INHIBITION EFFECT OF PHENOL-FORMALIN-ANILINE-UREA RESIN ON THE CORROSION OF MILD STEEL IN 1M SULPHURIC ACID MEDIUM

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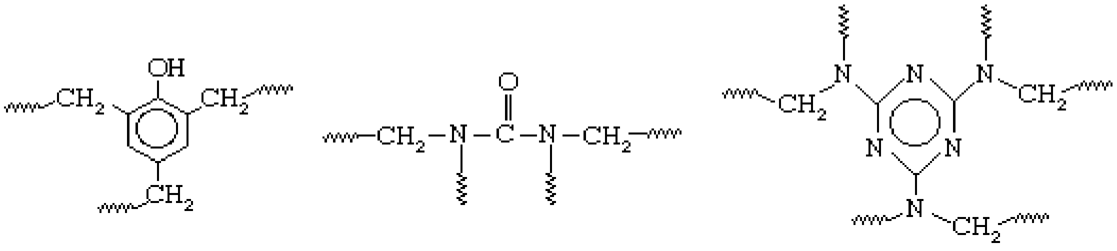
Abstract**:** The inhibition of the corrosion of mild steel in 1 M sulphuric acid solution by the resin has been studied using weight loss, electrochemical impedance and potentiodynamic polarisation methods. Inhibition was found to increase with increasing concentration of the resin. The adsorption of the inhibitor was also supported by scanning electron microscopy technique. Polarisation curves showed that resin behaves as mixed-type inhibitor in 1 M sulphuric acid.

Keywords: **Phenol-formalin-aniline-melamine-urea resin, infrared, scanning electron microscope, mild steel, sulphuric acid**

I. INTRODUCTION

Mild steel is an important material which is extremely useful because of its low cost to manufacture reaction vessels, cooling towers and pipelines. In particular, its application in steam generators and ballast tanks are worthy to mention. Because of the extreme corrosive environment in industries its usefulness in strategic applications is much affected by corrosion phenomena. The corrosion process is controlled by protective coatings. Corrosion problems are also solved by adding suitable substances which will reduce the corrosion rate. We already know that the use of inhibitors is one of the most practical methods for protection against corrosion in acidic media. Inhibitors are used to prevent metal dissolution as well as acid consumption. As acidic media, HCl and H_2SO_4 are widely used in the treatment of steel and ferrous alloys. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decreases or prevent the reaction of the metal with the media [1]. The use of inhibitors is one of the most practical methods for protecting metals or alloys from corrosion. Compared with organic and inorganic salt corrosion inhibitors, using organic corrosion inhibitors is an effective, inexpensive and less pollution means of reducing the degradation of metals or alloys in many fields of applications and which has been extensively investigated during the last decade[2]-[8]. The mechanism of inhibition of corrosion by organic compounds vests with its ability to be adsorbed and to form a protective layer on the metal surface which can markedly change the corrosion resisting property of the metal [9]-[10]. In case of organic inhibitors the mode of action is controlled by many factors such as, nature of the functional groups, availability of π-electron density, steric factor, molecular weight etc [11]-[18].Organic compounds containing the hetero atoms such as nitrogen, sulphur and oxygen having one or two lone pairs of electrons are widely used as inhibitors and few examples are some Schiff bases, thiourea and amine melamine formaldehyde[19]-[20].Among the heteroatom nitrogen, sulfur and oxygen the efficiency in corrosion inhibition is in the order S>N>O. Apart from the structural aspects the other factors affect the goodness of organic inhibitor are the pH of the medium, temperature, time duration and composition of the metal[21]-[22]. The corrosion of mild steel in acid solution causes considerable loss. In order to reduce the corrosion of mild steel several techniques have been adopted. The high performance of the present investigation is attributed to the presence of rich π-electrons and its large molecular size [23]-[26].



phenol formaldehyde urea formaldehyde melamine formaldehyde

aniline-formaldehyde

Scheme-1.Constituents of Phenol- formalin -aniline –melamine- urea (resin)

II MATERIALS AND METHOD

2.1 PREPARATION OF RESIN

Sulphuric acid (98%) is added to phenol solution, maintain the temperature between 105-115˚C for 3 hours. The phenol sulphonic acid is formed it is added with urea, water and formalin (37%). To this mixture add causticlye (40%) slowly, maintain the temperature to 90-95˚C in one vessel (I) for 2 hours.. In another vessel (II) sodiumbisulphite is added to water to get a homogeneous solution. After getting homogeneous solution formalin is added to the solution and heated to 70˚ C, then aniline is added slowly after that formalin (37%) is again added to the heated solution. The solubility should be checked with water and maintained for 2 hours. In this method separately prepare urea, water, formalin and finally add melamine. The prepared mixture added to the vessel II and maintained for 2 hrs at 80-85˚C. The resultant solution (II) is mixed with (I) and run for another 1 hour. It is then converted into powder form (resin) by putting in an oven at 150 ˚ C for half an hour. It is readily soluble in water. The presences of various functional groups in the resin are confirmed by FT-IR spectroscopy

2.2 Preparation of Mild Steel Specimens

Corrosion tests are carried out on electrodes cut from sheets of mild steel strips containing 0.01%Al, 0.05% Mn, 0.21% C, 0.05%S and the remaining of the iron is used for the measurement. In the present study mild steel is used as the specimen for determining corrosion rate. Mild steel 1cm × 1cm is abraded with emery paper washed with conductivity water.

2.3 Weight Loss Method

Weight loss is a non-electrochemical technique for the determination of corrosion rates and inhibition efficiency which provides more reliable results when compared with electro chemical techniques under experimental conditions. After accurate weighing, the specimens are immersed in a 100 ml beaker which contained 50 ml of H_2SO_4 with and without addition of different concentrations of inhibitor. After one hour the specimens are taken out washed, dried and weighed accurately. Then the tests are repeated at different temperatures, different concentrations of inhibitor. In all cases duplicate experiments were performed and the mean values are reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in mmpy.The corrosion rate and inhibition efficiency IE (%) were calculated according to the Equations (1) and (2) respectively.

$$\text{Corrosion rate (mmpy)} = 534\ W/\ \rho A\ t \qquad (1)$$

Where W is the weight loss (mg), ρ is the density of the specimen (gcm^{-3}), A is the

area of the specimen (cm^2), and *t* is the exposure time (hours).

Inhibition efficiency is defined as follows

$$\text{IE (\%)} = ((CR^o - CR)/\ CR^o) \times 100 \qquad (2)$$

Where CR^o- Average weight loss without inhibitor, CR- Average weight loss with inhibitor

2.4 Electrochemical Studies

2.4.1 Potentiodynamic Polarisation Study

Electrochemical measurements were performed in a conventional three electrode cell consisting of mild steel as working electrode (WE), platinum as counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. To minimize ohmic contribution the Luggin capillary was close to working electrode (WE) which was in the form of a square embedded in a PVC holder using epoxy resin so that the flat surface was only surface in the electrode. By using emery paper, the mild steel (WE) surface was abraded and degreased with acetone at room temperature before used. The area of the working electrode surface is 1 cm^2. The anodic and cathodic potentiodynamic polarization curves of mild steel specimen were obtained in the inhibited and uninhibited solution. Measurements were carried out in 1M H_2SO_4 solution having different concentrations of the present inhibitor by changing electrode potential automatically from -600 to -300 mV. The current density curves are obtained by linear extrapolation of the anodic and cathodic branches of the Tafel plots.

2.4.2 AC Impedance Spectra

Electrochemical Impedance Spectroscopy (EIS) studies were carried out in a frequency range of 100 kHz to 10 mHz with amplitude of 10 mV using AC signals at open circuit potential (OCP) with scan rate of 1 mVs^{-1}. Computer programs automatically control the measurements performed at rest potentials after 30 minutes of exposure. Before recording the curves the test solution is de-aerated and magnetically stirred for few minutes in the cell with nitrogen. Nyquist plots were drawn from these experiments and the best semicircle can be fitted through the data points in the Nyquist plot.

The charge transfer resistance (R_{ct}) values have been obtained from the diameter of semicircles of Nyquist plots. The inhibition efficiency has been calculated by using the following equation

$$IE (\%) = [(R_{ct} – R^{o}_{ct})/ R_{ct})] X 100 \qquad (3)$$

R_{ct} - charge t ance without inhibitor

2.5 Scanning Electron Microscopy (SEM)

The mild steel specimen immersed in 1M H_2SO_4 for 1 hour was taken out and washed with distilled water, dried and taken SEM micrograph. Similarly the mild steel specimen immersed in resin solution containing acid for 1 hour was taken out, rinsed with double distilled water, dried and subjected to surface examination by scanning electron microscopy (SEM) using HITACHI S-3000H instrument.

2.6 FT IR Spectroscopy

IR spectroscopy is used to study the structure of the inhibitors used in the present work. In order for IR absorbance to occur two conditions must be met: There must be a change in the dipole moment of the molecule as a result of a molecular vibration (or rotation). The change (or oscillation) in the dipole moment allows interaction with the alternating electrical component of the IR radiation wave. Symmetric molecules (or bonds) do not absorb IR radiation since there is no dipole moment. If the frequency of the radiation matches the natural frequency of the vibration (or) rotation, the IR photon is absorbed and the amplitude of the vibration increases

2.7 EDX Spectroscopy

Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum.

To stimulate the emission of characteristic X-rays from a specimen a beam of X-rays is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured.

III. RESULTS AND DISCUSSION

3.1 Analysis of Weight loss Method

The weight loss method of obtaining corrosion rate and inhibition efficiency is useful because of its simple nature and reliable results. Weight loss data of mild steel in 1M H_2SO_4 in the absence and presence of various concentrations of the inhibitor are listed in Table1.1. The data shows that corrosion rate decreases and inhibition efficiency increases with the increase in the inhibitor concentration. The values of corrosion rate and inhibition efficiency are obtained by the equations (1) and (2) in the corrosion of mild steel at different concentrations in 1M H_2SO_4 after one hour immersion are given in Table 1.1.

Table 1.1 Variation of corrosion rate of mild steel and inhibition efficiency (%) with increasing concentration of resin in 1M H_2SO_4

S.No	Inhibitor concentration (mM)	Corrosion rate (mmpy)	Inhibition efficiency (%)
1	0	0.867	
2	0.5	0.497	42.67
3	1	0.401	53.74
4	1.5	0.262	69.78
5	2	0.198	77.16
6	2.5	0.039	95.50

3.2 Electrochemical studies

Table1. 2 Potentiodynamic polarization parameters in different concentrations of resin at 303 K for the corrosion of mild steel in 1M H_2SO_4

Conc. mM	E_{corr} (mv/SCE)	I_{corr} (mA/cm^2)	β_c (mv/dec)	β_a (mv/dec)	IE %
0	-423	2257	126.7	220.3	
0.5	-368	585.3	125	26.6	74.06
1.0	-350	309.8	116.1	54.1	86.20
1.5	-324	252.6	134.2	61.2	88.80
2.0	-330	203.1	129.8	30.3	91.0
2.5	-.300	110.1	128.6	315.8	95.12

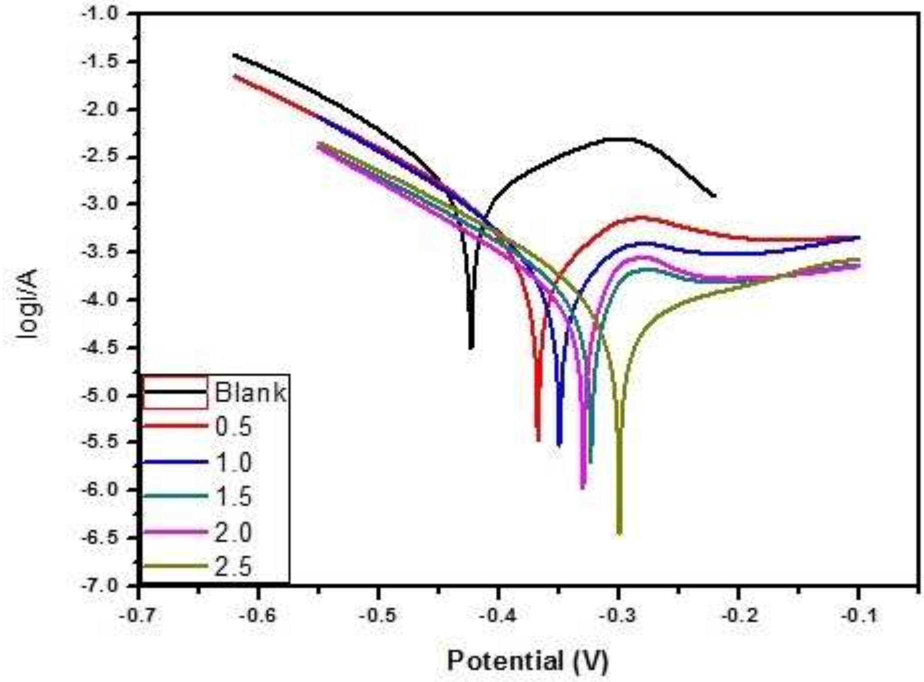


Figure1.1 Polarization curves of mild steel in 1M H_2SO_4 with and without resin at various concentrations

Electrochemical measurements are performed in a conventional three electrode cell consisting of a mild steel working electrode (WE), platinum counter electrode (CE) and saturated calomel electrode as the reference electrode. By using emery paper, these electrodes are degreased and dried at room temperature before used. The area of the working electrode is 1 cm^2. The current density (I_{corr}) curves obtained by extrapolation of the Tafel lines.

Potentiodynamic polarization measurements were carried out for this system and the details are given Table 1.2. The kinetic parameters obtained by this method Figure 1.1 such as E_{corr}, I_{corr}, anodic and cathodic tafel slopes (β_a & β_c) are given in Table 2. It is observed that with the increasing concentration of inhibitor the corrosion potential (E_{corr}) shifts slightly towards the cathodic direction. For the blank, E_{corr} is -423 mV and at higher concentration of inhibitor 2.5 mM its value is -300 mV. These observations indicate that there is a dismal effect on corrosion potential with increase in the concentration of the inhibitor. However there is a progressive change in the values of anodic and cathodic Tafel slopes. This clearly shows that the mechanism of anodic dissolution of metal and cathodic hydrogen evolution steps is affected by the inhibitor. Here it is understood that the inhibition is due to the adsorption of the inhibitor on the mild steel surface. The values of βc and β_a show increasing trend indicating the inhibitive action is of mixed type[22-23]. From the Potentiodynamic polarization measurements the inhibition efficiency is obtained using the equation.

$$IE\% = \frac{I_{corr} - I_{corr}(\text{inhibitor})}{I_{corr}} \times 100 \qquad (4)$$

Where I_{corr} and $I_{corr\ (inhibitor)}$ are the values of corrosion current densities of mild steel without and with the inhibitor respectively. The inhibition efficiency increases with the increase in concentration of the inhibitor

3.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) studies were carried out in a frequency range of 100KHz to 10 MHz with amplitude of 10 mV using AC signals at open circuit potential (OCP). The charge transfer resistance (R_{ct}) values have been obtained from the diameter of semicircles of Nyquist plots.

Table1. 3 Electrochemical impedance parameters of mild steel at different concentrations of resin in 1 M H_2SO_4

Conc.mM	**R_{ct} Ω cm^2**	**C_{dl} μF cm^{-2} 10^{-7}**	**IE %**
0	15.583	10.22	
0.5	64.946	2.45	76.00%
1.0	118.837	1.33	86.08%
1.5	144.803	1.09	89.03%
2.0	147.457	1.07	89.40%
2.5	199.633	0.79	92.20%

The effect of the inhibitor concentration on the impedance behaviour of mild steel in 1M H_2SO_4 has been determined Table 1.3 and the Nyquist plots are given in Figure1.2. The impedance spectra show slight semicircle and R_{ct} significantly increases with increase in concentration of inhibitor and C_{dl} tends to decrease. This decrease in C_{dl} may be due to decrease in local dielectric constant and/or an increase in the thickness of protective layer at electrode surface which enhances the corrosion resistance of the mild steel. The increase in R_{ct} values is attributed to the formation of protective film at the metal-solution interface.

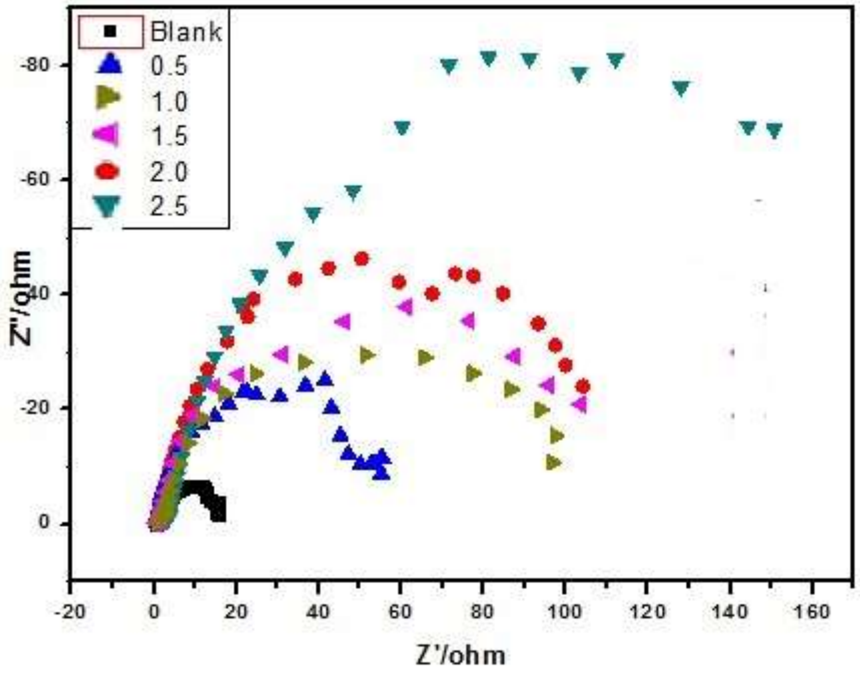


Figure 1.2 Nyquist plots for mild steel immersed in 1M H_2SO_4 solution without and with resin at various concentrations.

3.4 Scanning Electron Spectroscopy (SEM)

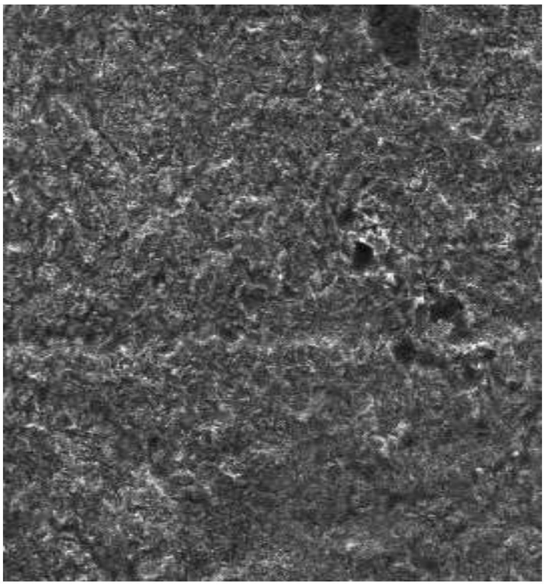
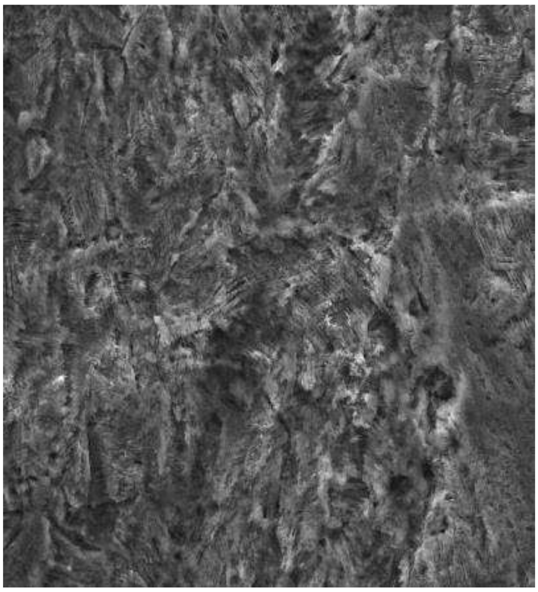


Figure 1.3 SEM micrograph of mild steel after 1 hour immersion in 1M H_2SO_4



SEM micrograph of mild steel after 1 hour immersion in the presence of resin in 1M H_2SO_4

The mild steel specimen immersed in 1M H_2SO_4 for one hour was taken out and washed with distilled water, dried and taken SEM micrograph. Similarly the mild steel specimen immersed in inhibitor solution containing acid for one hour was taken out, rinsed with double distilled water, dried and subjected to surface examination by scanning electron microscopy (SEM) using HITACHI S-3000H instrument.

3.5 IR Spectroscopy

Infrared spectrum of resin was taken in KBr pellet form in the region 750-4000 cm^{-1}. The mild steel specimens of size 1cm × 1cm were prepared and immersed in 100 ml of 1M H_2SO_4 solution containing 2.5 mM of inhibitor and were then dried. The infrared spectrum was applied to study the mild steel surface. The characteristic IR absorption bands of resin are as follows:

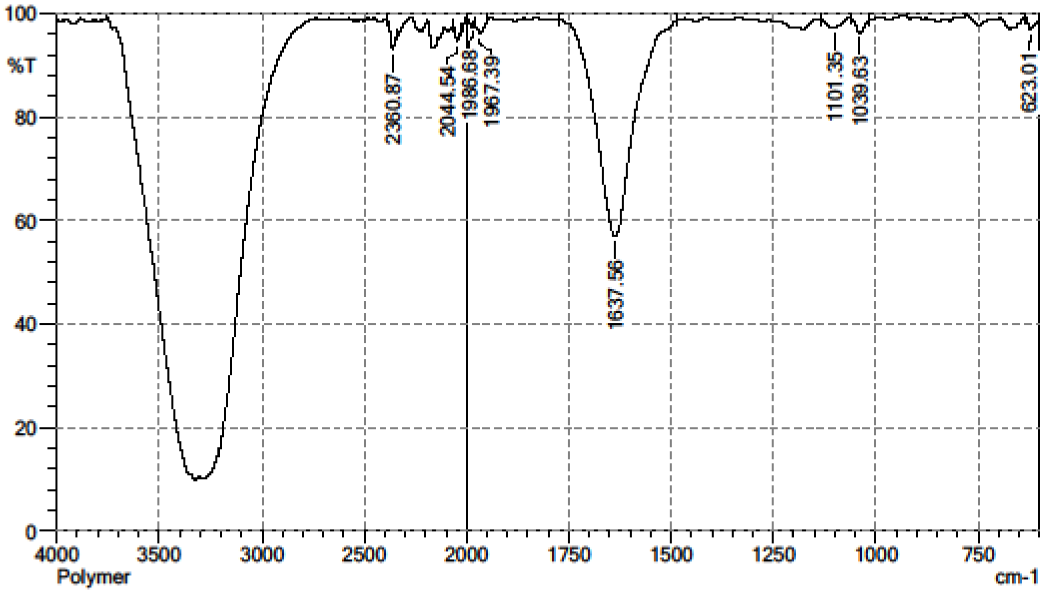


Figure 1.4 Infrared spectrum of resin

From Infrared spectrum of the compound, a broad band 3352 cm^{-1} is attributed to both O-H groups and N-H groups:at 1047 cm^{-1} is attributed to ether linkage groups:at 1639 cm^{-1} is attributed to C=O groups: at 1967&1986 cm^{-1} are attributed to C-H groups.

3.6 EDX SPECTROSCOPY

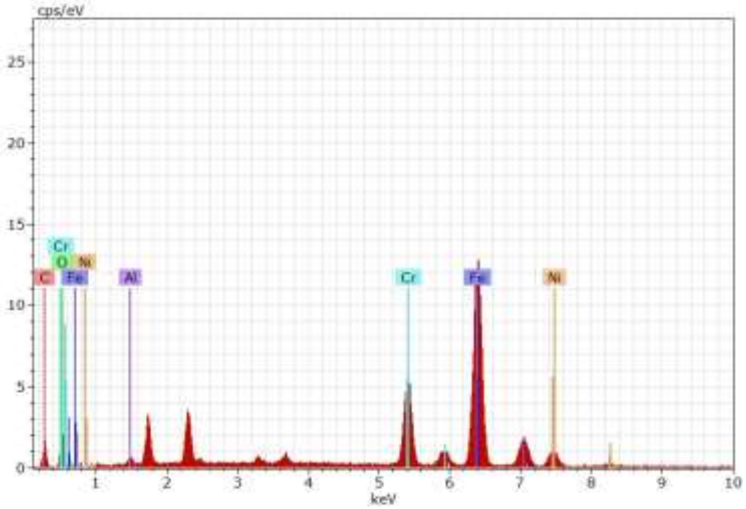


Figure 1.5 EDX spectrum of resin

IV. MECHANISM

Electrostatic interaction of protonated molecules with already adsorbed sulphate ions donor-acceptor interactions between the π-electrons of aromatic ring and vacant d-orbital of surface iron atoms, interaction between unshared electron pairs of hetero atoms and vacant d-orbital of iron surface atoms. Generally, two ways of adsorption are considered on the metal surface in acid media. In the first way, the neutral molecules may be adsorbed on the surface of mild steel involving the displacement of water molecules from the mild steel surface and the sharing electrons between the hetero atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor–acceptor interactions between π-electrons of the aromatic/heterocyclic ring and vacant d-orbitals of surface iron atoms. In second way, since it is well known that the steel surface bear's positive charge in acid solution it is difficult for the protonated molecules to approach the positively charged mild steel surface due to the electrostatic repulsion[24]. Since sulphate ions have a smaller degree of hydration, they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated inhibitors adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Thus, there is a synergism between adsorbed sulphate ions and protonated inhibitors. Thus, inhibition of mild steel corrosion in 1M H_2SO_4 due to the adsorption of resin constituents on the mild steel surface.This assumption could be further confirmed by Infrared analysis of mild steel surface. The high performance of the present investigation is attributed to the presence of rich π-electrons and its large molecular size [25-28].

V. CONCLUSION

. Resin is a good inhibitor for mild steel corrosion in 1M H_2SO_4 solution. Inhibition efficiency increases with increasing concentration of inhibitor and IE % values obtained from different methods are in reasonable agreement.

. Polarization curves measurements indicate that resin acted as mixed type inhibitor.

. The Infrared analysis showed that the inhibition of mild steel corrosion occurred due to the formation of a protective film on the metal surface through adsorption of constituents of resin.

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