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CORROSION INHIBITION OF MILD STEEL BY USING MIXED LIGAND METAL COMPLEXES

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ABSTRACT

Chiral mixed ligand (CML) metal complexes of the type [M(PMINAP) (aa)·$2H_2O$], where M is Ni (II), PMINAP is sodium salt of p-methoxyisonitrosoacetophenone and aa is chiral amino acid have been tested for inhibitive action on corrosion of mild steel in 1 M HCl. The inhibition was investigated by using weight loss, corrosion potential, potentiodynamic polarization and surface analytical techniques. The change in electrochemical parameters observed by variation on inhibitors concentration 100 ppm, 200 ppm and 500 ppm, favours its adsorption. The compounds influence the anodic dissolution of mild steel as well as hydrogen evolution reaction in 1 M HCl. Morphology of the mild steel specimens was examined using scanning electron microscopy in presence and absence of inhibitor. The inhibitions were due to adsorption of complexes on metal surface. Mechanism of adsorption of CML Ni (II) complexes on the surface of mild steel is proposed for its inhibition behavior. The adsorption characteristics of the inhibitor were approximated by Langmuir adsorption isotherm.

Key words: CML Ni (II) complexes, Mild steel, Inhibitors, Electrochemical techniques, Scanning electron microscopy.

INTRODUCTION

Corrosion is the destruction or deterioration of a material because of reaction with its environment, which is an irreversible interfacial reaction resulting in consumption of the material or dissolution into the component of the enviornment[1]. Corrosion of the metal is generally electrochemical in nature. Corrosion touches all-inside and outside the home, on the road, on the sea, in the plant and in aerospace vehicles. Total annual cost of floods, hurricanes, tornadoes, fires, lightning and earthquakes are less than the cost of corrosion[2].

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Mild steel is the most widely used engineering material in transportation, chemical processing industries, petroleum production and refining, pipeline industries, mining, marine applications, nuclear power and fossil fuel power plant, constructions and metal processing equipments[3]. Corrosion failure can disrupt production or cause unintended release of chemicals into the environment. Acid solutions are generally used for the removal of rust and scale in industrial processes.

Hydrochloric acid was widely used in the pickling of steel and ferrous alloys. During the course of pickling there is the danger that metal dissolution from already cleaned metal surface will occur after the removal of the oxides, scale or other coatings. This involves the loss of metals as well as more acid consumption. The mild steel corrosion also involves formation of nascent hydrogen, which gets dissolved in metal in atomic form. That gives rise to decrease in the ductility of metal known as pickling brittleness.

Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of construction. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations, or in process solutions containing appreciable amounts of hydrochloric acid. This acid is very corrosive to most common metals and alloys.

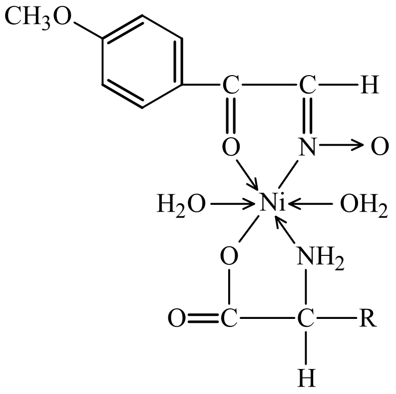
Inhibitor is a substance that, when added in small concentration decrease the corrosion rate. Inhibitor added to the acid to prevent the disadvantages associated with the metal corrosion in pickling[4]. Many compounds are used to inhibit mild steel corrosion in acid solutions[5-9]. The compounds containing heteroatom such as nitrogen, sulfur, phosphorous, oxygen etc. and aromatic ring, heterocyclic ring, double bond, triple bond in their structure serves as good corrosion inhibitors of metals with great effectiveness especially in aggressive acidic enviornment[10-12]. Compounds containing more than one heteroatom like nitrogen and sulfur in their structure serves as excellent corrosion inhibitor than those containing nitrogen and sulfur alone[13].

Rhodanine azosulpha and some antibacterial compounds have been reported[14,15] as efficient corrosion inhibitors in acidic media. The inhibitive capabilities of antifungal drugs clotrimazole and fluconazole on corrosion of aluminum in acid has been reported[16]. Some quinoline derivatives have been found effective corrosion inhibitor for mild steel in acid medium[17].

In continuation to our studies on chiral mixed ligand Ni(II) complexes, the present work deals with inhibition property of the complexes towards corrosion of mild steel in 1 M hydrochloric acid.

EXPERIMENTAL

Mild steel coupons having composition weight percentage (C-0.16%, Si-0.10%, Mn-0.40%, P-0.013%, S-0.02% and remaining as iron) have been used for electrochemical polarization and weight loss studies. Mild steel specimens coupons of 1.0 cm × 3.0 cm × 0.025 cm were washed with soap solution, rinsed with doubled distilled water, degreased with acetone and finally dried. Then surface of mild steel coupons were polished successively by different grades of metallographic emery papers 1/0, 2/0, 3/0 and 4/0 obtained from Sianor, Switzerland, so as to get the surface free from scratch and other apparent defects. The polished samples repeatedly washed with soap solution, rinsed with doubled distilled water, degreased with acetone and finally dried. The acid solutions used were made from AR grade HCl obtained from Merck chemicals. 1 M HCl solution was prepared in double distilled water. All the chiral mixed ligand nickel (II) complexes having different concentrations 100 ppm, 200 ppm, and 500 ppm were prepared in 1 M HCl solution as the corrosion inhibitor. The chemical structure of CML Ni (II) complexes is shown in Fig. 1.



R = (CH_3)	(Ala)
R = $CH\ (CH_3)_2$	(Val)
R = $CH_2 - CH\ (CH_3)_2$	(Leu)
R = $(CH_2)_2S - CH_3$	(Met)
R = $CH_2 - C_6H_5$	(Phe)

Fig. 1: Chemical structure of the CML Ni (II) complexes

Weight loss measurements

Weight loss measurements were carried out in a glass vessel with 100 mL of 1 M HCl solution with and without 100 ppm, 200 ppm and 500 ppm concentration of inhibitors. The immersion time for weight loss was 24 h at 30 ± 1°C. After immersion the coupons were withdrawn, rinsed with double distilled water, washed with acetone, dried and weighed. The experiment was carried out in duplicate and the average value of weight loss was noted.

Electrochemical measurements

Electrochemical measurements were carried out by means of impendence equipment, Electrochemical Measurement system, DC 105, containing software of DC corrosion techniques from M/s Gamry Instruments Inc., (No. 23-25) 734, Louis Drive, Warminster, PA-18974, USA has been used for performing corrosion potential and polarization experiments. Electrochemical studies were performed in three electrode, saturated calomel electrode as reference electrode, spectroscopic grade graphite rod as counter electrode and Pyrex glass vessel with mild steel coupon as working electrode.

Electrochemical measurements were carried out on the steady state open circuit potential (OCP). The variation of corrosion potential of mild steel in 1 M HCl was measured against saturated calomel electrode in absence and presence of various concentrations of inhibitors. The time dependence of open circuit potential for different experiments was recorded for one hour exposure period. The same sample was used for potentiodynamic polarization (PD) experiments. Potential was swept between - 0.5 to + 0.5 V at the scan rate of 5 mV/s. Different electrochemical results obtained from potentiodynamic polarization. The polarization studies were carried out in unstirred solutions.

The electrochemical polarization studies (corrosion potential and potentiodynamic polarization) mild steel specimens were polished as described earlier leaving a working area 1 cm^2 of the flag and a small portion at the tip for providing electrical contact. Rest of the surface was coated with enamel lacquer including side edges. The test specimen was connected to the working electrode holder through the tip of the tail. About 50 mL of the corrosive medium was taken in a mini corrosion testing electrochemical cell. This volume was appropriate to permit desired immersion of electrodes. The surface treatments were carried out immediately before each experiment of corrosion test.

Scanning electron microscopy analysis

The surface morphology of corrosion product on mild steel sample after 24 h immersion in 1 M HCl in the absence and presence of 500 ppm of representative complex [Ni (PMINAP) (Ala)$\cdot 2H_2O$] was studied by SEM. The accelerating voltage for SEM pictures was 10.0 KV.

RESULTS AND DISCUSSION

Weight loss measurement

Weight loss data of mild steel in 1 M HCl in the absence and presence of 100 ppm, 200 ppm and 500 ppm concentration of inhibitors were obtained and are given in Table 1. Inhibition efficiencies (IE %) were calculated according to previous report[18].

$$(\text{IE }\%) = (W_o - W_{corr}) \times 100/W_o$$

Where W_{corr} and W_o are the weight loss of mild steel in the presence and absence of inhibitor, respectively. The results show that the inhibition efficiencies increase with increasing inhibitor concentration. The results obtained from the weight loss measurements were in good agreement with those obtained from the electrochemical methods.

Table 1: Weight loss data for inhibition of corrosion on mild steel exposed to 1 M HCl with different concentration of CML Ni(II) complexes

Inhibitor	Conc. (ppm)	Weight loss (mg)	Surface coverage (θ)	Inhibition efficiency (IE %)
Blank	-	286	-	-
[Ni(PMINAP)(Ala)·2H_2O]	100	86	0.6993	69.93
	200	76	0.7342	73.42
	500	70	0.7552	75.52
[Ni(PMINAP)(Val)·2H_2O]	100	64	0.7762	77.62
	200	60	0.7902	79.02
	500	55	0.8076	80.76
[Ni(PMINAP)(Leu)·2H_2O]	100	80	0.7202	72.02
	200	74	0.7412	74.12
	500	57	0.8006	80.06
[Ni(PMINAP)(Met)·2H_2O]	100	72	0.7482	74.82
	200	45	0.8426	84.26
	500	35	0.8776	87.76
[Ni(PMINAP)(Phe)·2H_2O]	100	79	0.7237	72.37
	200	65	0.7727	77.27
	500	53	0.8146	81.46

Adsorption isotherm

Corrosion inhibition of metal may involve either physisorption or chemisorption of the inhibitors to the metal surface and subsequent interference with either cathodic or anodic or both reaction occurring at the adsorption sites. The electrostatic attraction between the charged hydrophilic groups and the charge active centers on the metal surface leads to physisorption. The existing data show that most of the inhibitors are adsorbed on the metal surface by displacing water molecules on the surface and forming a compact barrier film[19]. The availability of non bonded (lone pair) and *p*-electrons in alkenes, alkynes and aromatic rings in inhibitor molecules may involve in chemisorption. The strength of the coordinate covalent bond thus formed depends upon the electron density and polarizability of the donor atom of the functional group[20]. Chemical adsorption has free energy of adsorption and activation energy higher than physical adsorption and hence, usually it is irreversible.

The surface coverage values θ (defined as $\theta = \text{IE}\ \% /100$) increases with increasing inhibitor concentration as a result of adsorption of more inhibitor molecules on the mild steel surface. If molecular adsorption at the metal/solution interface is the mechanism through which the corrosion inhibition occurs, several adsorption isotherm can be tested. The simplest, being the Langmuir isotherm based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not. Under these circumstances, the proportionality between surface coverage θ and bulk concentration C of the adsorbing compound is as follows[21].

$$KC = \theta/(1- \theta)$$

where K is the equilibrium constant. It is convenient to rearrange the equation, yielding:

$$C/\theta = C + 1/K$$

The plot of log $(\theta/1- \theta)$ against the log C gave straight lines with the slope of unit (Fig. 2), which indicates that the adsorption of these compounds on the mild steel surface obeys the Langmuir isotherm. Adsorption parameters of all inhibitors are mentioned in Table 2.

Table 2: Adsorption parameters of CML Ni(II) Complexes

Inhibitor	C	log C	θ	1-θ	θ/(1- θ)	log θ/(1- θ)
[Ni(PMINAP)(Ala)·$2H_2O$]	0.000100	-4.0000	0.6993	0.3007	2.3256	0.3665
	0.000200	-3.6989	0.7342	0.2658	2.7622	0.4413
	0.000500	-3.3010	0.7552	0.2448	3.0850	0.4893
[Ni(PMINAP)(Val)·$2H_2O$]	0.000100	-4.0000	0.7762	0.2238	3.4683	0.5401
	0.000200	-3.6989	0.7902	0.2098	3.7664	0.5760
	0.000500	-3.3010	0.8076	0.1924	4.1975	0.6230
[Ni(PMINAP)(Leu)·$2H_2O$]	0.000100	-4.0000	0.7202	0.2798	2.5740	0.4106
	0.000200	-3.6989	0.7412	0.2588	2.8640	0.4570
	0.000500	-3.3010	0.8006	0.1994	4.0150	0.6037
[Ni(PMINAP)(Met)·$2H_2O$]	0.000100	-4.0000	0.7482	0.2518	2.9714	0.4730
	0.000200	-3.6989	0.8426	0.1574	5.3532	0.7286
	0.000500	-3.3010	0.8776	0.1224	7.1700	0.8555
[Ni(PMINAP)(Phe)·$2H_2O$]	0.000100	-4.0000	0.7237	0.2763	2.6193	0.4182
	0.000200	-3.6989	0.7727	0.2273	3.3995	0.5314
	0.000500	-3.3010	0.8146	0.1854	4.3937	0.6428

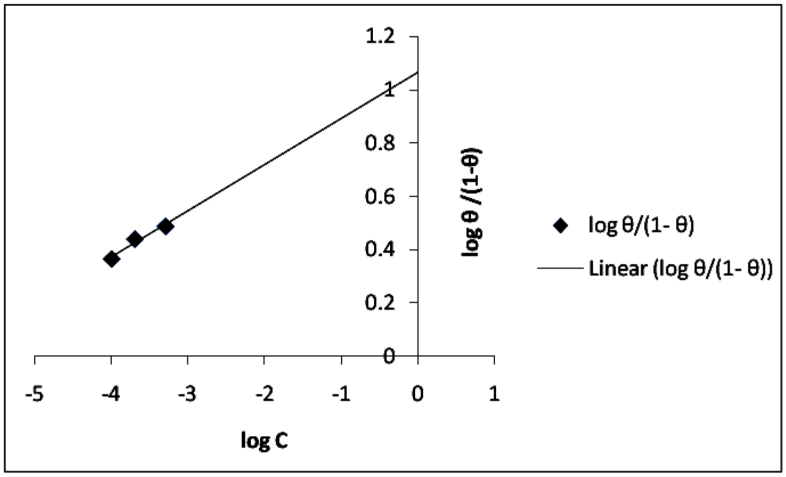


Fig. 2: Adsorption isotherm of [Ni(PMINAP(Ala)·$2H_2O$] complex

Open circuit potential measurements (OCP)

The electrochemical behavior of mild steel in 1 M HCl was studied by monitoring change in corrosion potential (E_{corr}) with time. The change in OCP of mild steel in absence and presence of 100 ppm, 200 ppm and 500 ppm concentrations of inhibitor [Ni (PMINAP) (Ala.) $2H_2O$] as representative complex in 1 M HCl is shown in Fig. 3.

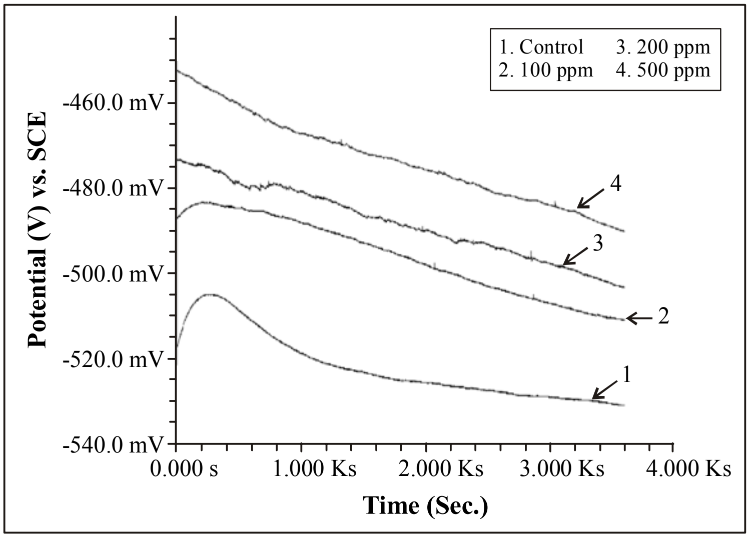


Fig. 3: Corrosion potentential of mild steel exposed to 1 M HCl solution with different concentrations of complex [Ni(PMINAP)(Ala)·$2H_2O$] in ppm

The change in OCP of mild steel in absence and presence of inhibitors were measured for period of one hour with sample period of one data per second. The potential attains steady state after exposure of 0.9 hour. The steady state potential is in equilibrium state at which $I_{ox.}$ is equal to the I_{red}. It has been observed that OCP of mild steel from moment of immersion in 1 M HCl tends towards more negative value in absence of inhibitor. This shows corrosiveness of medium, which is due to breakdown of pre-immersion, air formed oxide film on the metal surface. In the presence of various concentrations of inhibitors the steady state potential of mild steel shifts more toward positive value. This is due to adsorption of inhibitor on metal surface resulting in passivation of metal.

The influence of various concentration 100 ppm, 200 ppm and 500 ppm of representative [Ni(PMINAP)(Ala)·$2H_2O$] complex on OCP of mild steel in 1 M HCl is given in Fig. 3 show that at 500 ppm concentration the complex exhibit good inhibition performance. All CML Ni (II) complexes at 500 ppm concentration shown good inhibition efficiency.

Potentiodynamic polarization measurement

Potentiodynamic polarization curves for mild steel in 1 M HCl solution in the absence and presence of various concentration 100 ppm, 200 ppm, and 500 ppm of representative [Ni(PMINAP)(Ala)·2H_2O] complex at 30°C is shown in Fig. 4.

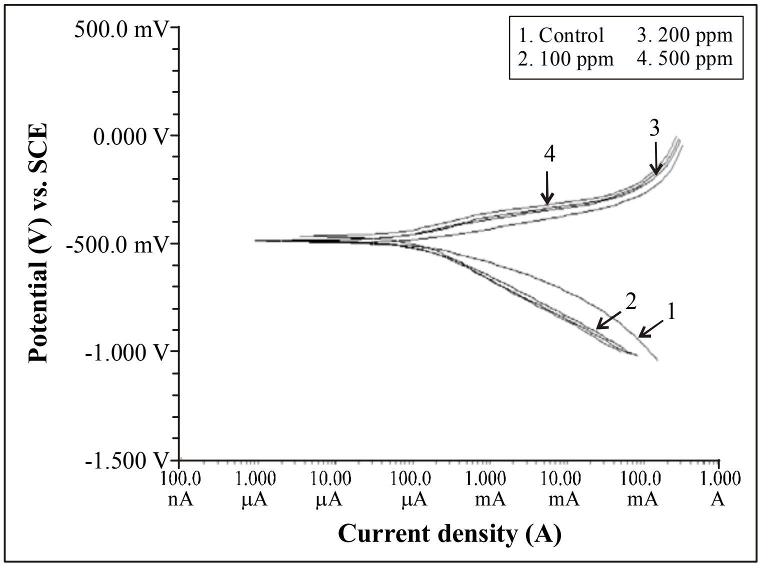


Fig. 4: Potentiodynamic polarization curve of mild steel exposed to 1 M HCl with different concentrations of complex [Ni(PMINAP)(Ala)·2H_2O] in ppm

The corrosion inhibition efficiency was calculated by using the following Equation:

$$\text{Inhibition efficiency (IE\%)} = 100\ (i_o - i)/i_o$$

Where i_o and i are the corrosion densities in the absence and presence of inhibitor in the solution, respectively. Various corrosion parameters such as corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (βa, βc), the corrosion current density and the inhibition efficiency (IE%) are given in Table 3.

The experimental results derived from polarization curves shown that in the presence of these compounds I_{corr} decreases significantly at all of the studied concentrations. The presence of CML nickel (II) complexes resulted in a slight shift of the corrosion potential towards the active direction in comparison to the result obtained in the absence of the inhibitor. This phenomenon may be due to the existence of a phenyl ring having high electron density[22,23]. Among the CML nickel (II) complexes of methionine complex shows maximum inhibition efficiency of 88.89% at 500 ppm, than other complexes, which may be attributed due to the presence of sulphur in its structure.

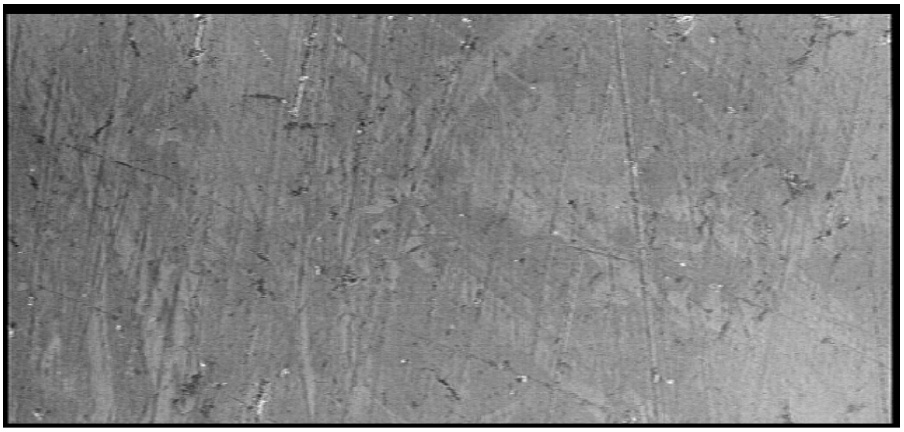
Table 3: Electrochemical parameters for inhibition of corrosion of mild steel exposed to 1 M HCl with different concentration of CML Ni(II) complexes.

Conc. of complex (ppm)	B_a (V/dec.)	B_c (V/dec.)	$I_{corr.}$ (μAcm^{-2})	$E_{corr.}$ (mV)	$C_{orr.}$ rate (mpy)	Inhibition efficiency (%)
Control	99.10e-3	167.4e-3	262.0	-492.0	119.9	-
[Ni(PMINAP)(Ala)·$2H_2O$]						
100	81.10e-3	168.7e-3	76.20	-484.0	34.82	70.92
200	83.00e-3	170.4e-3	67.90	-482.0	31.02	74.08
500	79.40e-3	176.2e-3	61.40	-462.0	28.04	76.56
[Ni(PMINAP)(Val)·$2H_2O$]						
100	82.70e-3	159.6e-3	55.40	-506.0	25.32	78.85
200	66.00e-3	174.4e-3	50.30	-486.0	22.97	80.80
500	58.90e-3	170.5e-3	47.30	-471.0	21.61	58.90
[Ni(PMINAP)(Leu)·$2H_2O$]						
100	118.6e-3	167.8e-3	70.90	-524.0	32.41	72.94
200	133.7e-3	171.8e-3	66.30	-529.0	30.30	74.70
500	129.6e-3	177.2e-3	49.60	-519.0	22.67	81.07
[Ni(PMINAP)(Met)·$2H_2O$]						
100	62.70e-3	165.9e-3	63.80	-485.0	29.15	75.65
200	72.50e-3	157.6e-3	37.50	-508.0	17.11	85.69
500	64.10e-3	162.8e-3	29.10	-485.0	13.31	88.89
[Ni(PMINAP)(Phe)·$2H_2O$]						
100	73.40e-3	168.2e-3	69.80	-505.0	31.91	73.36
200	73.50e-3	172.3e-3	56.60	-503.0	25.88	78.40
500	74.00e-3	174.4e-3	44.60	-497.0	20.40	82.98

The unchanged Tafel slopes βa and βc in the presence of CML nickel (II) complexes is indicative that the inhibitor acted by merely blocking the reaction sites of the metal surface without changing the anodic and cathodic reaction mechanisms. The results demonstrate that the hydrogen reduction is inhibited and that the inhibition efficiency increases with inhibitor concentration. In the anodic region, the polarization curves of mild steel show that the addition of CML nickel (II) complexes decreases current densities in a wide range of potential. These results suggest that CML nickel (II) complexes act as a mixed-type inhibitor of the corrosion of mild steel in HCl medium. Similar behavior has already been reported for other compounds[24,25]. The results obtained from electrochemical measurements were further supported by SEM analysis.

Scanning electron microscopy (SEM)

SEM micrographs obtained from unexposed and exposed specimen coupons in 1 M HCl for 24 h in the absence and presence of 500 ppm [Ni(PMINAP)(Ala)·$2H_2O$] complex are shown in Fig. 5. The accelerating voltage for SEM scanning was 10 KV. It could be visualized from Figure 5b that the specimen surface was rougher and was strongly damaged in the absence of the inhibitor. Figure 5c shows SEM micrograph of the mild steel surface after immersion in 1 M HCl containing 500 ppm solution of complex [Ni(PMINAP) (Ala.)·$2H_2O$]. It could be observed that extent of damage to mild steel surface is very less, the rate of corrosion was reduced considerably in the presence of inhibitors, it revealed that there was a good protective film adsorbed on metal surface, which acted as a barrier and was responsible for the inhibition of corrosion.



(a)

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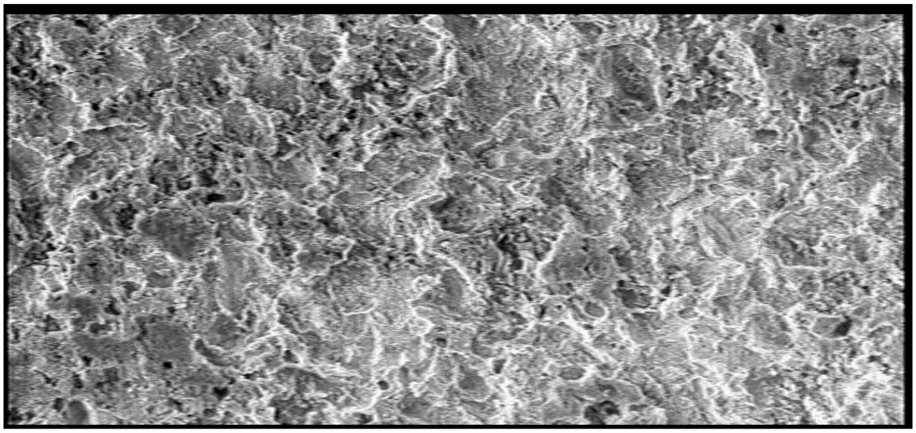
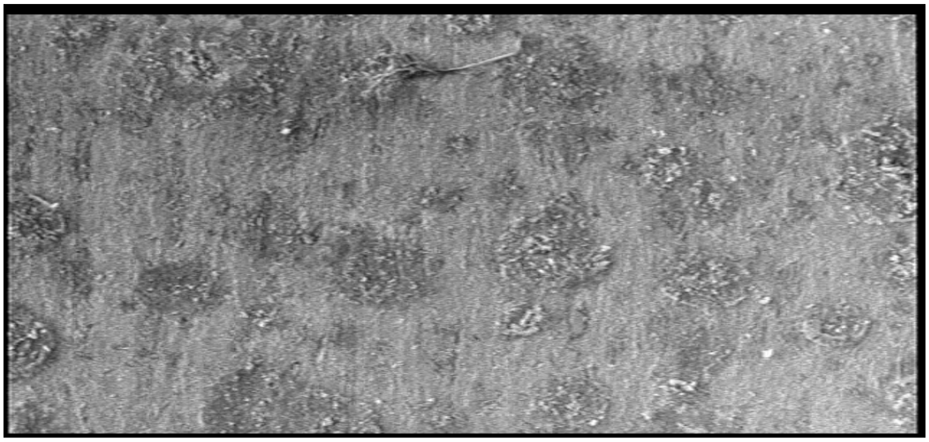


(b)



(c)

Fig. 5: SEM micrograph of mild steel samples (a) unexposed polished mild steel surface (b) after immersion in 1 M HCL solution in absence of inhibitor (c) after immersion in 1 M HCl solution in presence of 500 ppm complex of [Ni(PMINAP)(Ala)·2H_2O)]

Mechanism of corrosion inhibition

Electrochemical and weight loss methods have been employed to study the behavior of mild steel in acid media, in the presence of CML Ni(II) complexes. The increase of inhibition efficiency with increasing inhibitor concentration indicate that a higher coverage of inhibitor on the surface was obtained in a solution with higher concentration of inhibitor. The first stage in mechanism of corrosion inhibition in acid media is adsorption of inhibitor molecule on the metal surface[26]. In most inhibition studies, the formation of donor-accepter surface complexes between *p*-electrons of inhibitor and the vacant *d*-orbital of metal were postulated[6,27].

The process of adsorption is influenced by the nature and charge of the metal, chemical structure of inhibitor and the type of aggressive electrolyte. The zero charge potential (PZC) is the metal potential measured against the reference electrode at which the ionic double layer is absent at the electrode and the electrode is best able to adsorb substance dissolved in the electrolyte. The ability of an electrode to adsorb the molecule is reduced in the presence of potential difference at the ionic double layer. This is because the field pulls in water molecules having high electric constant, dislodging complex from the surface. Thus, the adsorption capacity of an electrode is a maximum close to the zero charge potential. The charge of the metal surface can be determined[28] from the potential of zero charge on the correlative scale (ψ_c) by the equation:

$$\psi_c = E_{corr} - E_{q=0}$$

where, $E_{q=0}$ is the potential of zero charge. However, value of E_{corr} obtained in HCl is -492 mV *versus* SCE[29]. The value of ψ_c in hydrochloric acid is positive and hence, the mild steel surface acquires positive charge. Accordingly, chloride ions (in HCl solution) are firstly adsorbed on the metal surface and consequently, the mild steel surface becomes negatively charged. Due to electrostatic attraction, the molecules of the complexes are adsorbed (physiosorption) and high inhibition is expected[30]. CML nickel (II) complexes get adsorbed on the mild steel surface through unshared pair of electrons present on metal chelates and shows higher efficiency in HCl solution.

Besides, electrostatic interaction, chemisorptions of these compounds is most probable through the vacant d-orbitals of iron which acts as an acceptor of electrons. Hence, d-p bonds are also formed by the overlap of vacant 3d-orbitals of Fe-atom with p-orbital electrons of donor atoms of the ligands in the complexes. Thus, CML nickel (II) complexes are strongly adsorbed on the mild steel surface.

CONCLUSION

The results proved that present CML nickel (II) complexes displayed good corrosion inhibition for mild steel in 1 M HCl solution. The complexes works as mixed type of inhibitor because both cathodic and anodic curves are shifted in positive direction. The percentage inhibition efficiency increases with increasing the concentration of the inhibitor. SEM examination of mild steel surface showed the presence of protective surface film formed on mild steel surface which inhibits metal dissolution in HCl and retards hydrogen evolution and supports to the mixed-type inhibitor activity.

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