Poly (acrylic acid) and Sodium gluconate as effective corrosion inhibitors for mild steel in chloride environment

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Abstract : The aim of the present work was to study the corrosion inhibition of mild steel using a ternary formulation. This new ternary inhibitor formulation, viz., Polyacrylic acid (PAA), with nickel ions and Sodium gluconate (SG) was used to protect mild steel from corrosion in a low-chloride environment. The weight loss studies showed that 89% inhibition efficiency was achieved with the ternary system consisting of 50 ppm Ni^{2+} ions, 200 ppm PAA, and 600 ppm SG. Electrochemical methods (potentiostatic polarization and electrochemical impedance studies) and Surface characterization techniques (FT-IR, SEM, EDAX and AFM) are also used to ascertain the nature of the protective film. The mechanical aspect of corrosion inhibition is proposed.

Keywords : Mild steel, Polarization, EIS, FT-IR, SEM, EDAX, AFM.

1. Introduction

Corrosion inhibitors are widely used as an economical method of corrosion control [1, 2]. Environmental restrictions imposed on heavy metal-based corrosion inhibitors oriented scientific researchers towards the study of non-toxic and environmentally friendly corrosion inhibitors [3]. The influence of several organic compounds containing polar functions such as nitrogen, oxygen, phosphorous or sulphur on the corrosion inhibition behavior of mild steel in aqueous solutions has been documented [4-8]. These groups of atoms or bonds facilitate electronic interactions between organic corrosion inhibitors and metal surface thereby aid adsorption of the inhibitors onto metal surface. The quest for eco-friendly compounds as corrosion inhibitors has shifted research focus to exploring potential application of polymers as corrosion inhibitors in the past few years.

The use of polymers as corrosion inhibitors has attracted considerable attention recently because: (i). they have low cost and are stable to metallic materials in aqueous media, (ii). possession of multiple adsorption sites and (iii) through their functional groups, they form complexes with metal ions, and on the metal surface, these complexes occupy a large area, thereby blanketing the surface and protecting the metal from corrosive agents present in the solution [9-13]. The inhibitive power of these polymers is related structurally to the cyclic rings, heteroatom (oxygen and nitrogen) that are regarded as centers of adsorption. Some polymers have been reported to inhibit the corrosion of mild steel in various aqueous media [14-17]. Recently, polyacrylic acid reported to be very effective corrosion inhibitors for the protection of mild steel in aqueous media to promote eco-friendly environment.

The aim of the present work is to determine the inhibitive effect of Polyacrylic acid (PAA), SG and Ni^{2+} ions on the corrosion of mild steel in 60 ppm chloride medium by chemical and electrochemical methods. Surface characterization techniques (FT-IR, SEM, EDAX and AFM) are also used to ascertain the nature of the protective film.

2. Experimental methods

2.1. Materials

Polyacrylic acid (PAA), Nickel sulphate ($NiSO_4.6H_2O$), Sodium gluconate (SG) and other reagents were analytical grade chemicals. The molecular structures of Polyacrylic acid and Sodium gluconate are shown in Fig.1 and Fig.2 respectively. All the solutions were prepared by using double distilled water. pH values of the solutions were adjusted by using 0.01 N sodium hydroxide and 0.01 N sulphuric acid solutions. An aqueous solution consisting of 60 ppm of sodium chloride has been used as the control throughout the studies.
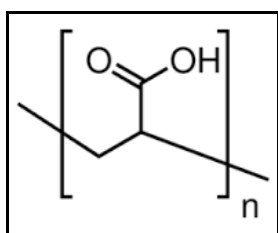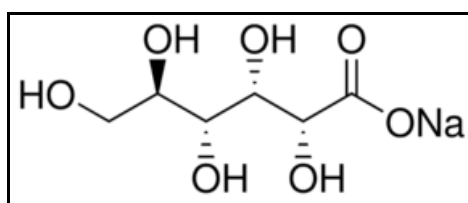

Fig.1. Polyacrylic acid (PAA)   **Fig.2. Sodium Gluconate (SG)**

2.2. Preparation of specimens

For all the studies, the specimens taken from a single sheet of mild steel of the following composition were chosen: C, 0.1-0.2%; P, 0.03-0.08%; S, 0.02-0.03%; Mn, 0.4-0.5% and the rest iron. For gravimetric measurements and surface analytical techniques, the polished specimens of the dimensions, 4 cm x 1.0 cm x 0.1 cm, were used while for other (electro chemical) studies, the dimensions of the specimens were 1.0 cm x 1.0 cm x 0.1 cm. Prior to all measurements, the specimens were polished successively using 1/0 to 6/0 emery papers, decreased with trichloroethylene and washed thoroughly with double distilled water and dried.

2.3. Weight loss measurements

Weight loss experiments are the easiest way to find the corrosion rate (CR) and inhibition efficiency (IE). In all gravimetric experiments, the polished specimens were weighed and immersed in duplicate, in 100 ml control solution in the absence and presence of inhibitor formulations of different concentrations, for a period of seven days. Then, the specimens were reweighed after washing and drying. The weights of the specimens before and after immersion were determined by the Mettler electronic balance, AE 240 model with a readability of 0.1 mg. Accuracy in weighing up to 0.0001g and its surface area measurement up to 0.1 cm^2. Corrosion rates of mild steel in the absence and presence of various inhibitor formulations are expressed in mdd. The corrosion rate was calculated according to the following equation.

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2) \times \text{Period of immersion (days)}} \text{ (mdd)} \qquad (1)$$

Where, m is the Loss in weight (mg), d is the Surface area of the specimen (dm^2) and d is the Period of immersion (days). Inhibition efficiencies (IE) of the inhibitor were calculated by using the formula,

$$\text{I.E} = 100\,[1- W_2/W_1]\,\% \qquad\qquad (2)$$

Where, W_1 is the weight loss in the absence of inhibitor, W_2 is the weight loss in the presence of inhibitor.

2.4. Electrochemical studies

Electrochemical impedance spectroscopic (EIS) studies and potentiostatic polarization studies were carried out using an electrochemical workstation CHI model 660A (USA) electrochemical analyzer. The mild steel specimens used as working electrode while platinum and calomel electrodes were used as counter electrode and the reference electrode, respectively. Impedance measurements were carried out at E_{corr} potential at the range of 100 kHz to 10 MHz at amplitude of 10 mV. The impedance diagrams are given in Nyquist representation. The impedance and polarization parameters such as double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) were computed from the polarization curves and Nyquist plots. The IE values were calculated from potentiodynamic polarization measurements using the equation (3).

$$IE_P\ (\%) = \left[\frac{I_{corr} - I'_{corr}}{I_{corr}} \right] \times 100$$

(3)

Where, I_{corr} and I'_{corr} are the corrosion current densities in case of the absence and presence of the inhibitor respectively. From impedance measurements, the IE values were calculated from the following relation,

$$IE_I\ (\%) = \left[\frac{R_{ct(i)} - R_{ct(b)}}{R_{ct(i)}} \right] \times 100$$

(4)

Where, $Rct_{(b)}$ and $Rct_{(i)}$ are the charge transfer resistance values in the absence and presence of the inhibitor respectively.

2.5. Surface studies

The mild steel specimens were immersed in various test solutions for a period of seven days. Then, they were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Energy Dispersive X-Ray Analysis (EDAX) and Atomic force microscopy (AFM).

2.5.1. Fourier Transform Infrared Spectroscopy

The mild steel specimens were immersed in various test solutions for a period of seven days. On completion of the seventh day, the specimens were taken out and dried. The protective film formed on the metal specimens was scratched and mixed with KBr and pellets were obtained and the FT-IR spectra were recorded using Spectrum RXI Spectrophotometer over a range of 4000 - 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.5.2. Scanning Electron Microscopy and EDAX

The surface morphology of the formed layers on the mild steel surface after its immersion in control solutions containing 60 ppm chloride ions in the absence and in the presence of the inhibitor were carried out. After seven days, the specimens were taken out, washed with distilled water and dried. The SEM - EDAX photographs of the surfaces of the specimens were investigated using a VEGA3-TESCAN model scanning electron microscope.

2.5.3. Atomic Force Microscopy

The atomic force microscope was used for surface morphology studies. The protective films were examined with atomic force microscope (AFM) using A100 model (A.P.E Research, Italy). The topography of the entire samples from a scanned area of 20 μm x 20 μm is evaluated for a set point of 20 nm and a scan speed of 10 mm/s. The three dimensional topography of surface films gave various roughness parameters of the film.

3. Results and Discussion

3.1. Weight loss measurements

The Weight loss measurements were carried out to calculate the corrosion rate (CR) and inhibition efficiency (IE) for the mild steel in an aqueous solution containing 60 ppm chloride ions in the absence and presence of various inhibitor formulations consists in various amounts of PAA, Ni^{2+} ions and SG are given in Table.1. The inhibition efficiency was represented as a function of SG concentration in Fig.3.

Table.1. Inhibition efficiency (IE) and Corrosion rate (CR) by Weight loss measurements of MS in the presence of inhibitor

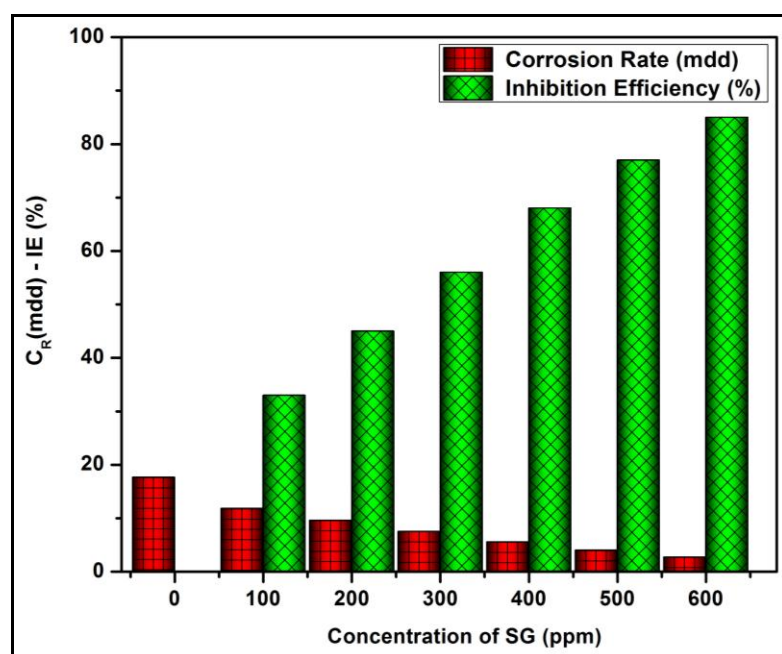| Ni^{2+} (ppm)	PAA (ppm)	SG (ppm)	Weight loss (g)	I.E (%)	Corrosion rate (mdd)	Surface Coverage (θ)
60 ppm Cl⁻	--	--	0.0136	--	17.66	--
50	200	100	0.0091	33	11.81	0.3308
50	200	200	0.0075	45	09.74	0.4485
50	200	300	0.0060	56	07.14	0.5588
50	200	400	0.0043	68	05.58	0.6838
50	200	500	0.0031	77	04.02	0.7720
50	200	600	0.0015	89	01.94	0.8897

Fig.3. Inhibition efficiency as a function of concentration of SG

It can be seen from the results of the ternary formulations, that for lower concentration of 50 ppm Ni^{2+} and 200 ppm PAA with 600 ppm SG, the maximum inhibition efficiency of only 89% is achieved. It is apparent that the inhibition efficiency increased with the increase in inhibitor concentration in the presence and absence of SG. This behavior can be explained based on the strong interaction of the inhibitor molecule with the metal surface resulting in adsorption. The extent of adsorption increases with the increase in concentration of the

inhibitor leading to increased inhibition efficiency. The maximum inhibition efficiency was observed at an inhibitor concentration of 600 ppm. Generally, inhibitor molecules suppress the metal dissolution by forming a protective film adsorbed to the metal surface and separating it from the corrosion medium.

3.1.1. Effect of pH

The influence of pH on corrosion rate of mild steel in the presence of inhibitor system and the maximum inhibition efficiency obtained in the gravimetric measurements were studied. When the pH is changed from 7 to 5 (addition of dil H_2SO_4) the inhibition efficiency is altered very much lowered. When the pH is changed from 7 to 9 (addition of dil NaOH) the inhibition efficiency is very much lowered, the system consisting of 50 ppm of Ni^{2+}, 200 ppm of PAA and 600 ppm of SG, the inhibition efficiency increases from 9% to 12%. This is due to the fact at this pH, when NaOH is added, Ni^{2+} is precipitated as $Ni(OH)_2$. Hence Ni^{2+} is not transported from the bulk of the solutions towards the metal surface. Hence inhibition efficiency decreases. However, interestingly when pH is changed from 7 to 11, the inhibition efficiency decreases to some extent but still the system shows some inhibition efficiency. The reasons for this decrease in inhibition efficiency in more alkaline and acidic environments are explained under the mechanistic aspects.
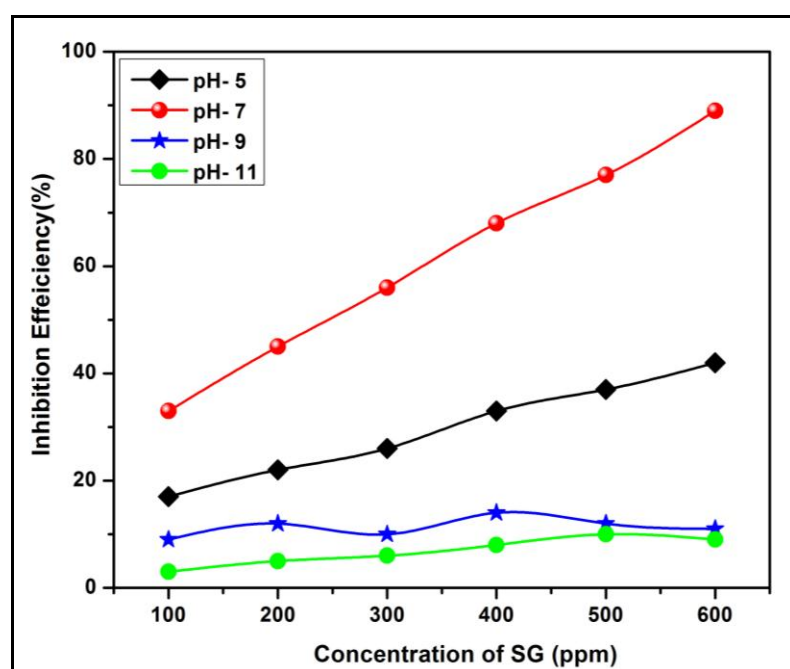

Fig.4. Effect of pH

3.2. Electrochemical measurements

3.2.1. Potentiodynamic Polarization Studies

The potentiodynamic polarization studies were carried out to determine the kinetics of the cathodic and anodic reactions. Fig.5. Shows the potentiodynamic polarization curves for mild steel electrodes in control solution at pH 7 in the absence and presence of inhibitor combinations. Electrochemical kinetic parameters, i.e., the corrosion potential (E_{corr}), corrosion current density (I_{corr}), and anodic and cathodic tafel slopes (β_a and β_c), obtained from extrapolation of the polarization curves are listed in Table 2. When mild steel is immersed in 60 ppm Cl^- medium, the corrosion potential (Ecorr) is - 598 mV/dec and the corrosion current is 129 $\mu A/cm^2$. When 600 ppm SG to 200 ppm of PAA and 50 ppm Ni^{2+} are added to 60 ppm Cl^- medium the corrosion potential is found to be - 619 mV/dec and corrosion current is 16.8 $\mu A/cm^2$. The corrosion current decreases from 129 to 16.8 $\mu A/cm^2$.
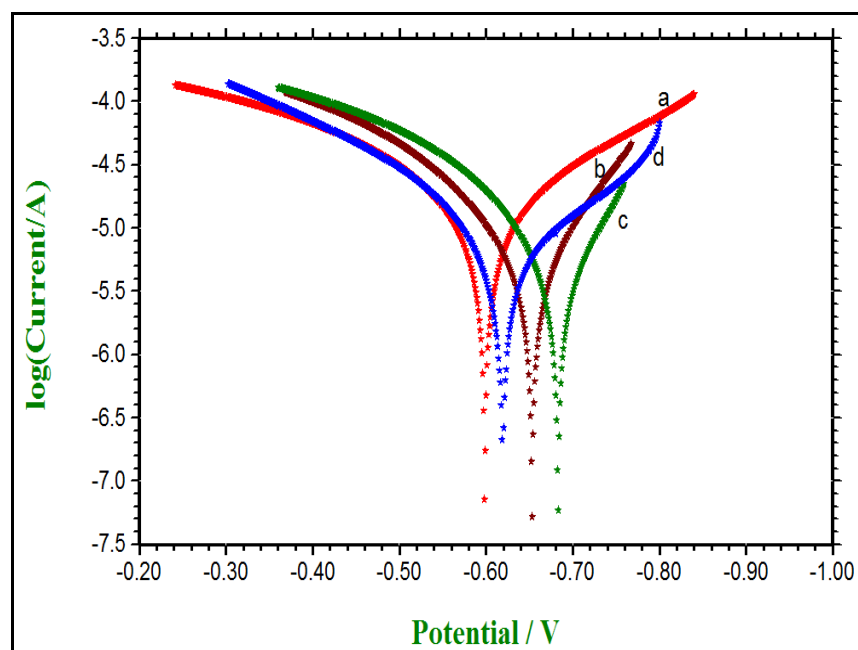
Fig.5. Potentiodynamic polarization curves of MS in a). 60 ppm Cl⁻ b). 600 ppm SG c). 50 ppm Ni²⁺ b). 60 ppm Cl⁻ + 50 ppm Ni²⁺ + 200 ppm PAA + 600 ppm SG

This shows that the formulation functions as a cathodic inhibitor controlling both anodic and cathodic processes but more predominantly cathodic process. This suggests, indicate that protective film is formed on the metal surface.

Table.2. Corrosion parameters of mild steel immersed in the absence and presence of inhibitor obtained from potentiodynamic polarization studies

Concentration (ppm)			Tafel parameters				IE_P (%)
PAA	Ni²⁺	SG	E_{corr} (mV/SCE)	I_{corr} ($\mu A/cm^2$)	β_a (mV/dec)	β_c (mV/dec)	
0	0	0	-598	129.0	192	198	--
0	0	600	-639	114.2	166	187	--
0	50	0	-670	107.9	153	186	--
200	50	600	-619	16.8	183	176	87

3.2.2. Electrochemical Impedance Studies

Nyquist plots for mild steel immersed in 60 ppm of Cl⁻ solution at pH 7 in the absence and presence of formulations are shown in Fig.6. The impedance parameters, charge transfer resistance (R_{ct}), Double layer capacitance (C_{dl}) from the Nyquist plot values are shown in Table 3. When mild steel is immersed in 60 ppm Cl⁻ medium the R_{ct} value is found to be 112 (Ω cm²). The C_{dl} value is 25.00 ($\mu F/cm^2$). When 600 ppm SG to of 200 ppm PAA and 50 ppm Ni²⁺ are added to 60 ppm Cl⁻ medium the R_{ct} value has increased from 112 to 693 (Ω cm²) and the C_{dl} value has decreased from 25.00 to 1.90 ($\mu F/cm^2$). The increase in Rct values and decrease in double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in 60 ppm Cl⁻ medium. This behavior means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film.
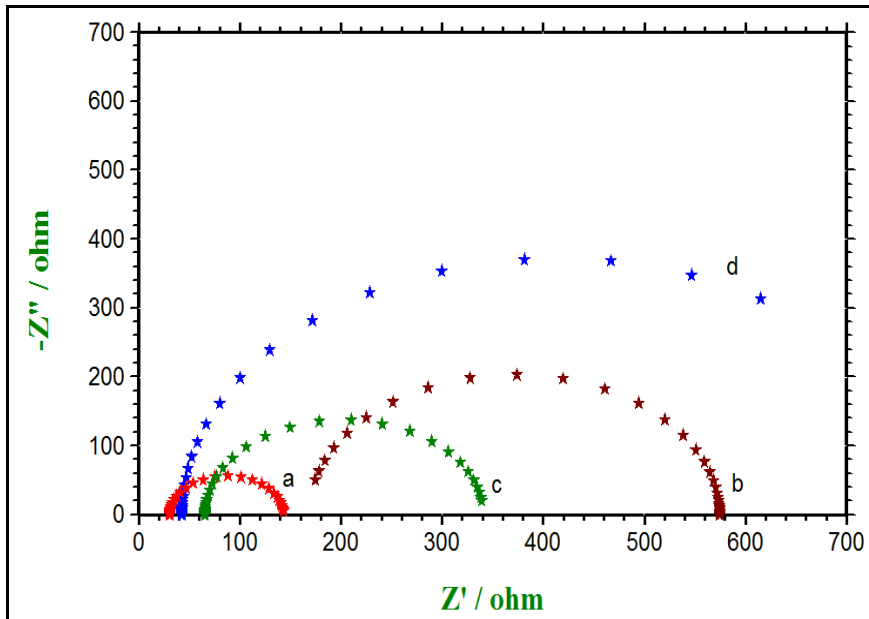
Fig.6. Electrochemical impedance curves of MS in a). 60 ppm Cl⁻ b). 600 ppm SG c). 50 ppm Ni²⁺ b). 60 ppm Cl⁻ + 50 ppm Ni²⁺ + 200 ppm PAA + 600 ppm SG

Table.3. Corrosion parameters of mild steel immersed in the absence and presence of inhibitor obtained from electrochemical impedance studies

Concentration (ppm)			Charge Transfer Resistance R_{ct} (Ω cm^2)	Double Layer Capacitance C_{dl} (μF/cm^2)	IE_{imp} (%)
PAA	**Ni²⁺**	**SG**			
0	0	0	112	25.00	--
0	0	600	410	2.30	--
0	50	0	325	3.18	--
200	50	600	693	1.90	83

3.3. Surface Studies

3.3.1. Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectrum of pure PAA is shown in Fig.7.(a). The C=O stretching vibration at 1719 cm^{-1} and the broad absorption peak at 3448 cm^{-1} shows OH stretching vibration. The FT-IR spectrum of pure SG is shown in Fig.7.(b). The C=O stretching frequency appears at 1603 cm^{-1} and OH stretching frequency appears at 3314 and 3432 cm^{-1} respectively. The FT-IR spectrum of the film formed on the surface of the mild steel after immersion in the solution consisting of 60 ppm of Cl⁻, 50 ppm of Ni²⁺, 200 ppm PAA and 600 ppm of SG is shown in Fig.7.(c). It is observed that the OH stretching frequency of PAA decreases from 3448 cm^{-1} to 3405 cm^{-1}. This shift is caused by the electron cloud density from the O atom to Fe²⁺. This suggests that the O atom of the polyacrylic acid is coordinate to Fe²⁺ resulting in the formation of Fe²⁺ - PAA, complex on the metal surface.
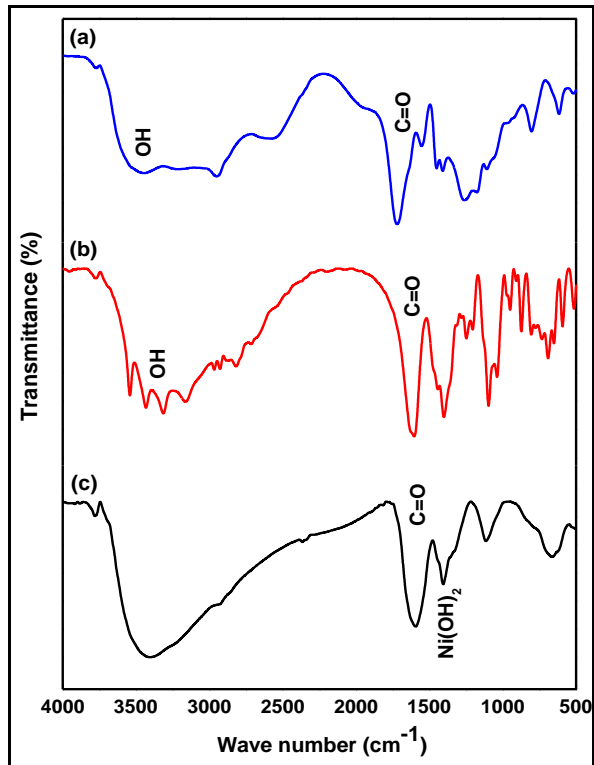
Fig.7. FT-IR Spectra of (a). Pure PAA (b). Pure SG (c). Surface film

The C=O stretching frequency of SG has decreased from 1603 cm^{-1} to 1593 cm^{-1}. This suggests that SG has coordinated with Fe^{2+} through an oxygen atom, resulting in the formation of Fe^{2+} - SG complex at the anodic sites on the metal surface. The peak at 1405 cm^{-1} is due to Ni(OH)$_2$ on the cathodic sites of the metal surface. Thus FT-IR spectral study leads to the conclusion that the protective film consists of Fe^{2+} - PAA complex, Fe^{2+} - SG complex and Ni(OH)$_2$.

3.3.2 Scanning Electron Microscopy (SEM)

SEM analysis provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extend of corrosion of mild steel. Fig.8.(a) show the metal surface immersion of 60 ppm Cl$^-$ solutions. This shows the roughness of the metal surface by the corrosive environment and there is formation of different forms of corrosion products.
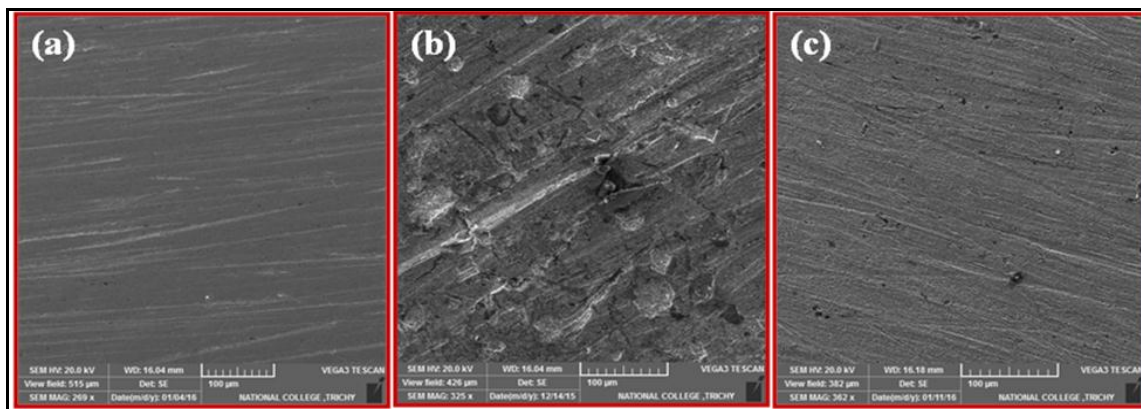

Fig.8. SEM images of MS: (a). polished mild steel (b). 60 ppm Cl$^-$ (c). 60ppm Cl$^-$ + 50 ppm Ni^{2+} + 200 ppm PAA + 600 ppm SG

Fig.8.(b) show the metal surface immersion of 600 ppm SG, 200 ppm PAA and 50 ppm Ni^{2+} are added to 60 ppm Cl^- medium gives metal surface incorporating into the passive film in order to block the active site present on the mild steel surface. Comparative examination of these images, clearly suggest that the surface of mild steel is smoothened to a very large extent in the presence of the combined inhibitor system. This smoothening might be due to the adsorption of the inhibitor molecules on it and thus the surface is fully covered.

3.3.3. Energy Dispersive X-ray Analysis (EDAX)

The composition of protective film formed on the mild steel surface was analyzed by EDAX as shown in Fig.9.(a,b,c). The EDAX spectrum of polished mild steel sample in Fig.4.10.(a) describes a unity of surface composition properties, in the absence of inhibitor molecules, mild steel immersed in 60 ppm Cl^- shown in Fig.9.(b), this observation prove that the apparent weakened surface area due to the increasing corrosion rate. Fig.9.(c) shows by adding 60 ppm Cl^-, 200 ppm PAA, 50 ppm Ni^{2+} and 600 ppm SG, the decrease of iron peak and appearance of Na, Cl, C, O and Ni peak was observed due to the formation of a strong protective film of the inhibitor molecules on the surface of mild steel sample. The action of inhibitor is related to adsorption and formation of a barrier film on the electrode surface.
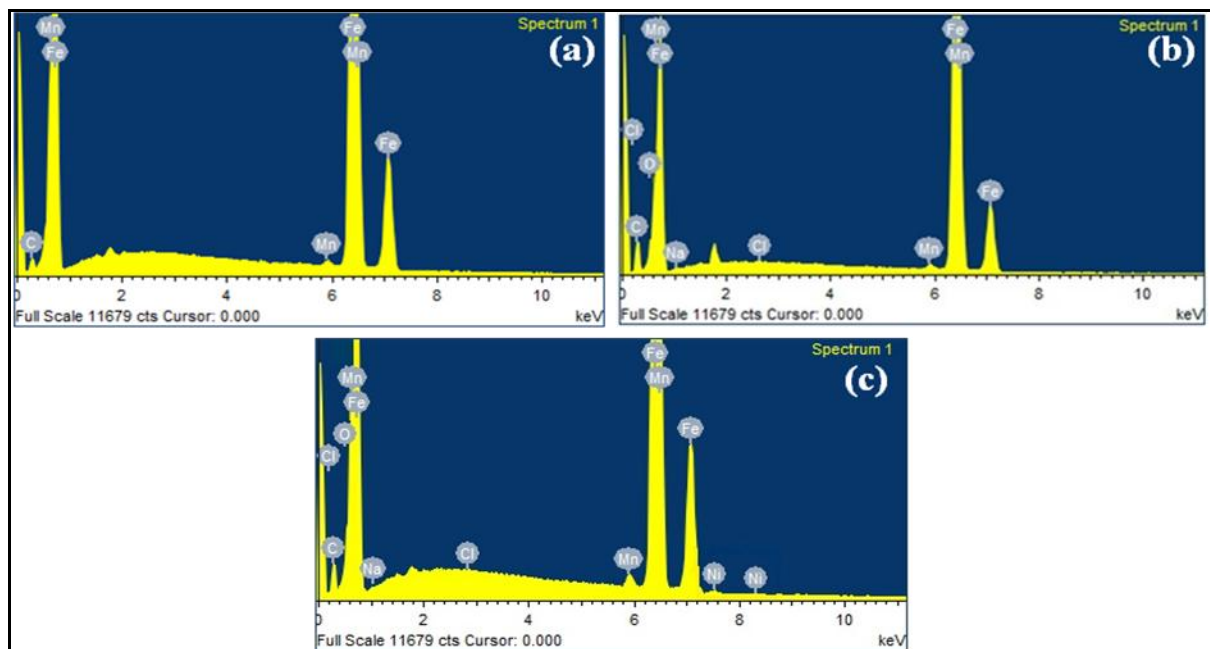

Fig.9. EDAX images of MS: (a). polished mild steel (b). 60ppm Cl^- solution (c). 60ppm Cl^- + 50 ppm Ni^{2+} + 200 ppm PAA + 600 ppm SG

3.3.4. Atomic Force Micrographs (AFM)

AFM is a dynamic tool to examine the surface morphology from nano to micro scale and has become a new choice to study the nature of protective layer formed over the surface of mild steel. The 2D & 3D AFM images of polished mild steel, 60 ppm Cl^- in mild steel and mild steel in 60 ppm Cl^- solution containing 50 ppm of Ni^{2+}, 200 ppm of PAA and 600 ppm of SG, respectively are shown in Fig.10.(a,b,c). As can be seen from the AFM images, the surface is very clear for polished mild steel (Fig.10.a). Whereas in mild steel immersed in 60 ppm Cl^- (Fig.10.b) the surface is severely damaged by the solution. In (Fig.10.c) the surface is protected from attack by the protective layer formed by the inhibitor molecules. From the results, it is clear that, the inhibition of mild steel corrosion in inhibitor is mainly due to the formation of a protective layer by adsorption of inhibitor molecules over the surface of mild steel. AFM data for mild steel is given in Table.4.
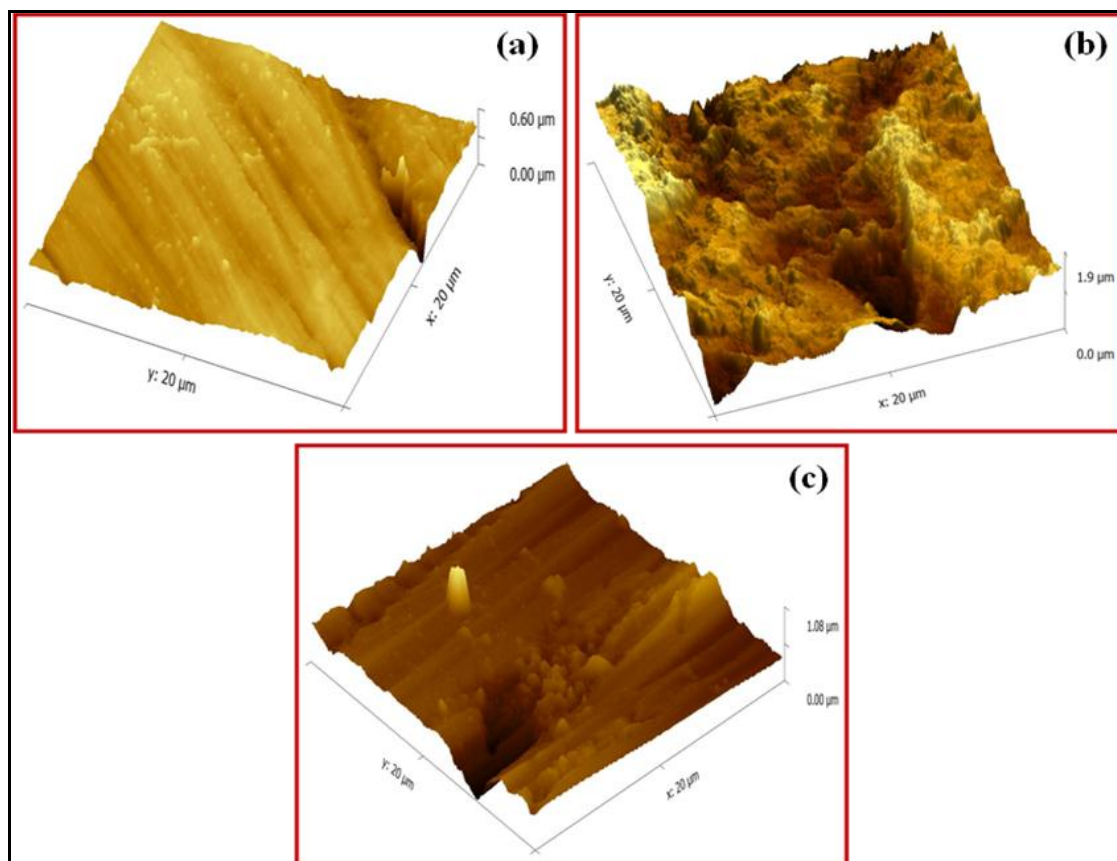
Fig.10. 2D & 3D AFM images of MS: (a). Polished mild steel (b). 60 ppm Cl⁻ (c). 60ppm Cl⁻ + 50 ppm Ni²⁺ + 200 ppm PAA + 600 ppm SG

Table.4. AFM parameters in different environments

Environment	Average Roughness (nm)	Root-mean-square Roughness (nm)	Maximum peak-to valley height (nm)
a). Polished mild steel	26	36	215
b). 60 ppm Cl⁻	218	279	1901
c). 60 ppm Cl⁻ + 50 ppm Ni²⁺ + 200 ppm PAA + 600 ppm SG	76	98	650

4. Mechanism of protection

In order to explain all the experimental results, the following mechanism of corrosion inhibition can be proposed. Mild steel undergoes initial corrosion to form Fe^{2+} ions at anodic sites:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

(5)

And the cathodic reaction is:

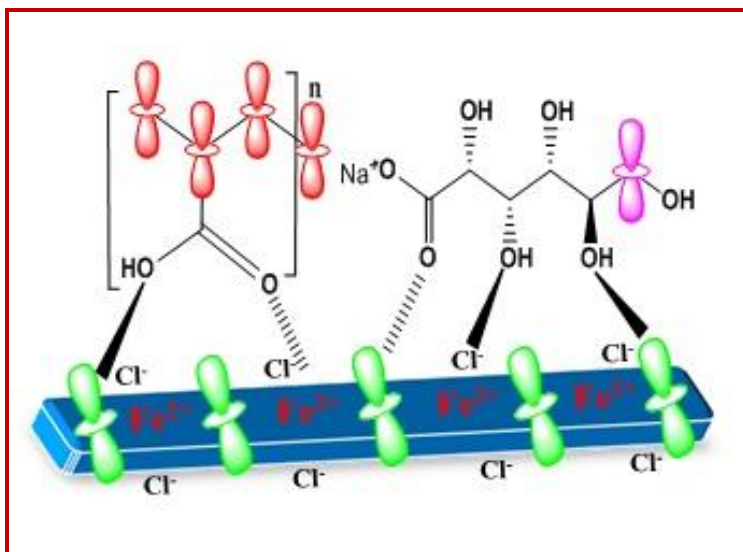$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

(6)

Fig.11. Pictorial representation of mechanism of adsorption of inhibitors on MS surface

When the environment containing 60 ppm Cl^- ions 50ppm Ni^{2+}, 200 ppm PAA, 600 ppm SG was prepared, a [Ni^{2+}-PAA-SG] complex was formed in the solution. Besides this complex, the presence of free PAA, SG and Ni^{2+} ions. While the metal was immersed in this environment, the [Ni^{2+}-PAA-SG] complex diffused from the bulk of the solution onto the surface of the metal and further complexes with Fe^{2+} ions available due to initial corrosion. Free PAA and SG molecules diffuse from the bulk of the solution to the metal surface and form [Fe^{2+}-PAA-SG] complexes. These complexes fill the pores of the film formed on the surface and make it productive.

$$[Ni^{2+} - PAA - SG] + Fe^{2+} \longrightarrow [Fe^{2+} - PAA - SG] + Ni^{2+} \tag{7}$$
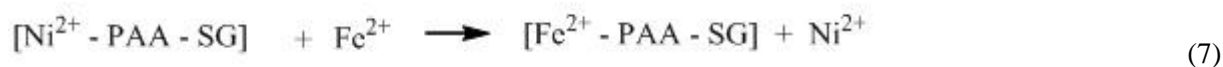
Free Ni^{2+} ions diffuse from the bulk of the solution to the metal surface and form $Ni(OH)_2$ at the local cathodic sites.

$$Ni^{2+} + 2OH^- \longrightarrow Ni(OH)_2 \tag{8}$$

Thus, PAA, Ni^{2+}, and SG play a very important role in the controlling corrosion through the formation of a protective film on the metal surface.

5. Conclusion

The ternary inhibitor formulation consisting 200 ppm PAA, 50 ppm Ni^{2+} ion and 600 ppm SG afforded an inhibition efficiency of 89% was achieved. This synergistic ternary inhibitor formulation is effective in the pH range 7.0. Further, this ternary inhibitor combination acts as a mixed inhibitor, predominantly cathodic in nature. The corrosion inhibition is established due to the formation of an inhibiting film, which has a very high charge transfer resistance. FT-IR, SEM, EDAX and AFM provide a pictorial representation on the nature of surface film formed in the absence and presence of inhibitor system. The protective film consist of [Fe^{2+}- PAA - SG] complex, small amounts of iron oxide, hydroxide and nickel hydroxide.

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