SYNTHESIS, CHARACTERIZATION AND CORROSION INHIBITON EFFICIENCY OF 5-(2, 4-dicholoro-phenyl)-1-phenyl-4, 5-dihydro-1H-pyrazol-3-yl]-phenyl-amine (CPP): ON MILD STEEL IN1M HYDROCHLORIC ACID

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ABSTRACT *5-(2,4-dicholoro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl]-phenyl-amine(CPP) was synthesized and characterized by elemental analysis, FT-IR,[1]H-NMR, [13]C-NMR study.The corrosion inhibition properties of5-(2,4-dicholoro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl]-phenyl-amine(CPP)for mild steel corrosion in HCl solution were evaluated by electrochemical impedance spectroscopy (EIS), and Potentiodynamic polarization. The inhibition efficiencyincreased with the concentration of inhibitor based on weight loss measurement. The UV-Visible absorption spectra of the solution containing the inhibitor after the immersion of mild steel specimen indicate the formation of a CPP–Fe complex. Scanning electron microscope (SEM)and EDAXsclearly revealed that surface morphology of the organic compound adsorbed and formed as a protective layer on the mildsteel.*

Keywords: *Mild Steel, HCl,Potentiodynamic polarization, EDAX's*

1. Introduction:

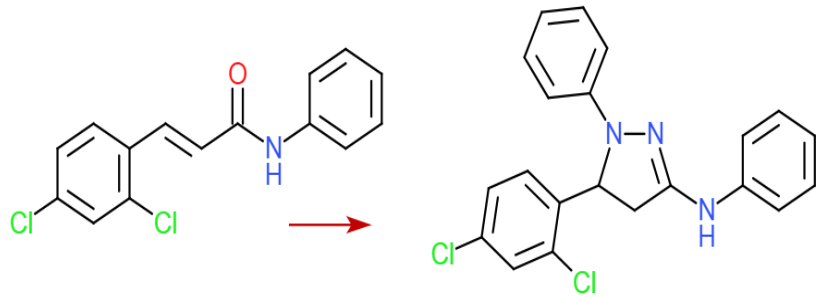
Corrosion is deterioration of metals due to chemical interaction with their environment. Mild steel is an alloy of carbon used in industries for the functional and aesthetic purpose. It is largely used in manufacturing applications such asmachinery, industries due to its workability without defect and economic feasibility [1, 2].Mild steel is corrosion resistance to the atmosphere owing to its mechanical property. Corrosion is the major problem forindustrial water supply and circulation system. Itis a continuous problem, often difficult to prevent completely. Protection against corrosion was carries out by adding inhibition in acidic medium [3-5]. Acid inhibitors organic compounds contain π-electrons, lone pair electrons, functional group mainly contain aromatic rings or heteroatoms like nitrogen, oxygen and sulfur which cause adsorption on the metal surface[6-13].Using hydrochloric acid solution, due to its dissolution and organic inhibitor which is protonated carries positive charge on the metal surface. The protonated organic inhibitor would be less adsorbed onto the metal surface leading to lower inhibition efficiencies due to the electrostatic interaction of positive charge.

The aim of the present work is study of corrosion protection of 5-(2,4-dicholoro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl]-phenyl-amine(CPP)on mild steel in 1.0 M HCl using chemical (weight loss) and electrochemical techniques (EIS, potentiodynamic polarization). SEM,EDAX Spectroscopic studied were also included to examine the changes in surface morphology and presence elements on mild steel surface in absence and presence of chalcone derivative. These factors favor the interaction of this corrosion inhibitor with the metal.

2. ExperimentalTechniques:

2.1. Synthesis of 5-(2,4-Dicholoro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl]-phenyl-amine(CPP):

The solution of 3-(2,4-dichloro-phenyl)-N-phenyl acrylamide (0.001 mol) was refluxed with phenyl hydrazine (0.001mol) in dry EtOH (30 ml) and catalytic amount of glacial acetic acid for at 80 ^{0}C for 8h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure, distillation. The residue obtained was recrystallized from EtOH giving brown solid. The yield of the product was 72%. The melting point of the solid was noted as 160^0 C.



3-(2,4-dichloro-phenyl)-N-phenyl acrylamide

5-(2,4-Dicholoro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl]-phenyl-amine

3. Analytical data for inhibitor;

Yield:84%,Mt.pt:126^{o}C, IR (KBr) cm-1: 3301(N-HStr), 1602(N-Hbend), 1442(C=CStr), 2923(C-H_{Str}), 1098(N-NStr), 868(C-Hdef), 1253(C=OStr). 1H NMR (DMSO) ppm: 0.879-0.826(-CH3), 1.755(-CH2), 6.8-8.0(PHENYL PROTON) 10.419(ALDEHYDE INDOLE).

4. Instrumentation:

The Melting point of the compounds was determined in Open Capillaries, using Eligo Digital melting point apparatus and expressed in degreeCelsius and the values were uncorrected. IR spectra of the compounds were recorded on Shimadzu 8201 Spectrophotometer using KBr and the values areexpressed in 4000-400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400 MHz Spectrophotometer using TMS as an internal standard and thevalues are expressed in δ ppm. All the solvents used were analytical grade. The purity of the compound was checked by TLC using silica gel plates.

5. Materials:

The mild steel specimen contain with a chemical composition of 0.26 % S, 0.13 % C, and rest iron (Fe).The specimen having dimension 1.0cm x4.0 x 0.2cm were polished to mirror finish .The mild steel is degrease with acetone and used for weight loss method.

6. Weight loss measurements:

Weight Loss method is probably the most widely used method of inhibition assessment [14, 17].The mild steel (MS) specimens were immersed in a 100ml beaker containing organic inhibitor with and without addition of different concentrations. All the aggressive acid solutions were open to air. After 2h the specimens were taken out, washed, dried, and weighed accurately. In order to getgood reproducibility experiments were carried out in triplicate. The average weight loss of three parallel MS sheetwas obtained. The inhibition efficient was calculated using the formula,

Inhibition Efficiency (IE):$100[1-(w_2-w_1)]$ %

Where w_1 is the weight loss value in the absence of inhibitor

andw_2 is the weight loss value in the presence of inhibitor.

7. Polarization measurements:

7.1. Electrochemical impedance spectroscopy:

The electrochemical measurements were carried out using CH1 ELECTROCHEMICAL WORKSTATION with impedance model 643, Austin, USA. Thecorrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). Aplatinum electrode was used as auxiliary electrode of surface area of 1 cm^2. The working electrode was mild steel. All potentials given in this study were referred to this reference electrode [18]. The working electrode was immersed intest solution for 30 minutes. The real part(Z') and the imaginary part (Z') of the cell impedance were measured in Ohms at various frequencies.AC impedance spectra were recorded with initials$E_{(v)}$ =0 V,high frequency limit was $1X10^5$Hz,low frequency limit was 1 Hz Amplitude=0.005v and quiet time t_q=2s.The valuesof charge transfer resistance Rt and double layer capacitance C_{dl} were calculated.

$C_{dl}=1/2\pi rR_1f_{max}$

Where f_{max} is maximum frequency.

8. Surface characterization analysis:

The mild specimens were immersed in different concentration of solution for 2hrs for various test.After 2hr themild steelspecimen weretaken out and dried. The film form layers on mild steel were examined by different surface analysis techniques.

Spectrophotometric measurement:

9. UV-Visible spectroscopy for surface analysis:

UV –Visible spectra were recorded in (Make: Perkin Elmer Model: Lambda 35 Range: 190nm to 1100nm) spectrophotometer.

10. FT-IR Spectroscopy methods:

FT-IR studies (Make: Perkin Elmer Model: Spectrum Two Range: 4000cm^{-1} to 400cm^{-1}) help to detect the chemical bond in the inhibitor. The film formed in the mild steel were removed carefully and mixed with KBr to form pallet then recorded.

11. Scanning Electron microscopy (SEM) analysis:

The surface of mild steel is examined for the morphological studies by SEManalysis. It is used to understand the surface morphology of the film with and without inhibitors in extent of corrosion of mild steel. The SEM micrographs of the surface are examined(VEGA3TESCAN).

12. Energydispersive Analysis of X-rays (EDAXs):

The element is present on themetal surface is examined by energy dispersive analysis of X-rays (EDAXs) the mild steel specimen with and without inhibitor solution for 2hrs .It is removed, dried and observed in EDAXs.It is detected by the EDAX's (Bruker).

13. Results and discussion:

13.1. Weight loss method:

The effect of concentration of corrosion inhibitor on the mild steel in 1M HCl was shown in table:1From the values the concentration is increases whereas inhibition efficiencyincreases.Theincrease in inhibition efficiently as due to the blocking effect on the surface of the metal by adsorption. It is due to presence of oxygenatom and double bond in corrosion inhibitor. This makes it surface film on mild steel.

TABLE 1: The mild steel immersed in a 1M HClwith and without inhibitor at various concentration and the inhibition efficiency (IE %) obtained Weight loss method.

S.NO	CONCENTRATION OF INHIBITOR	IE%	Θ(SURFACE COVERAGE)
1	10^{-3}M	83.33	0.8333
2	10^{-4}M	77.77	0.7777
3	10^{-5}M	72.22	0.7222
4	10^{-6}M	66.66	0.6666
5	10^{-7}M	61.11	0.6111

13.2.AC Impedance spectra:

AC impedance spectra have been used to confirm that protective layer formed on the metal surface. The AC Impedance spectra of mild steel immersed in 1M HCl with and without using corrosion inhibitor. From the figure 1.(Nyquist plots) and Figure 2(Bode plots),the following parameters are used for impedance spectra namely Charge transfer resistance(R_t)double layer capacitance(Cdl) and impedance lg(z/ohm) are given table3.if aprotective film formed over the mild steelsurface, then $R_t$value increases and the Cdl decreases.

Table 2: Polarization method containing corrosion parameters of mild steel in the presence and absence of corrosion inhibitor:

Systems	Ecorr(mV vs. SCE)	Icorr (A/cm^2)	ba(mv/dec)	bc(mv/dec)	LPR(Ω CM^2)
BLANK	-0.396	5.342e-003	6.281	3.487	8.3
10^{-3}M CPP+ 1M HCL	-0.453	1.438e-004	10.178	7.477	171.2

Table 3: The AC Impedance spectra of mild steel immersed in 1MHCl with and without using corrosion inhibitor.

Concentration	R_t,Ωcm^2	Cdl,Fcm^{-2}	Log($Zohm^{-1}$)
BLANK	13.710	$20.81X10^{-5}$	18.827
10^{-3}M CPP+1M HCL	25.269	$35.30X10^{-5}$	19.142

When mild steel is immersed in 1M HCl (blank solution), whereR_t value is 13.710, and Cdl value is 20.81X10^{-5}.When corrosion inhibitor is added, then the value becomes R_t value increased form13.710 to 25.269and the Cdl value decreases from 20.81X10^{-5}to35.30X10^{-5}. The impedance value increases from 18.827 to 19.142 .From the AC impedance spectra value reveals that the efficiency of corrosion inhibitor is high and protective film formed on mild steel surface.

Figure1: Nyquist plot:

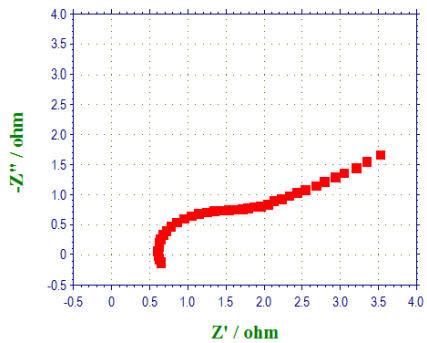


Figure:1(a)

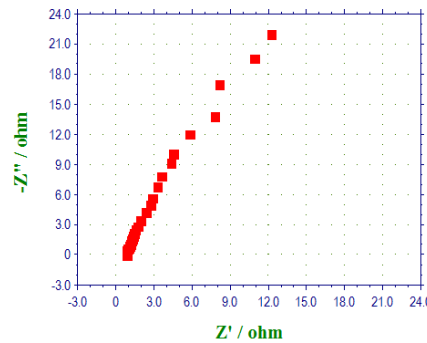


Figure:1(b)

Figure 1: AC Impedance spectra (Nyquist plots) of mild steel immersed in various test solutions)1(a) blanksolution, 1(b) Corrosion inhibitor solutionwith 1M HCl

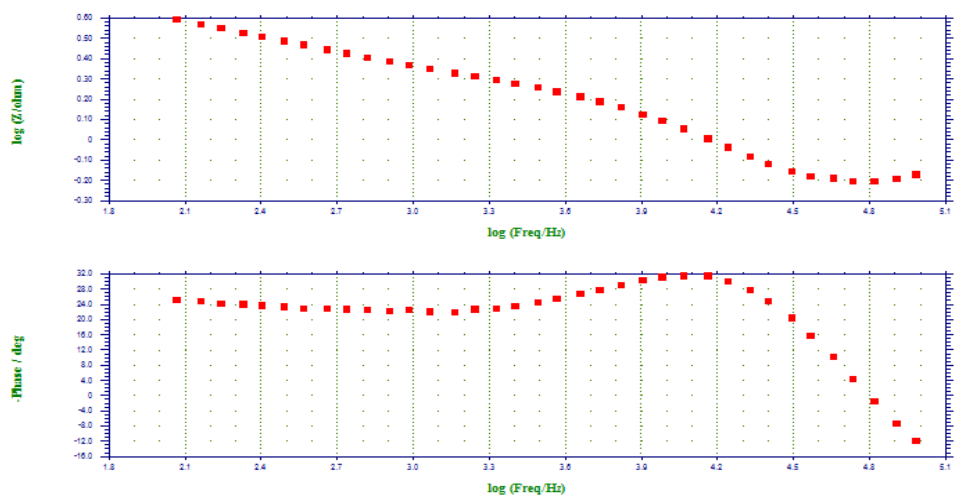


Figure 2: Bode plot:

Figure 2(a):AC Impedance spectra (Bode plots) of mild steel immersed in 1M HCl solution

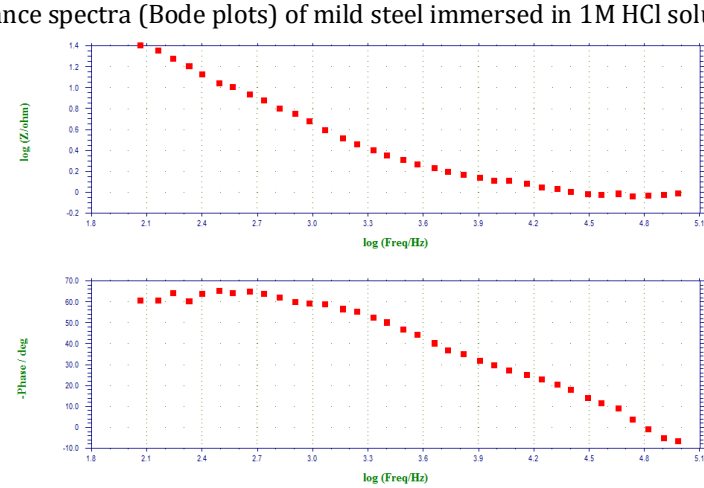


Figure 2(b):AC Impedance spectra (Bode plot) of mild steel immersed in corrosion inhibitor(CPP) solution.

13.3. UV Spectral Analysis:

From the figure:3(a) the UV absorption spectrum of the pure corrosion inhibitor.199.6,291.0,633.5,887.4and 1028.1 nm are the peak appears in the UV absorption spectra. From the figure:3(b) the new peak appears at 207.0, 292.3 and 663.2.The formation of corrosion inhibitor-Fe^{2+} ion formation confirm by increase intensity of peak.

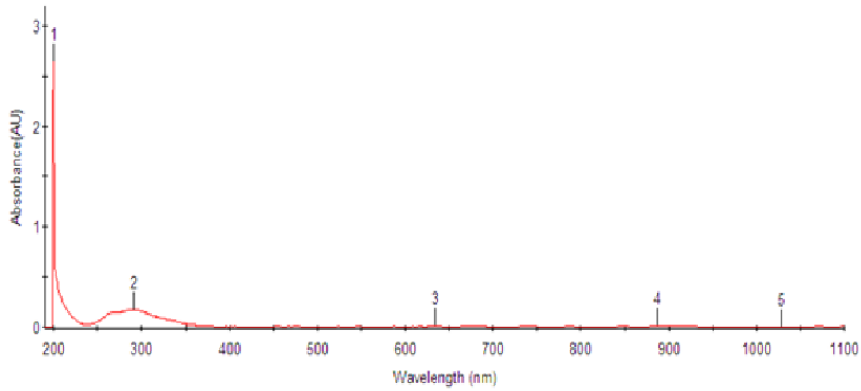


Figure 3(a): UV –absorption of spectrum of solution containing corrosion inhibitor (CPP).

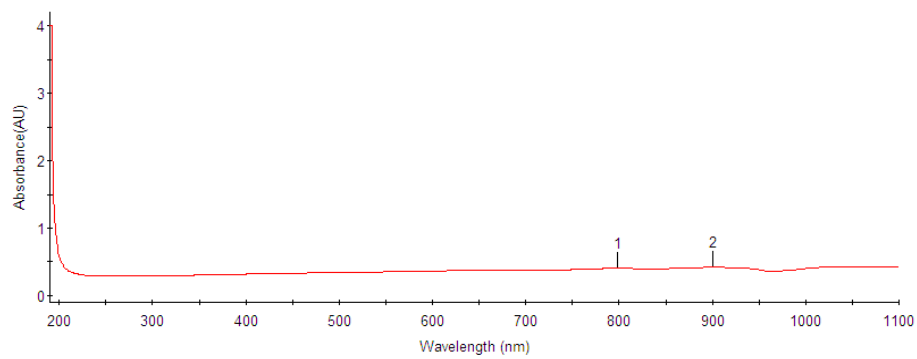


Figure 3(b): UV –absorption of spectrum of solution containing corrosion inhibitor-CPP-Fe^{2+} ion.

13.4. FT-IR Spectral analysis:

The FT-IR spectrum (KBr) of the protective film formed on the mild steel surface after immersion in a corrosion inhibitor for a period of 2hrs shown in figure 4(b).The N-H Stretchingfrequency has shifted from 3404.36cm^{-1} to3332.45cm^{-1}. The Aromatic C-H stretching frequency hasshifted from 2926.01 $cm^{-1}$to 2885cm^{-1}.TheAromatic C=C stretching frequency has shifted from 1442 cm^{-1} to1404 cm^{-1}.The addition peal obtained in the region of 3853.97 cm^{-1}due tocorrosioninhibitor-Fe^{2+} formation.

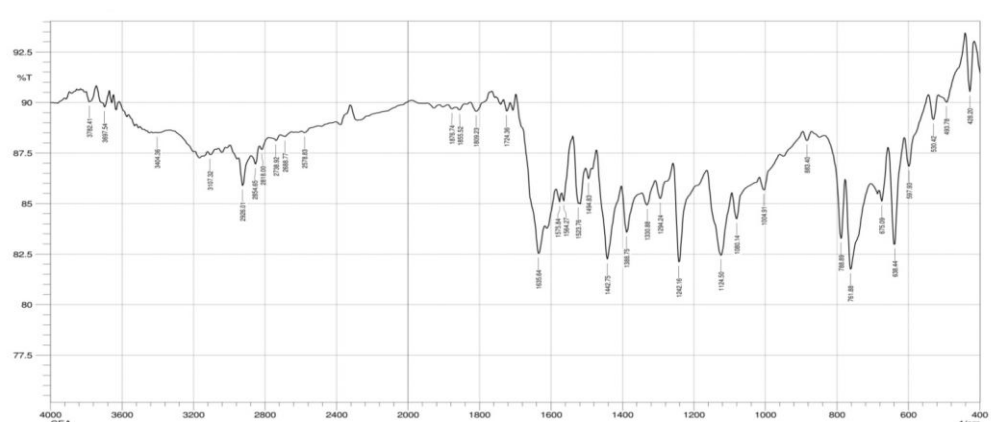


Figure 4(a):FTIR –spectra ofpure compound (CPP)

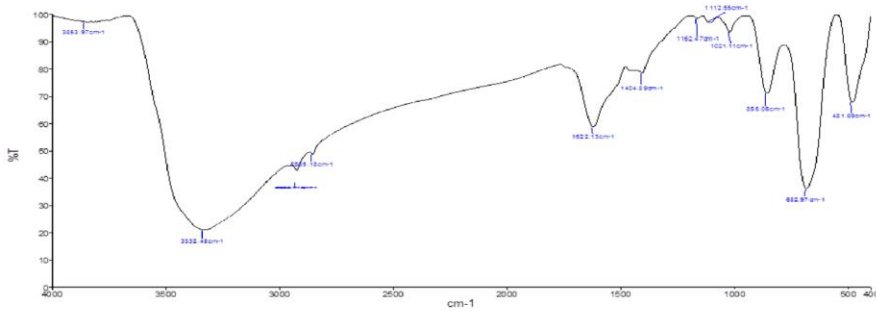


Figure 4(b): FTIR –Spectra of Protective film formed on mild steel surface containing corrosion inhibitor.

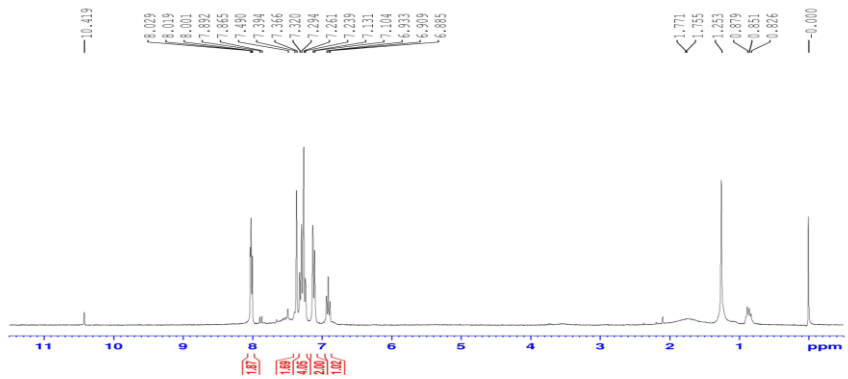


Figure 4(c):^{1}H-NMR –spectra of pure corrosion inhibitor (CPP)

13.5. Scanning electron microscope (SEM):

The metal specimen is immersed in the 1M HCl solution containing inhibitor for 2hrs.The specimen is taken out ,dried and observed under the investigation of SEM .The images of fresh metal is shown figure5(a). The metal surface has been damaged due to metal dissolution in 1M HCl is shown figure 5(b).The metal surface dipped in acid containing inhibitor is shown figure5(c).

The SEM images of smooth metal surface infigure 5(a) which indicate absence of any corrosion inhibitor formed on the metal surface. The figureSEM image of rough metal surface whichindicate highly corroded area. Thefigure5(c) SEM image of metal surface in presence of inhibitor isless corroded surface and smooth metal surfacewhich is due to strong adsorption of the inhibitor on metal surface and suppress the corrosion process.

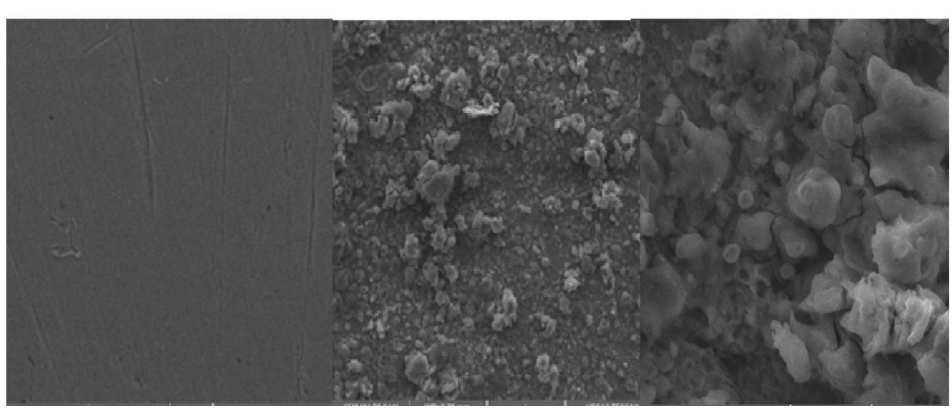


Figure: 5(a) Figure: 5(b) Figure: 5(c)

13.6. Energy Dispersive Analysis of X-rays (EDAXs):

The EDAXs spectra were used to detect the element present in the metal surface before and after exposure to the inhibitor solution. The main aim to use the spectra is the result obtained from chemical and electrochemical measurements that a protective film formed on the metal surface is measured.

Toachievethis EDAX examination of the metal surface were performed in the presence and absence of inhibitor.

The corresponding EDAXsprofile analysis the selected areas on SEM images of figure and its shows the concentration of iron(Fe).Carbon(C) are found higher in the fresh metal than inhibitor used metal surface. In EDAX spectra theOxygen concentration are found lower than that of the blank metal sample.it means that the corrosioninhibitor act as a protective layer against the penetration of the aggressive ions n the solution to the metal sample.The EDAX spectra data contain Fe, O, C, Cl atom covered on the mild steel surface.

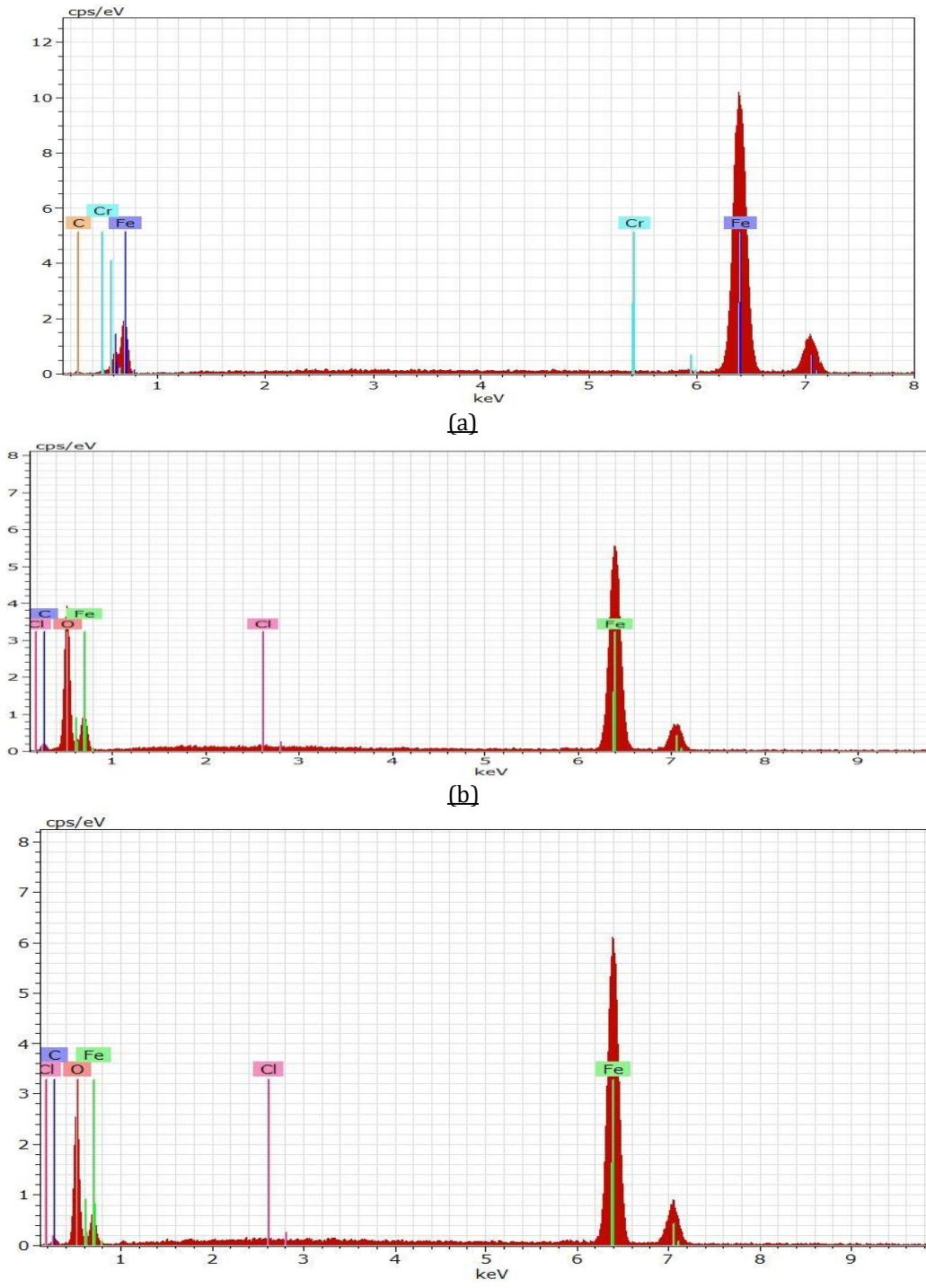


Figure (6): EDAX Spectra of (a) mild steel (b) mild steel immersion in 1M HCl(c) mild steel immersion containingcorrosion inhibitor.

14. CONCLUSION:

The compound 5-(2,4-dicholoro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl]-phenyl-amine(CPP)was found to be effective inhibitor in the acidic medium.it provides inhibitor efficiency upto 83.33% with corrosion inhibitor in 1MHCl,AC Impedance spectra measured that protective film is formed on metal surface.UV AND FT-IR detect that the protective film consistCPP-Fe^{2+}complex formed on metal surface. SEM s and EDAXs confirm the presence of protective film on the metal surface.

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