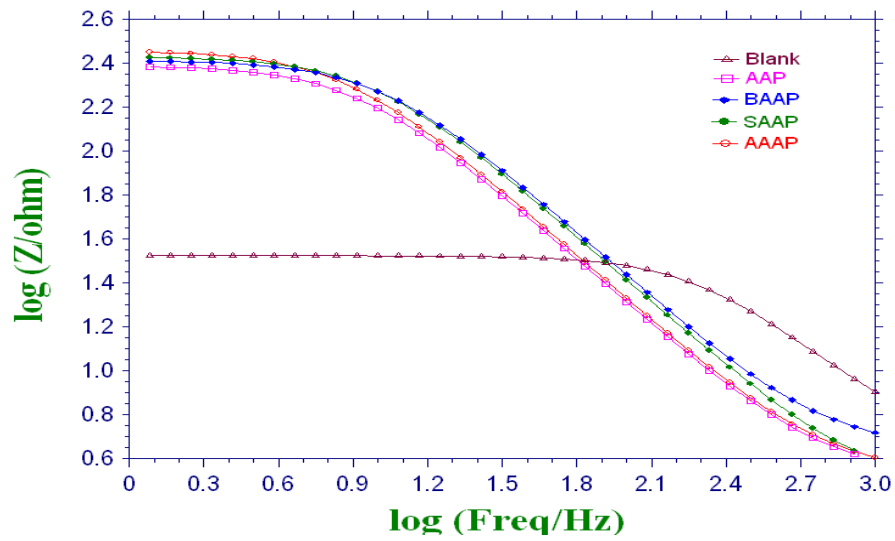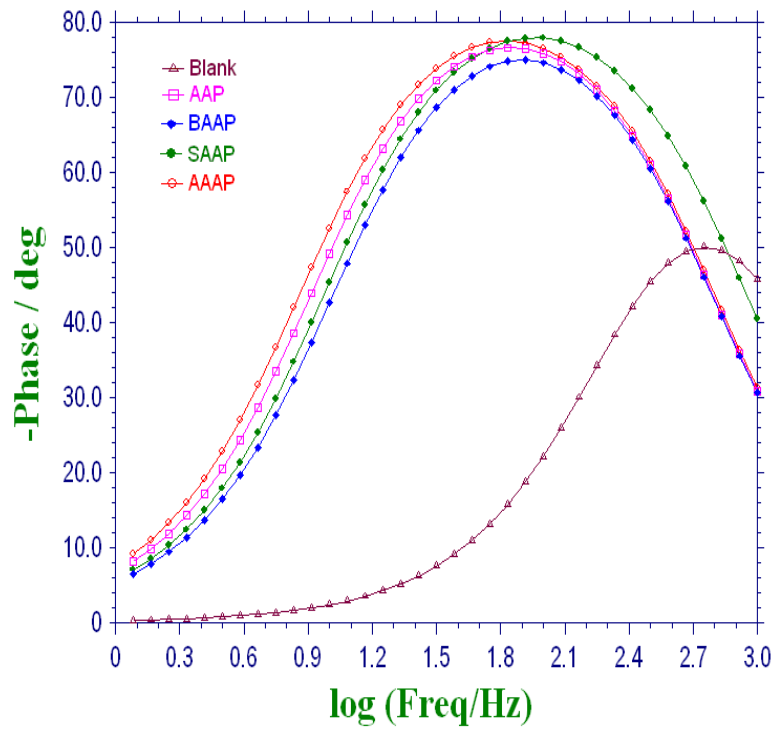
Figure 5

Figure 6

Bode plots of mild steel in 1M HCl in absence and presence of AAP, FAAP, SAAP and AAAP
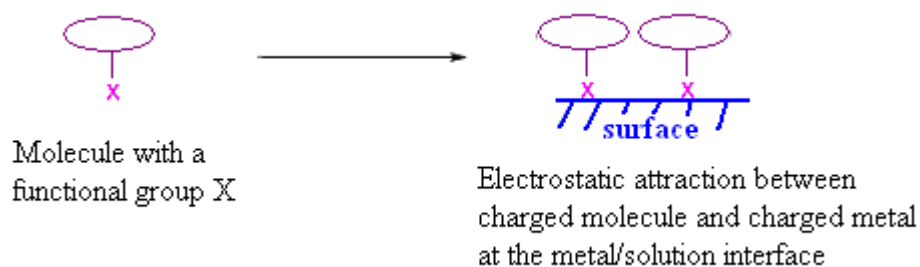
Figure 7

Schematic representation of adsorption of Schiff base at metal electrode

Adsorption Isotherm

Basic information on the interaction between the inhibitor and the mild steel surface can be proved by the adsorption isotherm and in general, inhibitors can function either by physical (electrostatic) adsorption or chemisorption with the metal. To obtain more information about the interaction between the schiff base molecules and the metal surface, different adsorption isotherms were tested. The fractional surface coverage θ at different concentrations of AAP, FAAP, SAAP and AAAP in 1 M HCl solution were determined from the potentiodynamic polarization measurements data [24] using the formula,

$$\theta = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \tag{4.1}$$

Where, i_{corr} and $i_{corr(inh)}$ are the values of corrosion current density of uninhibited and inhibited specimens, respectively.

$$Kc = \frac{\theta}{1-\theta} \tag{4.2}$$

Where, c is the concentration of the inhibitor, θ is the fractional surface coverage. The Langmuir isotherm, Eq. (4.2), which is based on the assumption that all adsorption sites are equivalent and that molecular binding occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied schiff bases. The adsorption equilibrium constant K is related to the free energy of adsorption ΔG_{ads} as,

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$

where, $C_{solvent}$ represents the molar concentration of the solvent, which in the case of water is 55.5 mol dm^{-3}, R is the gas constant and T is the thermodynamic temperature in K. The Langmuir isotherm, Eq. can be rearranged to obtain the following expression,

$$\frac{c}{\theta} = \frac{1}{K} + c$$

So that a linear-relationship can be obtained on plotting c/θ as a function of c, with a slope of unity. The

thermodynamic parameters K and ΔG_{ads} for the adsorption of the studied inhibitors on mild steel is obtained by Langmuir's adsorption isotherm and are given in. The negative values of ΔG^0_{ads} for the addition of inhibitors indicates that the process of adsorption of studied inhibitors are spontaneous in nature [25]. The free energy of adsorption (ΔG_{ads}) of all the studied inhibitors, in 1 M HCl was found to be equal to -11.26 kJ mol^{-1}, -11.54 kJ mol^{-1}, -11.69 kJ mol^{-1} and -12.10 kJ mol^{-1}, respectively.

It is well known that values of ΔG_{ads} in the order of -20 kJ mol^{-1} or lower indicate a physisorption while those about -40 kJ mol^{-1} or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [25,26]. The calculated adsorption values for the 4-amino antipyrine and its schiff bases show that the adsorption is of physical in nature, and there is no chemical interaction between the inhibitor molecule and the metal surface. This indicates that the adsorption of AAP, FAAP, SAAP and AAAP takes place through electrostatic interaction between the inhibitor molecule and the metal surface.

Thermodynamic parameters for the adsorption of AAP, BAAP, SAAP and AAAP in 1M HCl on the mild steel at 301 K

Table 3

Inhibitor	K (10^4 M^{-1})	ΔG_{ads} (kJ mol^{-1})
AAP	1.74	-11.26
BAAP	1.74	-11.54
SAAP	1.74	-11.69
AAAP	1.74	-12.10

Figure 8

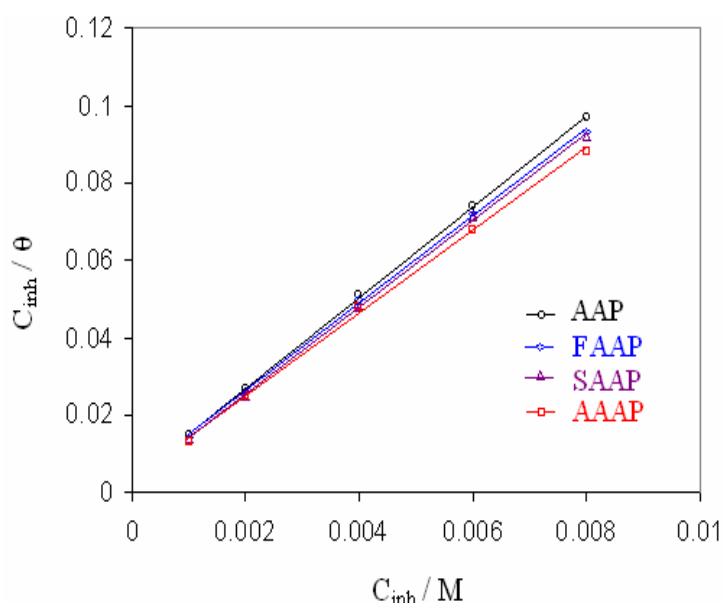## CONCLUSIONS

The following conclusions were drawn from the present investigation.

The inhibitive action of AAP and its Schiff bases (FAAP, SAAP and AAAP) against mild steel corrosion in HCl environment was studied using weight-loss method, potentiodynamic polarization and electrochemical impedance

technique.The presence of 4-Amino antipyrine and its Schiff bases hindered the mild steel corrosion in 1M HCl solution.The inhibition is due to the adsorption of inhibitor molecules on the mild steel surface and blocking its active sites.AAP, FAAP, SAAP and AAAP inhibit both anodic and cathodic reaction by adsorption on the mild steel surface.The results obtained from weight-loss measurements and electrochemical studies have the same tendency and they are in good agreement.The impedance measurements indicate that as the additive concentration is increased the polarization resistance increases where as the double layer capacitance decreases.

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