CHAPTER - 3

Materials and methods

CHAPTER III

MATERIALS AND METHODS

In any research work the materials and the methods adopted are the aspects, which decide and determine qualitatively and quantitatively the outcome of the research. In the present work, efforts have been taken to study **"Synthesis, Characterisation And Utilisation of Water Soluble Polyvinyl Alcohol-Selected Amino Acid Composites as Corrosion Inhibitors for Mild Steel in Acid Medium"**.

Efforts are taken to discuss the results in the three phases.

Phase I : Synthesis and characterisation of water soluble polyvinyl alcohol-selected amino acid composites.

Phase II: Utilisation of polymer composites as corrosion inhibitors for mild steel in acid medium-Weight loss methods and electrochemical measurements.

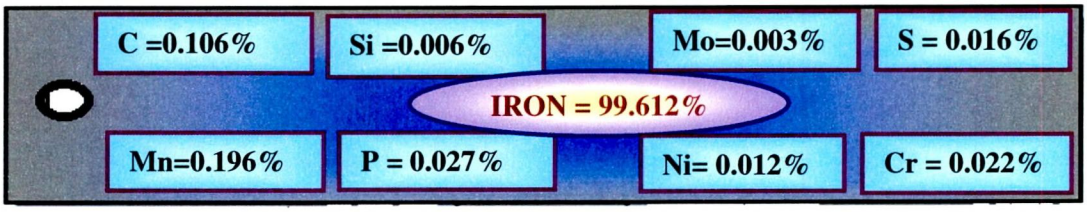
Phase III : Analysis the surface of mild steel in the presence and absence of polyvinyl alcohol- selected amino acid composites by surface analytical techniques.

In the current investigation reason for selection of the sample, preparation of the specimen, test media, selection of inhibitors, polymerization medium are presented in a detailed manner.

3.1 Phase I: Synthesis and Characterisation of Water Soluble Polyvinyl Alcohol- Selected Amino Acid Composites

3.1.1 SELECTION OF THE SAMPLE

Mild steel finds a variety of industrial applications for mechanical and structural purposes such as bridge work, buildings, boiler plants, steam engine parts, electroplating bath, pipes, tanks, automobiles etc., because of its low cost, easy availability and versatility. It is subjected to corrosion and the corrosion of mild steel is severe in the presence of aggressive medium such as acidic, basic and salty solutions. During industrial processes such as acid cleaning, etching and pickling the acidic solutions are made to come in contact with the metal. The metal suffers severe corrosion. To avoid corrosion, inhibitors are used. Several inhibitors have been synthesized and used as inhibitor for corrosion of mild steel in acidic and basic media. In response to the drive for environmentally friendly inhibitor, an attempt has been made with the water soluble polyvinyl alcohol-selected amino acid composites, to find out whether, they could inhibit the mild steel corrosion in acid medium. The mild steel samples used for this study were found to have the following elemental composition.



3.1.2 PREPARATION OF THE SPECIMEN

Commercially available mild steel sheet was procured and sheared into rectangular pieces of small bar (coupons) of area 5 X 1cm^2. A small hole was drilled at one end of the coupons to allow it for hooking. They were then thoroughly cleaned by buffing to produce a spotless finish and then degreased, washed with de-ionized water, dried and kept inside desiccators. The mild steel samples, with an active surface of 1×5 Cm^2 with 2 mm thickness are used for weight loss studies and one cm^2 area was used as the working electrode for electrochemical measurements following the ASTM standard procedure **(stated in ASTM, G 1-2, 1996a).**

3.1.3 TEST MEDIA

Among the commercially available acids the most frequently used acid is hydrochloric acid. At the present time, hydrochloric acid is the most important pickling acid. Large scale continuous treatment such as metal strip and wire pickling, as well as economic advantages in the regeneration of depleted pickling solutions a factor of increasing economic and ecological importance were the main reasons why hydrochloric acid gradually replaced sulphuric acid. It is used for the removal of oxide from the metallic parts, before coatings (acid pickling), removal of undesirable scales and rust (acid cleaning) and several other industrial processes. The exposures can be most severe but in many cases, corrosion inhibitors are widely used to prevent or reduce corrosion rates of metallic materials in these acid media. Hydrochloric acid is extensively used in industries, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Hence 1 M HCl was used for the present study.

3.1.4 POLYMERIZATION MEDIUM

In the present study the Chemical polymerization of polyvinyl alcohol-selected amino acids was carried out in acidic medium with the aim of obtaining well adherent PVA-selected Amino acids layer. Trials in several inorganic acids like sulphuric acid were proved to be unsuccessful also in terms of the formation of stable coatings on Fe, with the exception of nitric acid. This exception is probably associated with the property of Fe to be more easily passivated in nitric acid solution. However, part of this coating was readily removed by washing with water **(Trivedi, 1997).**

Then our focus was turned to the organic acids where the results were more promising for the dibasic acids especially for oxalic acid. The increase of the oxalic acid concentration (C_{ox}) favours polymerization of all the monomeric selected Aminoacids considered in the present study in the sense that it results in higher values of the polymer growth rate. Organic acid ranks among the most important chemicals in industry today. The reactive carboxylic group (COOH) makes a basic building block for many compounds such as drugs, pharmaceuticals, plastics and fibers. Therefore any acid whose pK_a value falls within that range would be suitable as a dopant (Table1).

Table 1 Dissociation constants of various acids

ACID	pK_a			
	K_1	K_2	K_3	K_4
α-Amino acetic acid (glycine)	2.35	9.78	-	-
Arsenic acid	2.22	6.98	11.4	
Trichloroacetic acid	0.89			
Dichloroacetic acid	1.26			
Oxalic acid	1.27	4.27		
Phorphoric acid	2.15	7.21	12.36	
Trifluroacetic acid	0			
Pyrophosphoric acid	0.96	1.86	6.68	9.40
Sulphamic acid	1.0			
Sulphuric acid	-4	1.92		
Sulphurous acid	1.76	7.19		
Hydrochloric acid	-7.0			
Hydrofluoric acid	3.17			
Benzene sulphonic acid	0.2			
p-Toluene sulphonic acid	0.3			
5-Sulphosalicylic acid	-.75	2.42	11.4	
Perchloric acid	-10			

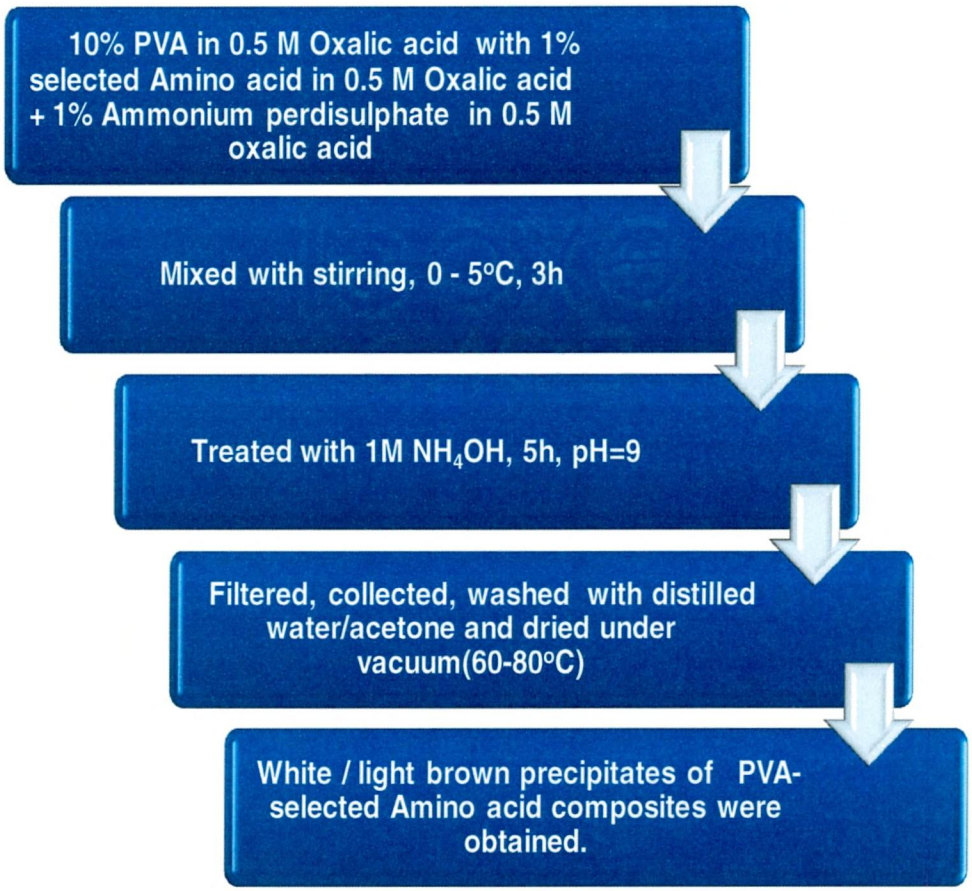
3.1.5 SYNTHESIS OF WATER SOLUBLE POLYVINYL ALCOHOL-SELECTED AMINO ACID COMPOSITES

A standard procedure was adopted to prepare polyvinyl alcohol-selected amino acid composites ***(Trivedi, 1997, Rupali Gangopadhyay et al. 2001, Mirmohseni, 2003)***. 1% Ammonium peroxydisulphate in aqueous solution of 0.5M oxalic (protonic) acid) is added dropwise to a stirred solution of 10% PVA and 1% selected Amino acids (Alanine, Valine, and Glutamic acid, Glutamine, Tyrosine and Trpytophan) in 0.5M aqueous solution of oxalic (protonic) acid, precooled to 0-5^{o}C. Ammonium peroxydisulphate is added very slowly to prevent the warming of the solution. After completion of the addition (addition time almost 30 minute), stirring is continued for 3 hours to ensure completion of the reaction. After keeping overnight, the PVA-selected Amino acids composites stable solution were treated with 1M

NH_4OH, kept for 5h and maintained at P^H=9. The polymer composites solution is then transferred to a 1000ml beaker and stirred with non-polar solvent (acetone/ methanol) and filtered acetone/methanol washing is desirable to remove the oilgomeric impurities. The PVA-selected Amino acids composites precipitates are filtered and dried under dynamic vacuum at 60-80°C for 8 h (figure -7).

The time of initial colouration on mixing of reactants depends upon the temperature and protonic acid used. When oxalic acid is used as a protonic acid, the colouration of solution occurs almost after 1minute at room temperature and around 0-5°C it is 3-5 minutes. The sequence of colouration is colourless colour (Alanine, Valine, Glutamic acid, Glutamine, Tyrosine and Trpytophan) → white colour (PVAALA, PVAVAL, PVAGLU and PVAGLN composites) / light brown colour (PVATYR and PVATRP composites) precipitates.

Figure-7 Flow chart showing the various steps involved in chemical synthesis of PVA-selected Amino acid composites



3.1.6 SELECTION OF INHIBITORS

3.1.6.1 Polymer as Corrosion Inhibitors

The use of polymers as corrosion inhibitors has drawn considerable attention due to their inherent stability and cost effectiveness. Due to presence of functional groups in polymers, they form complexes with metal ions and on the metal surface. These complexes occupy a large surface area thereby blanketing the surface and protecting the metals from corrosive agents present in solution. The effectiveness of these compounds as corrosion inhibitors has been interpreted in terms of their molecular structure, molecular size and molecular mass, hetero atoms present and adsorptive tendencies **(Sathiyanarayanan *et al.,* 1992)**.

3.1.6.2 Polyvinyl Alcohol

Polyvinyl alcohol is a synthetic linear polymer containing abundant secondary alcoholic groups. Polyvinyl alcohol is a semicrystalline, water soluble polymer, with low electrical conductivity. Polyvinyl alcohol is one of the popular precursor polymer range of industries including textiles, chemical and food for coating, adhesives, emulsifiers, colloidal stabilizers, film packaging etc. Due to the presence of multiple adsorption sites in the molecular structure of polymers, they should act as good corrosion inhibitors **(Umoren *et al.,* 2007a).**

3.1.6.3 Amino Acids

Most of the natural amino acids are alpha amino acids which contain carboxyl and amino groups bonded to the same carbon atom. Amino acids are non toxic, biodegradable, relatively cheap, completely soluble in aqueous media and easy to matrices for the fabrication of environmentally friendly, biodegradable and water soluble biopolymers. Polyvinyl alcohol based composites find applications in a wide produce with purities greater than 99%. Amino acids are ecofriendly inhibitors. Amino acids were reported as good toxic corrosion inhibitors ((**Oguzie *et al.,* 2007).**

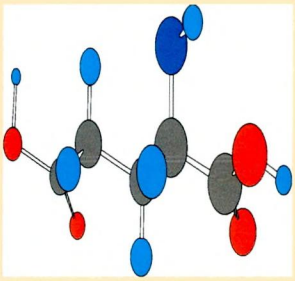
Syntheses of water soluble polymers are preferred as the available conducting polymers are insoluble in common solvents. This motivated us to carry out the present research work on synthesis and utilisation of PVA – selected Amino acid composites as corrosion inhibitors which are water soluble in nature (figure-8). Considering the technical process of pickling, good inhibitors must meet quite a number of requirements.

Required properties of inhibitors for acid pickling:

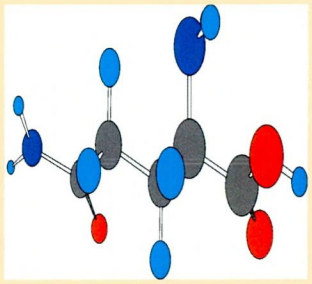
- Effective inhibition of metal dissolution.
- No over-pickling in the presence of higher iron salt contents
- No delay of the pickling process
- Effective at low concentrations and at higher temperature

- Effective also at higher temperature
- Thermally and chemically stable
- Good surfactant characteristics

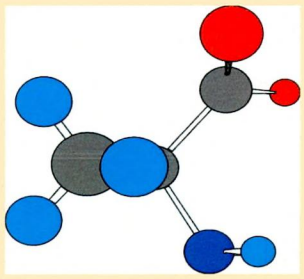
Figure-8 Structure of PVA and selected aminoacids for the present Research work



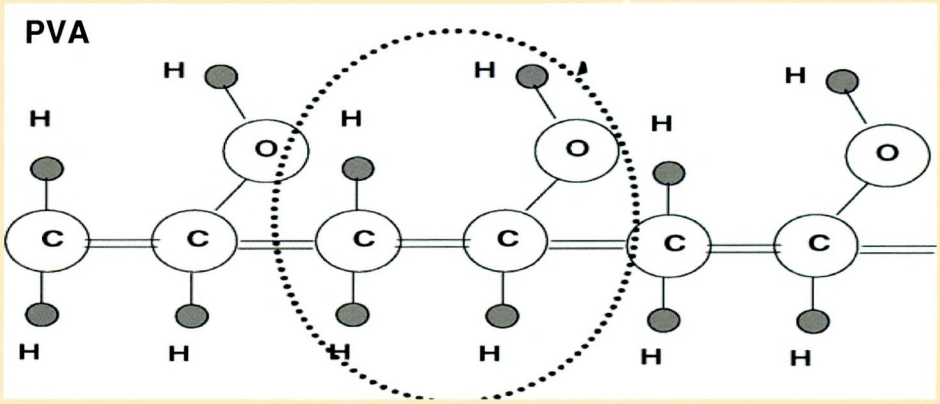
L-Glutamic acid

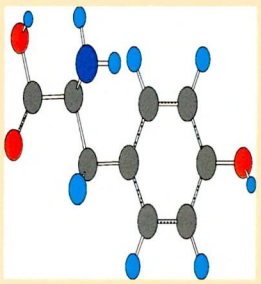


L-Glutamine

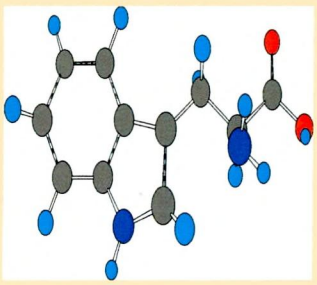


L-Alanine

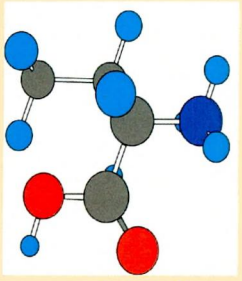




L-Tyrosine



L-Tryptophan



L-Valine

Most of the nitrogen, oxygen and sulphur containing organic compounds are found to effectively inhibit the corrosion of mild steel.

3.1.7 Characterization of Synthesised Water Soluble Polyvinyl Alcohol-Selected Amino Acid Composites

In order to obtain the physical properties of the, an exhaustive characterisation was developed as follows:

3.1.7.1 CHN elemental analysis:

In order to confirm the chemical composition of the synthesized CHN analysis was carried out using the **instrument Vario EL CHNS serial number 11035060**.

3.1.7.2 Conductivity measurements:

The conductivity of the PVA– selected Amino acid composites sample was measured by four probe technique and Solartron Electrochemical analyzer. The polymer composites samples were pressed into pellets of 1cm diameter at 3-ton pressure. Conductivity measurement of compressed pellets of the polymer composites was carried out using the **keithley** (Four probe methods). Solartron electrochemical analyzer was used to record Tafel polarization curve and Nyquist impedance curve. EIS measurements were carried out using ac signals of amplitude 10 mV peak to peak in the frequency range of 100 kHz to 0.1Hz. The EIS were analysed and fitted using Z plot (1260+1278) software and Tafel data were analysed **corrware-2 Instrument =1 solarton 1287[0,8].**

3.1.7.3 Infrared spectra:

The fundamental vibrations of the PVA– selected Amino acid composites were studied by FTIR analysis in the range 4000-400 Cm^{-1} using a **Bruker Tensor 27 FTIR system IR spectrometer**. Fourier transform infrared spectroscopy (FTIR) was used to characterize the presence of specific chemical group in the PVA-selected Amino acid composites.

3.1.7.4 UV-Visible spectra:

Aqueous solutions of PVA-Amino acids composites were subjected to UV-VIS Spectrophotometric characterization over 200-1100nm using **Aglient 8453 UV-Vis spectrophotometer**. The UV-Vis spectra give limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electrons in the σ and π orbital from the ground state to higher energy states.

3.1.7.5 Thermal Analysis:

TG/DTA and DSC has been used widely to study all physical processes involving the weight change, thermal degradation, phase transitions and crystallization of the polymer composites was carried out using the **instrument thermal analyzer**

(SDTQ600V8.3build101). The sample was heated at a rate of 20°C/min in protected nitrogen gas between 20°C and 1100°C of the samples was taken to carry out the experiment. TGA is a established techniques which measures the weight changes as a function of temperature or time. From the thermogravimetric curves the characteristic temperature of decomposition: temperature of initial decomposition (T_{di}) and temperature at maximum decomposition rate (T_{max}) of the polymer composites were determined to find out melting point (endothermic and exothermic peak) and any kind of phase transition of polymer composites, DTA curves were performed.

Differential Scanning Calorimetry (DSC) is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Differential scanning calorimetry (DSC) was measured at a heating rate of 10ºC/min in a helium atmosphere. To correct the baselines of DSC curves, an empty aluminum cell was scanned in the heating range, whereas DSC is more suitable to determine Tg because it directly measures the energy at a given temperature. The change in physical properties in polymer composites can be reflected in glass transition temperature (Tg) and melting point (Tm). It is well established that crystalline and amorphous phases in variable amount coexist in most of the polymeric materials.

3.1.7.6 XRD Powder Patterns:

The XRD data for PVA-Amino acids composites were obtained using **XPERT-PRO X-ray diffractometer** with Cu, K, α radiation (λ = 1.5418 Å). Finely crushed powder of the PVA-Amino acids composites was used for the analysis at a scan speed of 2 min^{-1}. The X-ray diffraction analysis is a useful tool to determine the structure and crystallization of the matrices. The chemical and micro structural modification of the polymer induced significant changes in the X-ray diffraction patterns

3.1.7.7 SEM-EDX Analysis:

Morphological studies of PVA-Amino acids composites were carried out on **JEOL model 6390 Scanning Electron microscope.**

3.2 Phase II: Utilisation of Polymer Composites as Corrosion Inhibitors for Mild Steel in Acid Medium-Weight Loss Methods and Electrochemical Measurements.

Corrosion techniques have been classified into two main categories

1. **Physico-chemical methods**
2. **Electrochemical methods**

Software Tools

- **Origin 8,SPSS 17, MS Excel**

3.2.1 PHYSICO-CHEMICAL METHOD (WEIGHT LOSS METHOD)

Weight loss measurements were carried out using a Denvar balance. Weighed samples in triplicate were immersed in 100 ml of acid solution (with and without inhibitor) for a specific time. The specimens were removed and washed with saturated sodium bicarbonate solution and water, dried and reweighed. The experiments were performed in 1M HCl solution without inhibitor and in the presence of polyvinyl alcohol-selected amino acid composites at different concentrations: 0.06%, 0.12%, 0.18%, 0.24%, 0.30%, 0.36%, 0.42%, 0.48%, 0.54% and 0.6% at various immersion times: 1/2h, 1h, 3h, 6h, 12h ,24h and 48h and at various temperatures 303K, 313K, 323K, 333K and 343K. Weight loss experiments were done according to ASTM standard procedure **(stated in ASTM, G 1-2, 1996a).**

From the obtained weight loss values, corrosion rate, surface coverage and Inhibition efficiencies were calculated using the following equations (6-8) **(Oguzie *et al.*, 2004)**

$$CR = \frac{543 \times W}{D \times A \times T} \quad (6)$$

Where W is the weight loss (g), D is the density of the mild steel (g/cm^2), A is the area of the specimen (cm^2) and T is the time of exposure (h).

$$IE\ (\%) = \frac{CR_0 - CR_i}{CR_0} \times 100 \quad (7)$$

$$\theta = \frac{CR_0 - CR_i}{CR_0} \quad (8)$$

Where CR_0 and CR_i are the corrosion rates in the absence and presence of inhibitor respectively.

3.2.2 Adsorption isotherms

Adsorption isotherms are usually used to describe the adsorption process. The establishment of adsorption isotherms that describe the adsorption of a corrosion inhibitor can provide important clues to the nature of the metal-inhibitor interaction. Adsorption of the organic molecules occurs, as the interaction energy

between the H_2O molecule and the metal surface is higher than that between the H_2O molecule and the metal surface **(Singh *et. al.,* 2010)**. The mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbates on the metal surface must be known. Various adsorption isotherms are tested graphically to fit a suitable adsorption for the inhibitor. Data were tested graphically by fitting various isotherms and statistical estimation of correlation for the curve fitting of isotherms have been used to investigate the goodness of fit of the isotherms using **SPSS 17 Package**

Langmiur	–	**Plot of log (C/θ) Vs log C**	(9)
Temkin	–	**Plot of θ Vs lnC**	(10)
Freundlich	–	**Plot of lnθ Vs lnC**	(11)
Frumkin	–	**Plot of θ Vs ln [θ/C (1- θ)]**	(12)
Flory- Huggins	–	**Plot of log (θ/C) Vs log (1- θ)**	(13)
Bockris-Swinkel's	–	**Plot of θ log (θ/1- θ) Vs log C**	(14)
El-Awady kinetic thermodynamic	–	**Plot of log (θ/1- θ) Vs log C**	(15)

In order to obtain the adsorption isotherms, the degree of surface coverage (θ) for various concentrations of the inhibitor has been calculated according to equation (9-15). Langmuir adsorption isotherm was found best fit for the adsorption of PVA-selected Amino acid composites on the mild steel in 1M HCl solution. Langmuir isotherm is given by following equation (16).

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (16)$$

Where K_{ads} is the equilibrium constant of the adsorption- desorption process, θ is the degree of surface coverage and C_{inh} is concentration of inhibitor in the bulk solution.

The equilibrium constant of adsorption deduced from the Langmuir adsorption isotherm is related to the free energy of adsorption of the inhibitor as follows **(Ashish Kumar Singh and Quraishi, 2010)**

$$\Delta G^{*}_{ads} = -2.303\ RT \times \log (55.5 K_{ads}) \qquad (17)$$

Where K is the equilibrium constant of adsorption, 55.5 is the molar concentration of water, ΔG^{*}_{ads} is the free energy of a adsorption of the inhibitor, R is the gas constant and T is the temperature.

3.2.3 Energy of Activation:

According to **Dehri and ozan, (2006)** the relationship between the temperature dependence of present inhibition efficiency (IE %) of a inhibitor and the activation energy found in its presence was given as follows:

a) Inhibitor whose IE% decreases with temperature increase, the value of activation energy (E_a) found is greater than that in the uninhibited solution.
b) Inhibitor whose IE% does not change with temperature variation, the activation energy (E_a) does not change with the presence or absence of inhibitors.
c) Inhibitor whose IE% increases with temperature increase, the value of activation energy (E_a) found is less than that in the uninhibited solution (**O.Radovici, 1965).**

The activation energy for the corrosion of mild steel in 1M HCl was calculated using the Arrhenius equation (**Eddy *et. al.,* 2010)**

$$\mathbf{CR = A \exp (-E_a / RT)} \qquad (18)$$

Where CR is the corrosion rate of mild steel, A is Arrhenius or pre-exponential constant, Ea is the activation energy for the corrosion of mild steel, R is the gas constant and T is the temperature. The logarithm of both sides of equation (18) yields equation (19)

$$\mathbf{\log CR = \log A - E_a/2.303RT} \qquad (19)$$

Applying the formula **Ea = - 2.303 x R x Slope**

Plots of log CR Versus 1/T for the corrosion of mild steel in the presence of various concentrations of PVA-selected Amino acid composites yields straight lines. From slopes and intercepts of the Arrhenius plot, the values of Ea and A were computed.

The transition state equation (20) was used to calculate some thermodynamic parameters (enthalpy of adsorption ΔH_a and entropy of adsorption ΔS_a for the adsorption of PVA-selected Amino acid composites on mild steel surface.

$$\mathbf{CR/T = R/Nh \times exp (\Delta S_a/R) \times exp (\Delta H_a/RT)} \qquad (20)$$

Where CR is the corrosion rate, R is the universal gas constant (8.31434 $JK^{-1}mol^{-1}$), T is the absolute temperature, A is the pre-exponential factor, h is Planck's constant (6.626176×10^{-34} JS) and N is Avogadro's number (6.02252×10^{23} mol^{-1}). From the logarithm of both sides of equation (20), equation (21) is obtained

$$\mathbf{\log (CR/T) = \log R/Nh + \Delta S_a/2.303R - \Delta H_a/2.303RT} \qquad (21)$$

Plots of log (CR/T) versus 1/T for PVA-selected Amino acid composites were linear. The slopes and intercepts of the transition state plots, the values of ΔS_a and ΔH_a are calculated.

3.2.4 Thermodynamic Parameters:

ΔG Adsorption:

The free energy of adsorption of PVA-selected Amino acid composites on the surface of mild steel is related to the equilibrium constant of adsorption according to equation (23)

$$\log C = [\log (\theta/1-\theta)] - \log B \quad (22)$$

Where $\log B = -1.744 - \Delta G_{ads}/2.303\ RT$

$$-\Delta G^{o}_{ads} = 2.303\ RT\ (1.744 + \log (\theta/1-\theta) - \log C) \quad (23)$$

where ΔG^{o}_{ads} is the free energy of adsorption θ is the degree of surface coverage and C is the concentration of inhibitor **(Umoren *et al.*, 2007).**

ΔH and ΔS Adsorption

The values of enthalpy of adsorption ΔH^{o}_{ads} and entropy of adsorption ΔS^{o}_{ads} were obtained from the basic thermodynamic equation (i,e) Gibb's Helmholtz equation (24)

$$\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T\Delta S^{o}_{ads} \quad (24)$$

The values of enthalpy of adsorption ΔH^{o}_{ads} and entropy of adsorption ΔS^{o}_{ads}, were obtained by plotting ΔG^{o}_{ads} (KJ/mol) Vs T (K). The slope of the straight line gives the value of ΔS^{o}ads and the intercept gives the value of ΔH^{o}_{ads} (**Eddy *et. al.*, 2010)**.

3.2.5 Electrochemical measurements:

An electrochemical measurement was done using the following techniques:

a. Potentiodynamic polarization method (tafel polarisation)
b. Linear polarisation resistance method
c. Electrochemical impedance spectroscopic technique.

3.2.5.1 POLARIZATION CELL, INSTRUMENTATION AND PROCEDURE

The experiments were performed in a classical three-electrode electrochemical cell. Mild steel specimen of one cm^2 area was used as the working electrode and platinum electrode as counter electrode and saturated calomel electrode as reference electrode as shown in the figure 9. Prior to each experiment the working electrode surface was polished with emery paper. Solartron Electrochemical analyzer (model 1280B) interface with an IBM computer and corrware and z-plot corrosion software were used for data acquisition and analysis. For polarization and impedance studies the period of immersion was for 30 minutes. Polarization technique was carried out using corrware software from a cathodic potential of -0.1 V to an anodic potential of -1 V with respect to corrosion potential at a sweep rate 2 mVs^{-1}. E versus log I curves were plotted. AC signals of 10 mV amplitude and a frequency spectrum from 20 kHz to 0.1 Hz were impressed and the Nyquist representation of the impedance data were analysed with Z view software.

The charge transfer values were obtained from the plots of Z' and Z". The values of (R_t+R_s) corresponds to the point where the plot cuts Z' axis at low frequency and R_s corresponds to the point where the plot cuts Z' axis at high frequency. The difference between R_t and R_s gives the charge transfer resistance (R_{ct}) values. The C_{dl} values were obtained from the relationship **(stated in ASTM, G 1-2, and 1996b).**

$$C_{dl} = \frac{1}{2\pi f_{max}} \times R_{ct} \qquad (25)$$

Where,

C_d = double layer capacitance

R_{ct} = charge transfer resistance

f_{max} = frequency at Z' value maximum.

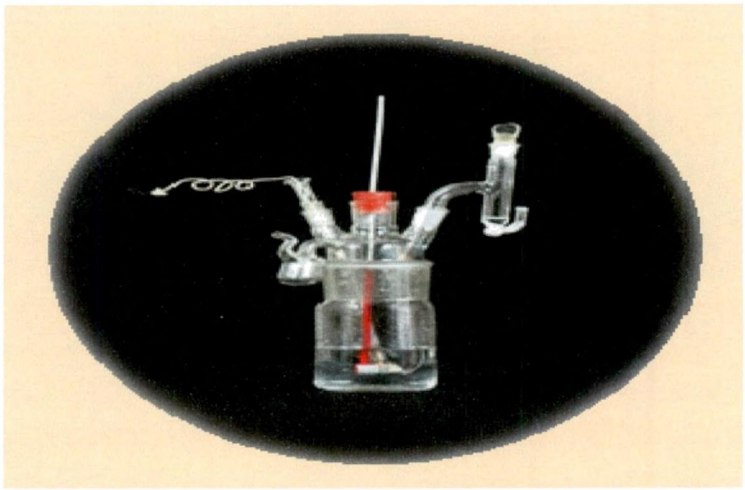


Figure -9 Classical three-electrode polarization cell

3.2.5.2 Potentiodynamic Polarization Method (Tafel Polarisation)

The values of corrosion potential (E_{corr}), corrosion current density (I_{corr}) anodic and cathodic Tafel slopes (b_a and b_c) can be evaluated from the anodic and cathodic region of Tafel plots. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). For Tafel polarization method, the corrosion inhibition efficiency (I.E. %) was evaluated from the measured Icorr values using the relationship **(Jeyapraba *et al.*, 2007).**

$$\text{I.E. (\%)} = \frac{I^{0}_{corr} - I^{i}_{corr}}{I^{0}_{corr}} \times 100 \qquad (26)$$

Where I^0_{corr} and I^i_{corr} are values of corrosion current density in absence and in presence of inhibitor, respectively.

3.2.5.3 Linear polarisation resistance method:

Polarization resistance values were determined from the slope of the potential- current lines,

$$R_p = A\frac{dE}{di} \qquad (27)$$

Where A is the surface area of the electrode, dE is change in potential and di is the change in current. The R_P values were used to calculate the inhibition efficiencies, I.E. %, using the relationship **(Jeyapraba *et al.*, 2007).**

$$\text{I.E.(\%)} = \frac{R^i_P - R^0_P}{R^i_P} \times 100 \qquad (28)$$

Where R^i_P and R^0_P are the polarization resistance in the presence and absence of inhibitor, respectively.

3.2.5.4 Electrochemical impedance spectroscopic technique

Electrochemical impedance measurements were carried over the frequency 20 kHz to 0.1Hz at open circuit potential. EIS behaviour of PVA-selected Amino acid composites at different concentrations and calculated. Inhibition efficiency can be obtained from Nyquist plot as follows **(Jeyapraba *et al.*, 2007)**

$$\text{I.E.(\%)} = \frac{R^i_{ct} - R^0_{ct}}{R^i_{ct}} \times 100 \qquad (29)$$

Where R^i_{ct} and R^0ct are the charge transfer resistance of mild steel in the presence and absence of inhibitors respectively.

From the measured double layer capacitance $C_{dl,}$ the surface coverage θ of inhibitor is given by

$$\theta = \frac{C^0_{dl} - C^i_{dl}}{C^0_{dl}} \qquad (30)$$

Where C^0_{dl} and C^i_{dl} are the double layer capacitance values in the presence and absence of inhibitor respectively.

3.3 Phase III: Analysis the Surface of Mild Steel in the Presence and Absence of Polyvinyl Alcohol- Selected Amino Acid Composites by Surface Analytical Techniques.

3.3.1 Scanning Electron Microscope:

Scanning electron microscopy (SEM) was used to study the morphology of corroded surface in presence and absence of inhibitors. The specimens were thoroughly washed with double distilled water before putting on the slide. The photographs have been taken from that portion of specimen from where better information was obtained. They were photographed at appropriate magnifications. To understand the morphology on the mild steel surface in absence and presence of inhibitors, the following cases have been examined.

- Polished mild steel specimen.
- Mild steel specimen dipped in 1M HCl acid medium.
- Mild steel specimen dipped in 1M HCl acid medium containing 0.6% PVA - selected Amino acid composites inhibitors.

A scanning electron microscope (SEM) was used to evaluate the change in the surface formation caused by contact with the process solutions, and to monitor the effect of adding of the inhibitor. **JEOL MODEL JSM 6360** was used to study the topography of the iron substrate after corrosion in the presence and absence of the inhibitor. Surface examination of the iron substrate in the presence and absence of the inhibitor was carried out by Scanning Electron Microscope.

3.3.2 FTIR Spectral Analysis:

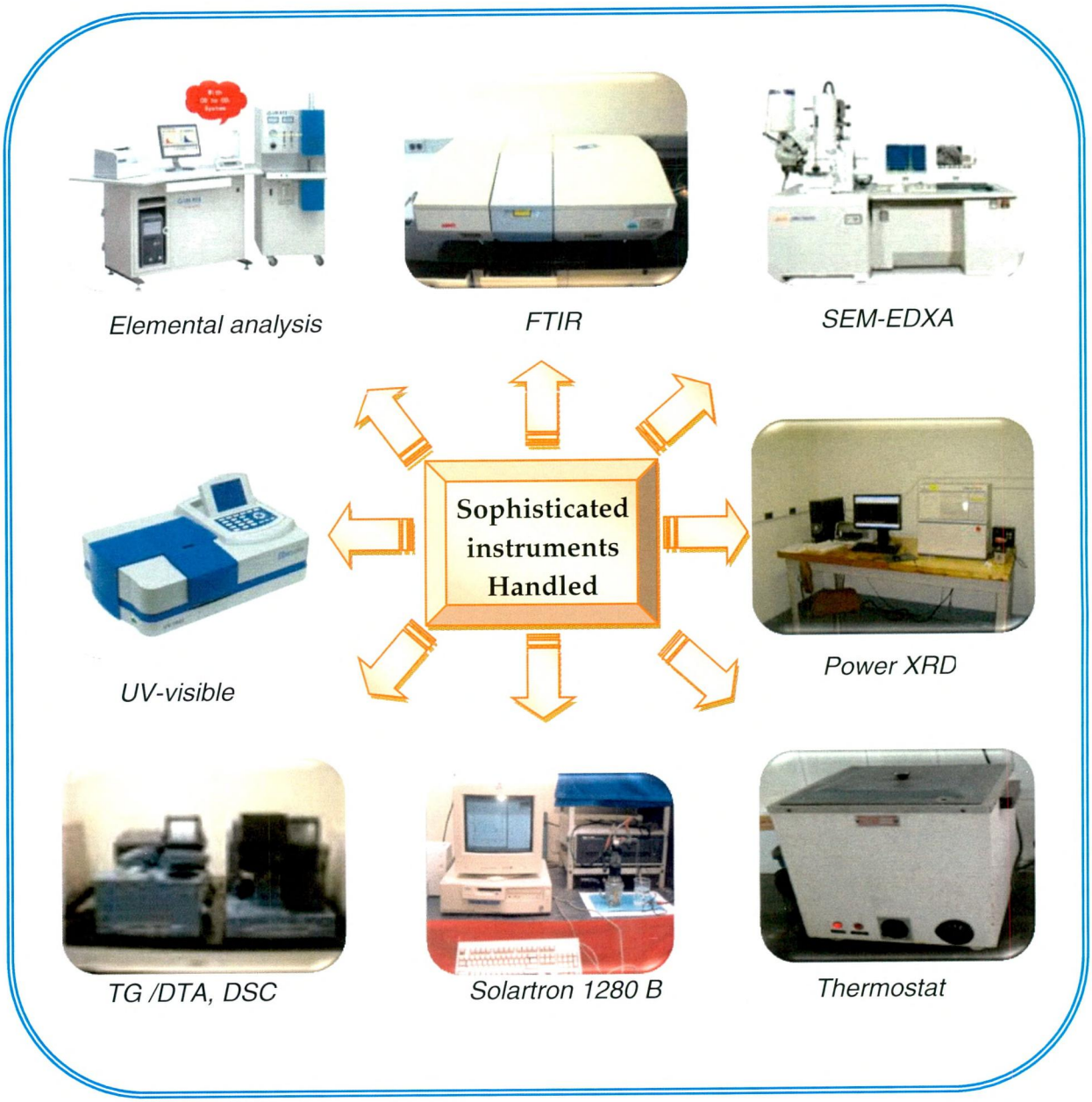
FTIR was recorded using **Nexus 670/ Thermo Electron Corporation Spectrometer** which extended from 4000 and 400 cm^{-1}**.** The interaction between the organic molecules and the metal surface has been studied by FTIR spectra. FTIR spectrometry was used to identify whether there was adsorption and to provide new bonding information on the mild steel surface after immersion (12h) in inhibited 1M HCl solution.

3.3.4 UV Spectrophotometric measurements:

PC based double beam spectrophotometer 2202 was used to confirm the possibility of the Fe-complex formation on mild steel surface. UV-visible absorption spectrophotometric method was carried out on the prepared mild steel samples after immersion in 1M HCl with and without addition of 0.6% PVA- Selected Amino acid composites at 303 K for 12h. Furthermore, it has been reported that change in position of the absorbance maximum and change in the value of absorbance indicate the formation of a complex between two species in solution.

3.4 List of Instruments used and Experimental plans.

Sophisticated Instruments handled during the present investigation are listed in Figure -10



Experimental plans carried out in the current investigation is depicted in the flow chart (Figure -11)

EXPERIMENTAL DESIGN