CHAPTER - 2

Review of literature

CHAPTER II

REVIEW OF LITERATURE

The present study on **"Synthesis, Characterisation And Utilisation of Water Soluble Polyvinyl Alcohol-Selected Amino Acid Composites as Corrosion Inhibitors for Mild Steel in Acid Medium"** is reviewed under the following topics:

- **ORGANIC COMPOUNDS AS CORROSION INHIBITORS**
- **AMINO ACIDS AS CORROSION INHIBITORS**
- **POLYMERS AS CORROSION INHIBITORS**
- **POLYMER COMPOSITE AS CORROSION INHIBITORS**

2.1 ORGANIC COMPOUNDS AS CORROSION INHIBITORS

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur or in some cases selenium and phosphorus. According to **Anand *et al.,* (1965)** the inhibiting properties of many compounds were determined by the electron density at the reaction center. With an increase in the electron density at the reaction center, the chemisorption bonds between the inhibitor and the metal are strengthened.

The effect of a new class of corrosion inhibitors, namely 2,5-disubstituted-1,3,4- oxadiazoles, on the corrosion of mild steel in 1 M HCl and 0.5 M H_2SO_4 were investigated by various corrosion monitoring techniques. Results obtained reveal that these compounds are very good inhibitors and behave better in 1 M HCl than 0.5 M H_2SO_4. Potentiodynamic polarisation studies clearly revealed the type of inhibitor. The oxadiazoles acts on the cathodic reaction without changing the mechanism of the hydrogen evolution reaction. Changes in impedance parameters (R_t and C_{dl}) were indicative of adsorption of the oxadiazole on the metal surface leading to the formation of a protective film which grows with increasing exposure time. The adsorption of oxadiazole derivatives on the mild steel surface in both acidic media followed a Langmuir adsorption isotherm (**Bentiss *et al.,* 2000**).

Sathiyanarayanan *et al.,* (2005a) investigated the inhibitive effect of triethylene tetramine (TETA) and hexamethylene tetramine (HMTA) for mild steel in 1 M hydrochloric acid in the concentration range of 10^{-6} to 10^{-2} M by weight loss, DC polarization methods and AC impedance spectroscopy. Results indicated that the addition of tetramines to the acid reduce the rate of metal attack. For both the amines, inhibition efficiency increases with the concentration of amine. The inhibition efficiency of the hexamethylene tetramine was less when compared to that of triethylene tetramine.

Bouklah *et al.,* (2006a) tested the effect of 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole (4-MOX) on the corrosion inhibition of steel in 0.5 M sulphuric acid using weight loss method, in the range of temperatures from 303 to 343 K. Results obtained revealed that 4-MOX performed excellently as a corrosion inhibitor for mild steel in sulphuric acid media and its efficiency attained more than 96.19% at 8×10^{-4} M at 333 K. The inhibition was assumed to occur via adsorption of the oxadiazole molecules on the metal surface.

Jabeera *et al.,* (2006) analysed the inhibitive effect of tartarate as a corrosion inhibitor with tungstate in preventing carbon steel corrosion in aqueous solutions. Open circuit potential measurements, weight-loss measurements and polarization studies were conducted to understand the domains of corrosion and passivation. Tartarate ions, even at low concentration, showed excellent synergistic corrosion inhibition characteristics. A mixture of 500 ppm each of the inhibitors was found to be optimum inhibitor combination. This inhibitor combination showed inhibition efficiency as high as 98%. Tartarate in the synergistic inhibitor combination did not reveal any dominant role in shifting the surface potential, even though it showed substantial passivation effect.

Bentiss *et al.,* (2007) examined the use of some 4H-triazole derivatives, namely 3,5-diphenyl-4H-1,2,4-triazole (DHT), 3,5-bis(4-pyridyl)-4H-1,2,4-triazole(4-PHT) and 3,5-bis(4-ethyltiophenyl)-4H-1,2,4-triazole (4-MTHT) for corrosion and dissolution protection of mild steel in normal hydrochloric acid solution. The inhibiting efficiency of the different additives was evaluated by means of weight loss and electrochemical techniques such as ac impedance measurements and polarisation curves. The experimental results obtained reveal that 4-MTHT is the best effective inhibitor and the inhibition efficiency was found to be in the following order: 4-MTHT > 4-PHT > DHT. The variation in inhibitive efficiency mainly depends on the type and nature of the substituents present in the inhibitor molecule. Polarisation curves show that these triazoles are mixed-type inhibitors in 1 M HCl. The inhibition efficiency increased with 4H-triazole derivatives concentration and attained a maximum value of 99.6% in the case of 4-MTHT at 5×10^{-4} M. The results obtained from weight loss and electrochemical studies were in reasonable agreement. The adsorption of 4H-triazole derivatives on the steel surface was found to obey the Langmuir isotherm model.

Quarishi *et al.,* (2008) analysed the corrosion inhibition of N-piperidinomethyl)-3-[(pyridine) amino] isatin (PPI) for mild steel in 1 N hydrochloric acid solution by weight loss and potentiodynamic polarization techniques. Various parameters (Ea, ΔG_{ads}, Q, ΔH, ΔS) for adsorption revealed a strong interaction between inhibitor and mild steel surface.

According to **Prabhu *et al.*, (2008)** the corrosion inhibition effect of 3-[(phenylimino)]quinoline-2-thione(PMOT),3{(E)-[4-chlorophenyl)imino] methyl} quinoline-2-thione(CPMQT) and 3{(E)-[4-fluorophenyl)imino]methyl}quinoline-2-thione (FPMQT) on mild steel in 1 mol dm^{-3} HCl using mass loss, polarization and impedance (EIS) methods at 300 K showed that the corrosion rate decreased significantly with increase in the concentration of inhibitors. The shape of polarization profiles of all the three compounds indicated their mixed-type nature of inhibition. The inhibition efficiencies decreased in the order FPMQT>CPMQT>PMQT. The adsorption of the compounds on the mild steel surface was found to obey Langmuir's adsorption isotherm.

Three benzotriazole derivatives namely, 1-(Phenylsulfonyl)-1H-benzotriazole (PSB), 1-(3- Pyridinylsulfonyl)-1H-benzotriazole (3PSB) and 1-(2-Pyridinylsulfonyl)-1H-benzotriazole (2PSB) were investigated for the corrosion of copper in 1M HNO_3 at different concentrations at 25±1°C using chemical (weight loss) and electrochemical (Tafel polarization method) measurements. Generally, inhibition efficiency of the investigated compounds was found to depend on the concentration and the nature of the inhibitors. Quantum chemical calculation results showed that the benzotriazole ring and heteroatoms are the active sites of the three inhibitors. The adsorption behaviour of the studied inhibitors on copper surface has been studied using molecular dynamics (MD) method and density functional theory. The results indicated that the three benzotriazole derivatives could adsorb on the copper surface firmly through the benzotriazole ring and heteroatoms, the three inhibitors afforded excellent corrosion inhibition performance (**Khaled *et al.*, 2009a**).

Rajalakshmi and Subhashini, (2010) studied the inhibition efficiency of Dicyloimine hydrochloride (DCI) on mild steel in 1 M HCl using weight loss method and electrochemical polarization studies. Results revealed that DCI acted as an effective inhibitor in HCl media forming a chemisorbed layer and behaved as a mixed inhibitor.

A molecular dynamics study for the adsorption of three benzimidazole derivatives and their inhibition characteristics was studied using chemical (weight loss) and electrochemical measurements (potentiodynamic polarization and electrochemical impedance spectroscopy, EIS). Results obtained from weight loss, dc polarization and ac impedance measurements were in reasonably good agreement and show increased inhibitor efficiency with increasing inhibitor concentration. The molecular dynamics study revealed that the benzimidazole ring as well as the side chain acts as the active sites in these inhibitors and they absorb on Fe surface by donating electrons to iron d-orbital (**Khaled *et al.,* 2010)**.

The corrosion inhibition of mild steel in a 2.5 M H_2SO_4 solution by 4-amino-5-phenyl-4H-1, 2, 4-trizole- 3-thiol (APTT) was studied at different temperatures, utilising open circuit potential, and potentiodynamic and impedance measurements. The results indicate that APTT performed as an excellent mixed-type inhibitor for mild steel corrosion in a 2.5 M H_2SO_4 solution and that the inhibition efficiencies increased with the inhibitor concentration but decreased proportionally with temperature. The kinetic and thermodynamic parameters for adsorption of APTT on the mild steel surface were calculated. A chemisorption mechanism of APTT molecules on the mild steel surface was proposed based on the thermodynamic adsorption parameters (**Musa *et al.,* 2010a)**.

Musa *et al.,* (2010b) reported the inhibition of the corrosion of mild steel in hydrochloric acid solutions by 4-amino-5-phenyl-4H- 1, 2, 4-trizole-3-thiol (APTT) inhibitor was studied using weight loss technique. Basic kinetic parameters of the corrosion inhibition process were obtained by reaction kinetic equations. Results show that the inhibition increased with increasing of inhibitor concentration. Kinetic calculations show that the maximum value of time for which the corrosion rate increases twice the initial one, while time for which the mass of the sample subjected to corrosion decreases twice the initial one were at 8×10^{-4} M of APTT. The dynamics were described by an exponential kinetic equation of self-accelerating reactions in the absence of inhibitor and by an equation of a zero order in its presence.

Nalini *et al.,* (2011a) carried out the synthesis of O-chlorophenyl-2-imidazoline (OCP2I) and its inhibition behaviour on mild steel corrosion in sulphuric acid and hydrochloric acid media, using weight loss method and electrochemical methods. The results of weight loss method reveal that, the inhibitor attained a maximum efficiency of 84.55% in H_2SO_4 at 200 ppm and 91.42% in HCl medium at 120 ppm of concentration. Thermodynamic parameters indicate physisorption mode of adsorption OCP2I was found to obey Langmuir and Temkin adsorption isotherms. Potentiodynamic polarization and impedance studies were conducted to investigate the mechanism of the inhibition and the present system was found to follow mixed mode of inhibition

A heterocyclic imidazoline, 3, 4, 5-Trimethoxy phenyl-2-imidazolines (TMP2I) was tested for its corrosion inhibition in 0.5 M H_2SO_4 and 1 M HCl using weight loss, Tafel polarisation and electrochemical impedance techniques. The results show that the inhibition efficiency increases with the increase in concentration of TMP2I and a higher efficiency of about 98% was obtained in both the acid media at 200ppm. The adsorption of TMP2I was found to obey Langmuir adsorption isotherm and occurs spontaneously. Cathodic and anodic polarization curves of mild steel in the presence of different concentrations of TMP2I at 30°C reveal that it is a mixed type of inhibitor **(Nalini *et al.*, 2011b).**

Nataraja *et al.*, (2011) investigated the corrosion inhibition effect of 2-[4-(methylthio) phenyl] acetohydrazide (HYD), 2-{[4-(methylthio) phenyl] acetyl} hydrazine carbothioamide (TAD) and 5-[4-(methylthio) benzyl]-4H-1, 2, 4-triazole-3-thiol (TRD) on steel in 1.0 M HCl was investigated by mass loss and electrochemical methods. The effect of concentration, temperature and immersion time was studied. The results indicated that the compounds are efficient, mixed type and pursue Flory–Huggins adsorption isotherm. The inhibition efficiency at lower concentration of inhibitor decreased with temperature while at higher concentration, it is retained and the calculated free energy attributes this to comprehensive adsorption. The efficiency stands in the order TRD > TAD > HYD and is confirmed by the Quantum studies.

Abdel-Rehim *et al.*, (2011) reported the corrosion and corrosion inhibition of iron in HCl solutions in the absence and presence of pyrazole (PA) by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Changes in impedance parameters (R_{ct} and C_{dl}) were indicative of the adsorption of PA on the iron surface. The adsorption of PA was found to obey Langmuir adsorption isotherm. The study suggests that the compound behaved as an anodic inhibitor.

The inhibition of mild steel corrosion in a 2.5 M H_2SO_4 solution by 4, 4-dimethyl-3-thiosemicarbazide (DTS) was studied at 30°C using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Quantum chemical parameters were calculated for DTS using PM3-SCF method. The molecular dynamic method was performed to simulate the adsorption of the DTS molecules on Fe surface. Results showed that DTS performed excellent as inhibitor for mild steel corrosion in a 2.5 M H_2SO_4 solution and indicated that the inhibition efficiencies increase with the concentration of inhibitor. Theoretical results indicated that DTS could adsorb on the mild steel surface firmly through heteroatom (**Musa *et al.*, 2011**).

2.2 AMINO ACIDS AS CORROSION INHIBITORS

The corrosion behaviour of a copper electrode in a 1 M HCl solution was studied potentiokinetically at different temperatures ranging from 25 to 55°C. The inhibition efficiency of four amino acids was then tested for three concentrations in the range 10^{-5}-10^{-3} M. The protection efficiency of each amino acid was calculated for different temperatures and concentrations. The amino acids function as a corrosion inhibitor in HCl solution through adsorption on the copper surface. The kinetic results, operating through a compensation effect, could well account for the variation of the inhibiting capacities of the various amino acids. The results reported in this paper elucidate the effect of temperature and the molecular structure on the inhibition efficiency. α-alanine was the most efficient of the four amino acids for inhibiting the corrosion of copper in HCl solution. (**Gomma *et al.,* 1994**).

Morad *et al.,* (2002) reported the action of four amino acids containing sulphur on the corrosion of mild steel in phosphoric acid solution with and without Cl^-, F^- and Fe^{3+} ions near and as the corrosion potential (E_{corr}) using both the polarization resistance method and electrochemical impedance spectroscopy (EIS). Both cysteine and N-acetyicysteine (ACC) showed higher inhibition efficiency than methionine and cystine. Adsorption of methionine on to a mid steel surface obeyed the Frumkin adsorption isotherm and had a free energy of adsorption value (ΔG°_{ads}) lower than those obtained in the presence of cystine, cysteine and ACC whose adsorption isotherms followed Langmuir.

The effect of some amino acid compounds: glycine, leucine, dl- aspartic, arginine and methionine on the corrosion behaviour of pure iron in citric acid solution at pH = 5 was investigated by weight-loss, polarisation and EIS measurements. Results obtained show that methionine was the best inhibitor and its efficiency reached 96% at 2×10^{-2} M. Polarisation measurements showed that the compounds tested were cathodic inhibitors. Methionine adsorbed on the iron surface according to the Temkin isotherm model (**Zerfaouia *et al.,* 2004**).

The inhibition effects of tryptamine (TA) on the corrosion behaviour of ARMCO iron in 0.5 M deaerated H_2SO_4 (in the 25–55°C temperature range) was studied in both short and long time tests (1, 24 and 72 h) by means of potentiodynamic curves (PCM) and electrochemical impedance spectroscopy (EIS). TA was found to be an effective ARMCO iron inhibitor furnishing 90-99% IP%. TA adsorption followed Bockris–Swinkels' isotherm (x = 1). The thermodynamic data indicated that, in the more concentrated solutions, TA also chemisorbed on the iron surface (**Moretti *et al.,* 2004**).

The inhibition effect of three amino acids - alanine, glycine and leucine against steel corrosion in HCl solutions has investigated by potentiodynamic polarization method. Corrosion data such as corrosion rate, corrosion potential (E_{corr}) and corrosion resistance (R_p) were determined by extrapolation of the cathodic and anodic Tafel region. Adsorption isotherm was investigated by weight-loss measurement. The effect of inhibitor concentration and acid concentration against inhibitor action was investigated. The inhibition efficiency (IE) depended on the type of amino acid and its concentration. The inhibition effect ranged from 28 to 91%. The amino acids acted as corrosion inhibitors in HCl solution through adsorption on the steel surface and adsorption followed Langmuir isotherm **(Ashassi-Sorkhabia *et al.,* 2004)**.

Corrosion inhibition of steel in hydrochloric acid by decylamides of α-amino acids derivatives was studied using gravimetric and electrochemical techniques. Protection efficiencies of 90% were obtained with 100 ppm of tyrosine and glycine derivatives, while alanine and valine derivatives reached only 80%. The order of increasing inhibition efficiency was correlated with the modification of the molecular structure of inhibitors. Potentiodynamic polarization curves indicated that both the decylamide of tyrosine and glycine acted primarily as anodic type inhibitors, whereas the decylamide of alanine and valine were of the cathodic type. Thermodynamic parameters and Flory–Huggins adsorption isotherms described the experimental findings. The number of active sites, equilibrium constant, enthalpy and change of free energy were computed for all inhibitors studied. This information suggested that organic molecules were adsorbed and displaced water molecules from the steel surface. X-ray photoelectron spectroscopy confirmed that species of N, C and O interacted with steel to form a continuous protective film (**Olivares *et al.*, 2006)**.

The corrosion inhibition of mild steel in sulphuric acid by methionine (MTI) was investigated using electrochemical techniques. The effect of KI additives on corrosion inhibition efficiency was also studied. The results reveal that MTI inhibited the corrosion reaction by adsorption onto the metal/solution interface. Inhibition efficiency increased with MTI concentration and synergistically increased in the presence of KI, with an optimum [KI]/[MTI] ratio of 5⁄5, due to stabilization of adsorbed MTI cations as revealed by AFM surface morphological images. Potentiodynamic polarization data suggest that the compound functioned via a mixed-inhibition mechanism (**Oguzie *et al.,* 2007)**.

Influence of hydrodynamic conditions on the behavior of l-methionine (l-MTI) as a green organic inhibitor was studied using mild steel rotating disc electrode. Electrochemical impedance spectroscopy (EIS) and polarization measurements were carried out in the absence and presence of inhibitor in 1 M H_2SO_4 solution under static conditions and at different rotation speeds; the inhibitor concentration was 5×10^{-3}M in all tests. The open circuit potentials (OCP) were measured versus time in all studied rotation speeds; it was found that the OCP shifted toward more positive potentials as the rotation speed increased. It was also found that the higher rotation speeds increased efficiencies were observed. This behavior could be attributed to the enhanced mass transport of inhibitor molecules from bulk to the metal surface in high rotation rates **(Ashassi-Sorkhabi *et al.,* 2008)**.

The inhibition effect of five amino acids (AA) on the corrosion of copper in molar nitric solution was studied by using weight loss and electrochemical polarization measurements. Valine (Val) and Glycine (Gly) accelerated the corrosion process; but Arginine (Arg), Lysine (Lys) and Cysteine (Cys) inhibited the corrosion phenomenon. Cysteine is the best inhibitor. Its efficiency increased with the concentration to attain 61% at 10^{-3} M. Correlation between the quantum chemical calculations and inhibition efficiency was discussed using semiempirical methods (AM1 and MNDO) (**Barouni *et al.*, 2008).**

Monte Carlo simulations technique incorporating molecular mechanics and molecular dynamics were used to simulate the adsorption of methionine derivatives, namely L-methionine, L-methionine sulphoxide and L-methionine sulphone, on iron (110) surface in 0.5 M sulphuric acid by **Khaled *et al.*, (2009b).** Results show that methionine derivatives have a very good inhibitive effect for corrosion of mild steel in 0.5 M sulphuric acid solution. Tafel polarisation studies showed that methionine derivatives function as mixed-type inhibitors, and their inhibition mechanism was adsorption assisted by hydrogen bond formation. Impedance results indicated that the values of the constant phase element tend to decrease with increasing methionine derivatives concentrations due to the increase in the thickness of the electrical double layer. In addition, both polarisation resistance and inhibition efficiency IE (%) tend to increase with increasing inhibitors concentrations due to the increase of the surface coverage, i.e., the decrease of the electrochemical active surface area. The quantum mechanical approach may well be able to foretell molecular structures that are better for corrosion inhibition.

The inhibiting effect of methionine and tyrosine on the corrosion of iron in 0.1M HCl was carried out by electrochemical measurements. Quantum chemical calculations were performed with an increase in the concentration of inhibitor, the effectiveness of inhibitor increased. The highest inhibition was determined as 97.8% at 100 ppm methionine and tyrosine adsorbed on the iron surface according to Langmuir isotherm **(Zor *et al.*, 2009)**.

To correlate the inhibition efficiencies of a total of 12 amino acids for the corrosion of nickel in acidic medium, with the structure a density functional theory (DFT) study was carried out using the B3LYP/LANL2DZ method. Quantum chemical descriptors such as the energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), and the energy gap (ΔG) were calculated. Equations were proposed using linear regression analysis to determine the most effective parameter on inhibition efficiency. The theoretically obtained results were found to be consistent with the experimental data reported (**Gokhan Gece *et al.,* 2010).**

The performance of three selected amino acids, namely alanine (Ala), cysteine (Cys) and S-methyl cysteine (S-MCys) as safe corrosion inhibitors for iron in aerated stagnant 1.0 M HCl solutions was evaluated by Tafel polarization and impedance measurements. Results indicated that Ala acts mainly as a cathodic inhibitor, while Cys and S-MCys function as mixed-type inhibitors. The order of inhibition effect was found to be cys > S-MCys > Ala. Molecular dynamics (MD) and density functional theory (DFT), were also employed to establish the correlation between the structure (molecular and electronic) of the three tested inhibitors and the inhibition efficiency. Experimental and theoretical results were in good agreement (**Amin *et al.,* 2010).**

Electrochemical corrosion behaviour of aluminum alloy Al7075 and its corrosion inhibition using L-glutamine in 3.5% NaCl solution under different hydrodynamic conditions was studied. The hydrodynamic conditions were simulated by using a rotating disc electrode. The results showed that an increase in rotation speed leads to a higher corrosion current density, while the charge transfer resistance decreases and corrosion potential shifts towards more positive values. The inhibition efficiency was found to depend on rotation speed. The efficiency was low in stagnant solution, but enhanced significantly under hydrodynamic conditions. The phenomenon was attributed to the increased mass transport of inhibitor's molecules to the electrode surface (**Ashassi-Sorkhabi *et al.,* 2010).**

The inhibition behavior of low carbon steel in 1 M HCl by L-tryptophan was investigated with weight loss experiment and Tafel polarization curve in the used temperature range (298–328 K). All the experimental results show that L-tryptophan exhibited excellent corrosion inhibition performance and the most effective concentration of inhibitor is 1.9×10^{-2} mol L^{-1}. The Tafel polarization curve results indicated that L-tryptophan acted more as a cathodic than anodic inhibitor. The adsorption of L-tryptophan on the surface of low carbon steel obeyed the Langmuir adsorption isotherm. The adsorption behavior of L-tryptophan at Fe surface (1 1 0) was also investigated by the molecule dynamics simulation method and density functional theory. The results indicated that the L-tryptophan could adsorb firmly on the Fe surface through the indole ring with p-electrons and nitrogen/oxygen atom with lone-pair electrons in its molecule (**Jia-Jun Fu *et al.,* 2010).**

Substituent constants and quantum chemical parameters were calculated from PM6, PM3, AM1, RM1 and MNDO. Hamiltonians were used to predict the corrosion inhibition potential of nine amino acids grouped under three skeletons.

Skeleton I consisted of cysteine (CYS), serine (SER) and amino butyric acid (ABU). Those in skeleton II included threonine (THR), alanine (ALA) and valine (VAL) while those in skeleton III are aromatic amino acids, which included phenylalanine (PHE), tryptophan (TRP) and tyrosine (TYR). The results obtained from quantum chemical parameters indicated that the trends for the variation of corrosion inhibition potentials of the studied amino acids in skeletons I, II and III are CYS> SER >ABU, THR > ALA > VAL and TRP> TYR > PHE, respectively (**Nnabuk O. Eddy *et al.,* 2010a).**

The corrosion inhibition behaviour of four selected amino acid compounds, namely L-cysteine, L-histidine, L-tryptophan and L-serine on mild steel surface in deaerated 1 M HCl solution were studied electrochemically by Tafel polarization and electrochemical impedance spectroscopy methods and computationally by the quantum chemical calculation and molecular dynamics simulation. Electrochemical results show that these amino acid compounds inhibit the corrosion of mild steel in 1 M HCl solution significantly. The electrochemical experimental results are supported by the theoretical data **(Jia-jun Fu *et al.,* 2010).**

Gokhan Gece and Semra Bilgic, (2010) evaluated the inhibition efficiencies of a total of 12 amino acids for the corrosion of nickel in acidic medium with the help of a density functional theory (DFT) study using the B3LYP/LANL2DZ method. Quantum chemical descriptors such as the energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), and the energy gap (ΔE) calculated reveal that theoretically obtained results were consistent with the experimental data reported.

Azza El-Sayed El-Shenawy, (2011) investigation the corrosion inhibition of 316 L stainless steel in 0.5 M H_2SO_4 by lysine investigated using open-circuit potential measurements, potentiodynamic polarization measurements and scanning electron microscopy (SEM) techniques. The open circuit potentials were measured in the absence and presence of different concentrations of lysine. It was found that the open circuit potential becomes more positive with increase in the concentration of lysine. Potentiodymanic polarization measurements reveal that the presence of lysine in acidic solution effects mainly the cathodic process and decreases the corrosion current to a great extent and shifts the corrosion potential towards more negative values. The maximum inhibition efficiency of lysine was achieved at (7×10^{-2} M).

The inhibition effect of four amino acids on the corrosion of 316L stainless steel in 1.0 M H_2SO_4 has been studied by open-circuit potential and potentiodynamic polarization measurements. The results reveal that Glycine, Leucine and Valine inhibit the corrosion process, whereas Arginine accelerated the corrosion phenomenon. Glycine has the highest inhibition efficiency, its efficiency increased with increasing the concentration to attain 84.2% at 0.1 M. Different behaviours were observed, in case of Arginine, corrosion rate increased with increasing concentration. These results show that the presence of Arginine at high concentration turns the surface of 316L stainless steel electrochemically active, probably dissolving the passivation layer and promoting the stainless steel anodic dissolution (**Abdel Ghanyl *et al.,* 2011)**.

Eddy *et al.,* 2011 studied the Inhibition and adsorption potentials of cysteine, glycine, leucine and alanine for the corrosion of mild steel in hydrochloric acid (HCl) solution semi empirical ab-nitio, gravimetric, gasmetric, thermometric and QSAR methods. The results obtained indicated that various concentrations of the studied amino acids inhibited the corrosion of mild steel in HCl solution through physiosorption. The inhibition potentials of the inhibitors decreased in the order, cysteine > leucine > alanine > glycine. The adsorption of the inhibitors on mild steel surface was found to be exothermic, spontaneous and supported the Langmuir adsorption model. Results obtained from quantum chemical studies show excellent correlations between quantum chemical parameters and experimental inhibition efficiencies (for gas and aqueous phases using density functional theory (DFT) and Moller-Plesset (MP2) perturbations.

The corrosion inhibition of Mg–Al–Zn alloy was investigated in stagnant naturally aerated chloride free neutral solutions using amino acids as environmentally safe corrosion inhibitors. The corrosion rate was calculated in the absence and presence of the corrosion inhibitor using the polarization technique and electrochemical impedance spectroscopy. The corrosion inhibition process was found to depend on the adsorption of the amino acid molecules on the metal surface. Phenyl alanine reveals remarkably high corrosion inhibition efficiency up to 93% at a concentration of 2×10^{-3} mol dm^{-3}. The corrosion inhibition efficiency was found to depend on the concentration of the amino acid and its structure **(Helal et *al.,* 2011).**

Fouda et al., 2011 the inhibition effect of three amino acids (valine (val), alanine (ala) and glycine (gly)) on the corrosion of Cu10Ni alloy in sulfide-polluted salt water (3.5 % NaCl + 16 ppm S^{2-}) using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM), scanning electron microscopy (SEM) and energy dispersive X-ray diffraction (EDX). The polarization measurements reveal that the tested compounds act as mixed-type inhibitors. Results obtained from the different techniques reveal that the inhibition efficiency (%IE) follows the sequence: val > ala > gly. A synergistic effect was observed between these inhibitors and KI. SEM showed a remarkable inhibiting effect of these additives due to the protective film formed on the alloy surface confirmed by the presence of the carbon and nitrogen atoms in the EDX spectra. The adsorption of these inhibitors was found to be of a physisorption mode and obey Langmuir's adsorption isotherm.

2.3 POLYMERS AS CORROSION INHIBITORS

2.3.1 Polymers as Corrosion Inhibitors for Mild Steel

Manickavasagam *et al.*, (2002) synthesised Poly(styrenesulphonic acid)-doped polyaniline and reported the influence of this polymeric compound on the corrosion inhibition of mild steel in 1M HCl using weight loss measurements, galvanostatic polarisation studies, electro permeation studies and a.c. impedance measurements. The polymer acted predominantly as an anodic inhibitor. Hydrogen permeation studies and a.c. impedance measurements clearly indicate a very effective performance of the compound as corrosion inhibitor. The adsorption of the compound on the mild steel surface was found to obey Temkin adsorption isotherm.

The inhibiting effect of 2, 6 ionen, 2, 10 ionen, polyvinylbenzyltrimethyl ammonium chloride (PVBTMA) and latex on low carbon steel in HCl solution was investigated by potentiodynamic polarization measurements and EIS technique over a temperature range 20-60°C at different inhibitor concentrations. It was found that the inhibition efficiencies increased with the increase in inhibitor concentration. Results obtained also reveal that the inhibitor behaved as anodic inhibitor **(Bereket *et al.*, 2003).**

Mekki Daouadji *et al.*, (2004) investigated two forms of polymers namely red form with molecular weight of (800,000 g mol^{-1}) insoluble in alcohol and green form with low molecular weight (44,000 g mol^{-1}) and soluble in alcohol obtained by polymerization of ortho-ethoxyaniline as corrosion inhibitors for mild steel in acidic media. The obtained results showed the adsorption of the polymer alcoholic form obeyed Temkin adsorption isotherm with no significant change as function with inhibition efficiencies for a series of molecular weights ranging from 123,000 to 124,000 g mol^{-1}.

Selvaraj *et al.*, (2004) reported the inhibition efficiency of polyvinyl pyrrolidone (PVP) in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-, in the absence and the presence of Zn^{2+} using weight loss method. Influence of pH, immersion period, N-cetyl- N,N,N-trimethyl ammonium bromide and sodium dodecylsulphate on the inhibition efficiency of the inhibitor system was investigated and the nature of the protective film analyzed by FTIR and fluorescence spectroscopy. In the presence of PVP, the protective film consisted of Fe^{2+} - PVP complex; the film was found to be UV fluorescent. In the presence of PVP and Zn^{2+}, the protective film consists of Fe $^{2+}$ - PVP complex and $Zn(OH)_2$; it was found to be UV-fluorescent.

The corrosion and inhibition behavior of mild steel in 1M HCl in the presence of poly(4- vinylpyridine) (P4VP) and potassium iodide (KI) was investigated using weight loss measurements, potentiodynamic polarization studies and impedance measurements. The inhibition efficiency increased with increasing P4VP concentration. The inhibiting action of P4VP was considerably enhanced by the addition of potassium iodide. The adsorption of this compound either alone or in combination with iodide ions on the metal surface was found to obey Lamgmir's adsorption isotherm. The presence of P4VP + KI in the solution decreased the double layer capacitance and increased the charge transfer resistance, both derived from Nyquist plots obtained from a.c. impedance studies. The variation of charge transfer resistance with time suggested that the inhibitive action of (P4VP + KI) depended mainly on the protective inhibitor film formed on the steel surface (**Larabi *et al., 2004*).**

Ashassi-Sorkhabi *et al.,* (2005) studied the inhibitive effects of different polyethylene glycols of varying molecular weight (200 – 10,000 g /mol) on carbon steel corrosion in 3 N H_2SO_4 using weight loss, polarization and electrochemical impedance spectroscopy. Results obtained showed that the PEGs were effective corrosion inhibitors for carbon steel in the acidic environment. It was found that PEG has an inhibiting effect on the corrosion process and the inhibition efficiency was more than 90%. The studied polymers were physically adsorbed on the carbon steel surface in the acid medium. The results from the three independent methods employed were in good agreement.

Rajendran *et al.,* (2005) investigated the corrosion behaviour of carbon steel using polyvinyl alcohol (PVA) in neutral aqueous solution containing 60ppm of Cl^- in the absence and presence of Zn^{2+} ions using weight loss method. It was found that a formulation consisting of 100ppm of PVA and 75ppm Zn^{2+} offered 81% inhibition efficiency to carbon steel immersed in a solution containing 60ppm of Cl^-. A synergistic effect on inhibition of a combination of PVA and Zn^{2+} was observed during the tests. Increase in pH and duration of immersion led to increase in inhibition efficiency of the PVA – Zn^{2+} system.

Umoren *et al.,* (2006) reported the corrosion inhibition of mild steel in H_2SO_4 at 30 – 60°C by polyethylene glycol (PEG) and polyvinyl alcohol (PVA) using weight loss and hydrogen evolution techniques. The inhibition efficiency of the inhibitor increased with increase in concentration and temperature. The inhibitors were found to obey Temkin, Freudlich and Langmuir adsorption isotherms. The phenomenon of chemical adsorption was proposed from the activation parameters obtained. PEG was found to be a better inhibitor than PVA.

Ashassi-Sorkhabi *et al.,* (2006) evaluated the inhibition effect of some Polyethylene glycols (PEGs) on carbon steel corrosion at 25°C in 0.5 N HCl as corrosive medium using weight loss, polarization and electrochemical impedance spectroscopy techniques. In order to study the effect of PEGs' structure on the inhibition efficiency, different molecular weights: 400, 1000, 4000 and 10,000 $gmol^{-1}$ was selected. Results obtained show the effectiveness of polyethylene glycols on corrosion inhibition of C-steel in HCl solution. The inhibition efficiency was found to increase with increase in mean molecular weight of the polymer and its concentration. The adsorption of the studied polymers on C-steel was found to obey Langmuir isotherm.

The corrosion inhibition of mild steel in 1 M H_2SO_4 using polyacrylamide (PA) in the presence of iodide ions was studied at 30–60°C using weight loss and hydrogen evolution methods. Results obtained showed that inhibition efficiency increased with increase in concentration of PA and decreased with increase in temperature. The inhibition efficiency of PA synergistically increased on addition of KI. The adsorption of PA alone and in combination with iodide ions on the metal surface was found to obey Freundlich, Temkin and Flory–Huggins adsorption isotherms at all temperatures studied. Phenomenon of physical adsorption was proposed from the values of Ea and ΔG_{ads} obtained. Synergism parameter evaluated is found to be greater than unity for all concentrations of PA indicating that the enhanced inhibition efficiency of PA caused by addition of iodide ion was only due to synergism. Adsorption of PA and (PA+ KI) on to mild steel surface was found to be in nature spontaneous (**Umoren *et al.,* 2007a).**

New macrocyclic polyether compounds containing a 1, 3, 4-thiadiazole moieties were prepared to study the corrosion inhibitive effect of mild steel in normal hydrochloric acid solutions by weight loss and EIS methods. The results of these investigations have shown enhancement in inhibition efficiencies with the extent of the polyethylene glycol unit that forms a cavity. Data obtained from EIS show a frequency distribution and therefore a modelling element with frequency dispersion behaviour, a constant phase element (CPE) was used (**Lebrini *et al.,* 2007)**

The corrosion inhibition of mild steel in 1 N sulphuric acid solution by PEGME was studied in relation to the concentration of the inhibitor as well as the temperature using electrochemical polarization (galvanostatic and potentiostatic) techniques. The results were supplemented with scanning electron microscopy and infra-red spectroscopy. All the methods employed were in reasonable agreement. Adsorption of PEGME was found to follow the Langmuir's adsorption isotherm. PEGME acted as a mixed type of inhibitor (**Dubey *et al.*, 2007).**

The corrosion protection and/or adsorption of polyacrylamide (PAA) of number average molecular weight, *M n*, between 15,000 – 1,350,000 g mol^{-1} on mild steel and iron (99.99 % Fe) in 3 M HCl at room temperature was studied using spectrophotometry (the phenanthroline method), weight loss method and EIS techniques. It was found that the corrosion protection efficiency of the PAA – adsorbed layers strongly depended on both the molar concentration of PAA in the solution and its molecular weight, reaching limiting values between 85 and 96 %. The experimentally obtained results follow Langmuir adsorption isotherm (**Dragica chamovska *et al.*, 2007).**

The corrosion inhibition of mild steel in 1 M H_2SO_4 in the presence of polyvinylpyrolidone (PVP) and polyacrylamide (PA) as inhibitors at 30 – 60°C was studied using gravimetric and gasometric techniques **(Umoren *et al.,* 2008a)**. Results obtained indicate that increase in temperature increased the corrosion rate in the absence and presence of the inhibitors but decreased the inhibition efficiency. The inhibition efficiency increased with increase in concentration of the inhibitors. Both PVP and PA were found to obey Temkin and El- Awady *et al.* kinetic-thermodynamic adsorption isotherm at all the concentrations and temperatures studied. Physiosorption mechanism was proposed from the activation parameters obtained. PVP was found to be a better inhibitor than PA.

Gum Arabic (GA) (a naturally occurring polymer) was reported as an inhibitor for inhibition of mild steel corrosion in H_2SO_4 at 30 – 60°C using weight loss, evolution and thermometric measurements **(Umoren *et al.,* 2008b)**. Inhibition process was afforded by virtue of chemical adsorption of GA components onto mild steel surface following Temkin adsorption isotherm. Inhibition efficiency increased with increase in GA concentration as well as temperature rise. It was also found from the kinetic/thermodynamics studies that adsorption of GA onto mild steel surface was spontaneous.

The corrosion inhibition of mild steel in 1 M H_2SO_4 by polyvinyl pyrrolidone (PVP) and the synergistic effect of iodide ions were investigated using weight loss and hydrogen evolution methods in the temperature range of 30-60°C. The corrosion rates of mild steel decreased with the increasing concentration of PVP, while the inhibition efficiency (%I) increased. The inhibition efficiency of PVP decreased with rise in temperature, suggesting a physical adsorption mechanism, which was found to follow Freundlich and Temkin adsorption isotherms. The inhibiting action of PVP was considerably enhanced in the presence of iodide ions and values of the synergism parameter (S1) revealed synergistic interactions between PVP and iodide ions (**Umoren *et al.*, 2008c).**

The corrosion inhibition of mild steel in H_2SO_4 in the presence of gum arabic (GA) (naturally occurring polymer) and polyethylene glycol (PEG) (synthetic polymer) was studied using weight loss, hydrogen evolution and thermometric methods at 30-60°C. PEG was found to be a better inhibitor for mild steel corrosion in acidic medium than GA. The effect of addition of halides (KCl, KBr and KI) was also studied. Results obtained showed that inhibition efficiency (IE %) increased with increase in GA and PEG concentration, addition of halides and with increase in temperature. GA and PEG alone and in combination with halides were found to obey Temkin adsorption isotherm. Phenomenon of chemical adsorption was proposed from the trend of inhibition efficiency with temperature and values ΔG^o_{ads} obtained. The synergism parameter, SI evaluated was found to be greater than unity indicating that the enhanced inhibition efficiency caused by the addition of halides was only due to synergism **(Umoren *et al.,* 2008d).**

Quraishi and Sudhish Kumar Shukla, (2009) effectuated the corrosion inhibition of poly (aniline-formaldehyde) on mild steel in 1 N HCl by potentiodynamic polarization, linear polarization, and electrochemical impedance spectroscopy and weight loss measurements. Results obtained show that poly (aniline-formaldehyde) acted as mixed inhibitor and it inhibits mild steel corrosion through adsorption mechanism. It showed >90% inhibition efficiency at 10 ppm. AFM clearly revealed that surface roughness of inhibited mild steel sample is less than uninhibited mild steel.

The inhibition properties of the electro-prepared P (o-phenylenediamine), P(oPD), on the corrosion rate of mild steel (MS) in HCl solutions were investigated under different experimental conditions using weight loss and potentiodynamic polarization techniques. The data obtained from the two techniques were comparable and revealed that the presence of P(oPD) in the acid solutions suppresses the corrosion rate of MS indicating that the polymer acted as corrosion inhibitor. The inhibition efficiency (IE %) of the polymer enhanced with increasing concentration and decreased with increase in temperature. The inhibition occurred through adsorption and formation of barrier film on the metal surface which separated the metal from direct contact with the corrosive medium and hence protected the metal against the corrosion. Langmuir isotherm fitted well with the experimental data (**Abd El Rehim, *et al.*, 2010).**

2.3.2 Polymers as Corrosion Inhibitors for Iron

The inhibitive action of ortho-methoxy substituted polyaniline poly (o-methoxy-aniline), a new class of conducting polymer on the corrosion of iron in acidic chloride solution evaluated by Electrochemical Impedance Spectroscopy (EIS), Linear polarization Resistance (LPR), weight loss (WL) and by Logarithmic Polarization Technique (LPT). Inhibition efficiencies of nearly 80-88% were observed even at 25 ppm concentration. Double-layer capacitance studies indicate a strong adsorption of the polymer following Temkin adsorption isotherm **(Sathiyanarayanan *et al.,* 1994).**

Polarization and weight loss studies showed that both polyvinylpyrrolidonc and polyethylenimine are effective for the inhibition of low carbon steel over a wide concentration range of aqueous phosphoric acid solutions. Both polymers retard the anodic and cathodic corrosion reactions with emphasis on the former (**Jtanguo *et al.,* 1995).**

The corrosion rates of mild steel in neutral aqueous environment containing 60 ppm chloride in the absence and presence of polyacrylamide (PAA), phenyl phosphonate (PPA) and Zn^{2+} were evaluated by the weight-loss method. The formulation consisting of 50 ppm PAA and 50 ppm Zn^{2+} and also the 50 ppm Zn^{2+}±300 ppm PPA system showed synergistic effects (the inhibition efficiency of the latter remain the same after the addition of 50 ppm PAA) while the formulation consisting of 50 ppm PAA and 300 ppm PPA showed an antagonistic effect (**Susai Rajendran *et al.*, 1998).**

The influence of addition of poly (4-vinylpyridine) P4VP of two average degree of polymerization on the corrosion of Armco iron in 1M H_2SO_4 was studied using weight loss, potentiodynamic, polarization resistance and AC impedance (EIS) techniques. Results obtained show that both polymers reduce corrosion rates and that the compounds act essentially as cathodic inhibitors **(Abed *et al.,* 2001).** The inhibition efficiencies obtained from cathodic Tafel plots, polarisation resistance, EIS and gravimetric methods were in good agreement. The inhibitors were adsorbed on the iron surface according to the Frumkin adsorption isotherm. Polarisation measurements indicated that the compounds act essentially as cathodic inhibitors.

The effect of poly (4-vinylpyridine isopentyl bromide) (P4VPIPBr) in three degrees of quaternisation (6, 18 and 79%) on the corrosion of pure iron in molar sulphuric acid was investigated by potentiodynamic, polarisation resistance and weight loss measurements. The inhibition efficiency (I*E* %) of P4VPIPBr increased with its concentration to attain 100% around 5×10^{-6} M. I*E*% values obtained from the various methods were in good agreement. Polarisation measurements showed also that the compound act as a cathodic inhibitor and adsorbed on the pure iron surface according to the Frumkin adsorption isotherm model (**Chetouani *et al.*, 2003).**

The influence of poly(4-vinylpyridine-poly(3-oxideethylene)tosyle) P4VPPEO5000Ts, on the corrosion inhibition of iron in molar sulphuric acid solution was studied using weight-loss, polarisation resistance, potentiodynamic and EIS measurements. P4VPPEO5000Ts was found to be an excellent inhibitor and its inhibition efficiency increased with the increase of concentration to attain 100% at 2.5×10^{-8}M. Potentiodynamic polarisation studies clearly reveal that the inhibitor acted as a mixed-type inhibitor. Adsorption of this compound on iron surface followed Frumkin adsorption isotherm model **(Chetouani *et al.*, 2004).**

Octylphenol polyethylene oxide (OPPEO), was evaluated as an inhibitor for corrosion of low-carbon steel in 0.5M H_2SO_4. Potentiodynamic and potentiostatic methods and scanning electron microscopy were used to study the inhibition effectiveness of the OPPEO. The inhibition efficiency was found to increase with the inhibitor concentration and decrease with temperature. OPPEO showed higher constant protection efficiency near its critical micelle concentration. The activation energy of corrosion was found to be higher in presence than in absence of the inhibitor. The experimental data were fitted with the Flory–Huggins isotherm at a molecular ratio of 5:1. The Gibbs energy of adsorption decreased with the temperature. The inhibitor had relatively lower inhibition efficiencies at ambient and higher temperature. This was attributed to the molecular structure of the inhibitor (**Algaber *et al.*, 2004).**

The inhibitor performance of chemically synthesized water soluble poly(aminoquinone) (PAQ) on iron corrosion in 0.5 M sulphuric acid was studied in relation to inhibitor concentration using potentiodynamic polarization and electrochemical impedance spectroscopy measurements. On comparing the inhibition performance of PAQ with that of the monomer o-phenylenediamine (OPD), the OPD gave an efficiency of 80% for 1000 ppm while it was 90% for 100 ppm of PAQ. PAQ was found to be a mixed inhibitor (**Jeyaprabha *et al.*, 2005a).**

The influence of poly (aminoquinone) (PAQ) on corrosion inhibition of iron in 0.5M H_2SO_4 was reported using potentiodynamic polarization and electrochemical impedance spectroscopy measurement **(Sathiyanarayanan *et al.*, 2005b)**. The inhibitive performance of PAQ was compared to that of its monomer o-phenylenediamine (OPD) and was found that the inhibition performance of PAQ was better than OPD. This may be attributed to the presence of extensive delocalized π electrons. A maximum inhibition efficiency of 90% at 100ppm was obtained for PAQ while an efficiency of 80% at 1000ppm was obtained for OPD. PAQ was found to be a mixed inhibitor. Adsorption of PAQ followed Temkin adsorption isotherm.

The effect of polyvinylpyrrolidone (PVP) on the corrosion resistance of steel reinforced concrete was assessed by measuring the corrosion potential, linear polarization resistance and AC impedance during 60 days immersion in NaCl and NaCl + PVP solutions. Polarization resistance (R_p) values of PVP added reinforced concrete were much higher than those without PVP. The relationship between corrosion potential and linear polarization resistance was analysed. Results from corrosion potential measurements were well comparable with the linear polarization resistance data. AC impedance spectra reveal that the resistance of PVP mixed electrodes was also quite higher than the other electrodes. (**Gurten *et al.*, 2005)**.

The synergistic effect of halide ions on the inhibition of corrosion of iron in 0.5 M H_2SO_4 solutions by polyaniline was studied by polarization and impedance methods. Addition of 0.5 10^{-3}M I^- ions enhanced the inhibition efficiency of polyaniline at 10 ppm from 53% to 90%. However in the case of bromide and chloride ions, the inhibition efficiency of polyaniline at 50 ppm increased from 71% to 90%. The synergism parameter in all cases was found to be greater than 1. The synergistic effect may be attributed to enhanced adsorption of polyaniline by the adsorbed halide ions **(Jeyaprabha *et al.,* 2005c).**

The performance of water soluble polyaniline as corrosion inhibitor for iron in 0.5M H_2SO_4 was evaluated by potentiodynamic polarization, linear polarization, and electrochemical impedance spectroscopy and compared with the performance of the aniline monomer by **Jeyaprabha *et al.,* (2006a).** The results reveal that polyaniline acted as an efficient inhibitor, since the maximum efficiency of 84% was observed at a concentration of 100 ppm, whereas the monomer accelerated the corrosion. FTIR studies revealed that the polyaniline was strongly adsorbed on the iron surface and inhibits the corrosion effectively.

The inhibitive effect of poly(p-aminobenzoic acid) on iron in 1M HCl solution was investigated by polarization and electrochemical impedance spectroscopy and compared with that of monomer p-aminobenzoic acid **(Manivel *et al.,* 2006).** The effectiveness of poly (p-aminobenzoic acid) was very high in comparison with that of the monomer. The results show that both cathodic and anodic processes were suppressed by p-aminobenzoic acid and poly (p-aminobenzoic acid) of iron dissolution in 1M HCl by their adsorption on the iron surface. The inhibition efficiency of both p-aminobenzoic acid and poly (p-aminobenzoic acid) were found to increase with the inhibitor concentrations. Ultraviolet (UV) reflectance studies of the iron surface after exposure to inhibitor in the acid environment show that poly (p-aminobenzoic acid) was strongly adsorbed on iron surface.

A study was carried out to understand the effect of addition of cerium ions on the corrosion inhibition performance of polyaniline for iron in 0.5 M H_2SO_4. Techniques such as electrochemical impedance spectroscopy, potentiodynamic polarization and linear polarization resistance methods were employed to study the corrosion inhibition. Polyaniline was used in the concentration range of 10^{-100} ppm and the cerium ions concentration was maintained at 1×10^{-3} M. The inhibition efficiency of polyaniline at 10 ppm increased from 53 to 88% and for 50 ppm from 71 to 90% in the presence of cerium ions. The enhanced inhibition of polyaniline in presence of ceric ions may be due to the higher coverage of polyaniline-ceric complex (**Jeyaprabha *et al.*, 2006b).**

The corrosion behaviour of mild steel in sulphuric acid solution containing various concentrations of a copolymer formed between maleic anhydride and N-vinyl-2-pyrrolidone (VPMA) was investigated using weight-loss, polarization and electrochemical impedance techniques. The polymer acted as an effective corrosion inhibitor for steel in sulphuric acid medium. The inhibition process was attributed to the formation of an adsorbed film of co-polymer on the metal surface which protects the metal against corrosion. Scanning electron microscopy (SEM) studies of the metal surfaces confirmed the existence of an adsorbed film. The adsorption followed the Langmuir isotherm. The protection efficiency increased with increase in inhibitor concentration and decreased with increase in temperature and acid concentration. (**Ganesha Achary *et al.*, 2008).**

The inhibitive effects of polyvinylpyrrolidone PVP10 (Mol.Wt. 10,000) and PVP45 (Mol.Wt 45,000) on the corrosion properties of 316L stainless steel at different inhibitor concentrations and temperatures were investigated. Electrochemical techniques were used to determine the corrosion properties. The inhibition effect of the polypyrrolidone was found to increase with the molecular weight. E_{corr} showed an increase in corrosion potential with increasing concentration of the inhibitor. The corrosion potential for a 0.01M PVP10 reached a maximum of 0.26V after 72 hours compared to 0.32V for 0.005M PVP45. However, the curve of the PVP45 showe instability at different intervals of time indicative of frequent dissolutions/passivation processes. SEM revealed the formation of pits especially at low molecular weight of the polymers and fewer pits at 60°C in the case of PVP45 **(Khaled *et al.*, 2010).**

Corrosion inhibition and adsorption behaviour for pure iron in 0.5 M H_2SO_4 by polyacrylamide (PA) were investigated using electrochemical techniques. The effect of iodide ion additives was also studied. It was found that inhibition efficiency increased with PA concentration. Corrosion inhibition was afforded by adsorption of PA onto the metal following El-Awady kinetic–thermodynamic adsorption isotherm model via chemisorption mechanism. A mixed inhibition mechanism was proposed for the inhibitive effects of PA as revealed by potentiodynamic polarization technique. A synergistic effect was observed between PA and KI as evident from the values of synergism parameter found to be greater than unity (**Umoren *et al.,* 2010).**

2.3.3 POLYMERS AS CORROSION INHIBITORS FOR OTHER METALS

2.3.3.1 Polymers as Corrosion Inhibitors for Aluminium

Two polymers, polyvinylbenzyltrimethylammonium chloride (PVBA) and polydiallyldimethylammonium chloride (PDDA) were used to inhibit aluminium corrosion in primary cells with Al anodes and alkaline electrolyte by **Hirai *et al.,* (1985).** The results, reveal that the inhibitors inhibited cathodic corrosion reaction predominantly, which was preferable to the aluminium anode. The cathodic inhibiting effect from the result has due to the thicker double layer of the polymer cation.

The mechanism of corrosion of aluminium and the effect of polyethylene glycol (PEG) polymer as corrosion inhibitor in acidic medium was studied using weight loss method, potentiodynamic and galvanostatic polarization measurements (**Shukla *et al.,* 2003**) Differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry was used for the study of corrosion rates for the corrosion of aluminium in acidic medium at short time intervals. Results obtained reveal the corrosion inhibition efficiency of PEG was 94% after 24 h of immersion period.

The effect of two polyamide compounds on the corrosion behavior of aluminum metal in oxalic acid solution was investigated using potentiostatic and potentiodynamic anodic polarization techniques **(Abdallah *et al.,* 2004)**. The inhibition efficiency increased with increasing polyamide concentration until a critical value and then started to decrease in high polymer concentrations, indicating low inhibition efficiency. The inhibitive behavior of these compounds was due to adsorption of the polyamide compounds on the metal surface and formation of insoluble complexes. The adsorption process was found to obey Temkin adsorption isotherm.

The inhibition effect of some amino acids towards the corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 solution was investigated using weight loss measurement, linear polarization and SEM techniques. The results drawn from the different techniques are comparable. The used amino acids were alanine, leucine, valine, proline, methionine, and tryptophan. The effect of inhibitor concentration and temperature against inhibitor action was investigated. It was found that these amino acids act as good inhibitors for the corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 solution. Increasing inhibitor concentration increased the inhibition efficiency and with increasing temperature the inhibition efficiency decreased. It was found that adsorption of used amino acids on aluminum surface followed Langmuir and Frumkin isotherms (**Ashassi-Sorkhabi *et al.*, 2005).**

The corrosion inhibition of aluminum in H_2SO_4 in the presence of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) as inhibitors at 30–60°C was studied using gravimetric, gasometric, and thermometric techniques. The inhibition efficiency (%I) increased with increase in concentration of the inhibitors. Increase in temperature increased the corrosion rate in the absence and presence of inhibitors but decreased the inhibition efficiency. Both PEG and PVA were found to obey Temkin adsorption isotherm at all concentrations and temperatures studied. Phenomenon of physical adsorption was proposed from the activation parameters obtained. Thermodynamic parameters reveal that the adsorption process was spontaneous. PEG was found to be as better inhibitor than PVA (**Umoren *et al.*, 2007).**

The corrosion and inhibition behaviour of aluminium in hydrochloric acid (HCl) in the absence and presence of polyvinyl pyrrolidone (PVP), Polyacrylamide (PA) and their blends were studied in the temperature range of 30-60°C using weight loss, hydrogen evolution and thermometric techniques. The inhibition efficiency (%I) increased with increase in inhibitors concentration. Increase in temperature led to increase in corrosion rate but decreased the inhibition efficiency PVP was found to have the higher inhibition efficiency than PA which may suggest that the differences in their molecular structures play a significant role in the adsorption and hence inhibition process. Inhibition efficiency was enhanced on blending the two polymers; the optimum inhibition efficiency was obtained at 3:1 blending ratio for PVP: PA. The inhibitors (PVP and PA) obey Freundlich, Temkin and Flory-Huggins adsorption isotherms at all the temperatures. Results obtained from the kinetic and thermodynamic parameters indicate spontaneous adsorption of the inhibitors onto aluminium surface following physical adsorption mechanism (**Umoren *et al.*, 2008**).

Mohammed A. Amin *et al.*, (2009) studied the influence of three selected polyacrylic acids (PAAs) with different molecular weights (PAA1 = 1800, PAA2 = 11,000 and PAA3 = 14,000 g mol^{-1}) on the corrosion inhibition of Al in weakly alkaline solutions (pH 8 and 10) at 30 °C. Measurements were conducted under different experimental conditions using chemical (weight loss) and electrochemical (potentiodynamic polarization and impedance) techniques, complemented with ex situ energy dispersive X-ray (EDX) examinations of the electrode surface. The results demonstrated that these polymers inhibited the alkaline corrosion of Al. The inhibition effect of these polymers was due to their adsorption on Al surface. Polarization measurements showed that the three polymers act as mixed-type inhibitors. The inhibition efficiencies of these polymers increase with increasing concentration, molecular weight and immersion time. Results obtained from the chemical and electrochemical measurements were in good agreements.

2.3.3.2 Polymers as Corrosion Inhibitors for Copper

The inhibition of copper corrosion by polyvinylimidazole and benzimidazole at room and high temperature as well as in acidic water was assessed by surface-enhanced Raman scattering (SERS) **(Xue *et al.,* 1994).** The performance of polyvinylimidazole and benzimidazole was improved by coating the copper surface with their mixture.

The adsorption and inhibitive effects of polyvinylpyrrolidone (PVP) and polyethyleneimine (PEI) on copper in 2M H_2SO_4 at 30°C was investigated by the means of weight loss, potentiodynamic and in situ surface enhanced Raman scattering (SERS) techniques **(Schweinsberg *et al.,* 1996)** , according to result obtained, both polymer reduced the rate of anodic (metal dissolution) and cathodic (oxygen reduction) corrosion reaction. Also at all concentrations studied, PVP was found to be a better inhibitor than PEI.

The adsorption and inhibitive effects of polyvinylpyrrolidone (PVP) and polyethylenimine (PEI) on copper in 2 M H_2SO_4 at 30°C was investigated by means of weight loss, potentiodynamic and in situ surface enhanced Raman scattering (SERS) techniques. Both polymers reduce the rate of the anodic (metal dissolution) and cathodic (reduction) corrosion reactions. At all concentrations studied, PVP was found to be the better inhibitor. For PVP was adsorbed through oxygen whilst PEI showed coordination through the nitrogen atom (**Schweinsberg *et al.,* 1996).**

The effect of layers of poly (o-anisidine) (PVA) **(Shinde *et al.*, 2005, Pawar *et al.,* 2007)** poly (o-toluidine) (POT) and poly (o-anisidine-co-o-toluidine (OAOT) **(Pawar *et al.,* 2007, Torresi *et al.,,* 2005)** formed on copper surface on copper behaviour in 3% NaCl solution was reported. Results obtained indicate that they are efficient corrosion inhibitors and at concentration of 0.1 M, inhibition efficiency obtained was 85.81%, 98.00% and 99.66% for POA, POT and OAOT respectively.

Souza de *et al.,* (2007) reported that films formed in the presence of polyaniline (PANI) and poly (methylmethacrylate) (PMMA) protect copper surface against corrosion. The influence of polyaniline (PANI) and poly (orthomethoxyaniline (POMA) on corrosion inhibition of copper in 0.1 M NaCl was also studied. Best result was obtained for polyaniline which may be attributed to the fact that the polymer film was involved in the formation of oxide film on the polymer – metal surface. This oxide film increased the barrier effect of the polyaniline film hence greater corrosion inhibitor efficiency. The phenomenon of oxide formation was not observed with POMA.

2.3.4 Polymers as Corrosion Inhibitors for Other Metals

The effect of polyvinylpyrrolidone, poly-2-vinylpyridine and poly-4-vinylpyridine as inhibitors of corrosion behaviour of zinc metal in 1.0 M H_2SO_4 solution was reported using weight loss technique **(Mostafa Abo El-khair *et al.*, 1986).** The protection efficiency in the presence of polymers reached about 87% at an inhibitor concentration of 0.1 M.

The behaviour of corrosion inhibition of mild steel by various cationic and anionic polymers namely polyethyleneimine (PEI), its derivative (PEID), polyarylamine (PAAm) and polydicynodiamide derivative (PDCDA) as cationic polymers and polymaleic acid derivative (PMAD), polyacrylic acid derivative (PAAD) and polyacrylic acid (PAA) as anionic polymers were investigated by corrosion tests and physicochemical measurements **(Sekine *et al.*, 1992)** It was found that the cationic polymers lacked inhibition ability while the anionic polymers had more effective inhibition ability.

Poly(o-aminophenol), poly(o-aminothiophenol), poly(m-anisidine) prepared by chemical oxidation of their monomers using ammonium persulphate at 0^oC were evaluated as corrosion inhibitors for steel protection by measuring their corrosion rates in comparison with previously prepared polyaniline and the control sample **(Abd El-Ghaffar *et. al.*, 1998).** The polymers show a high performance as efficient corrosion inhibitors.

The effects of poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), sodium polyacrylate (NaPA), polyethylene glycol (PEG), pectin (P), and carboxymethyl cellulose (CMC) on the corrosion of cadmium in a 0.5 M hydrochloric acid (HCl) solution were studied with both electrochemical impedance spectroscopy and Tafel plot techniques **(Khairou *et al.*, 2003).** Measurements were carried out at cathodic, open-circuit, and anodic potentials. All the investigated polymers had inhibitory effects on both the cathodic and anodic processes, with a predominant anodic inhibiting action. The adsorption of most of the polymers obeyed a Temkin adsorption isotherm, and this indicated that the main process of inhibition was adsorption.

The corrosion behavior of mild steel in sulphuric acid solution containing various concentrations of a copolymer formed between maleic anhydride and N-vinyl-2-pyrrolidone (VPMA) was investigated using weight-loss, polarization and electrochemical impedance techniques. The polymer was found to as an effective corrosion inhibitor for steel in sulphuric acid medium. The inhibition process was attributed to the formation of an adsorbed film of co-polymer on the metal surface which protects the metal against corrosion. Scanning electron microscopy (SEM) studies of the metal surfaces confirmed the existence of an adsorbed film. The adsorption followed the Langmuir isotherm. The protection efficiency increased with increase in inhibitor concentration and decreased with increase in temperature and acid concentration (**Ganesha Achary *et al.,* 2008).**

The effect of polyethyleneimine (PEI) as corrosion inhibitor for ASTM 420 stainless steel in 30% aqueous NaCl was studied **(Finsgar *et al.,* 2009).** The results of linear polarization and cyclic polarization measurements indicate high inhibition effectiveness of the selected organics. Moreover, from cyclic measurements, it was deduced that PEI acted as an inhibitor against pitting corrosion. Immersion test in the presence of PEI show remarkable corrosion protection against uniform corrosion. X-ray photoelectron spectroscopy measurements show that PEI binding was mediated by electrostatic interactions between PEI and the substrate.

2.4 POLYMER COMPOSITE AS CORROSION INHIBITORS

The inhibitive effect of N-vinyl-2-pyrrolidone (NVP) and polyvinylpyrrolidone (PVP) of different average degrees of polymerization on acid corrosion of iron was investigated **(El-khair *et al.,* 1983).** It was found from the result obtained that PVP afforded a more efficient inhibition than NVP at very low concentrations. Protection efficiency of 98% was obtained.

The polymer-polymercomplexes [(PMAAN/PAAmM)n], composed of polymethacrylic acid [PMAAN, N = 1 (Mn = 1.0 x 10^4), 2 (Mn = 5.0 x10^3) and 3 (Mn = 2.5 x 10^3)] and polyacrylamide [PAAmM, M = 1 (Mn = 5.0 x 10^3) and 2 (Mn = 2.5 x 10^3)] were investigated as inhibitors for corrosion of mild steel in cooling water systems **(Morooka *et al.,* 2001).** The inhibition abilities of (PMAAN/PAAmM)n against corrosion and scale deposition were evaluated by corrosion tests and physicochemical methods. In a solution with low concentration of ionic species (LC solution), the corrosion inhibition abilities of (PMAAN/ PAAmM)n improved at an addition of the polymer higher than 50 ppm. This effect is due to the control of adsorption of the polymers on steel surfaces based on the formation of polymer complexes. In a solution with high concentration of ionic species (HCl solution), the corrosion inhibition abilities of (PMAAN/PAAmM)n were favourable at an addition of the polymer higher than 20 ppm. This effect may be attributed to the adsorption of the polymers on steel surfaces and the scale dispersion based on the formation of polymer-polymer complexes.

The effect of poly (4-vinylpyridine isopentyl bromide) (P4VPIPBr) in three degrees of quarterisation (6, 18 and 79%) on the corrosion of pure iron in molar sulphuric acid was investigated by potentiodynamic, polarisation resistance and weight loss measurements. The inhibition efficiency (IE %) of P4VPIPBr increased with increase in concentration to attain 100% around 5 x10^6 M. IE % values obtained from the various methods were found to be in good agreement. Polarisation measurements also show that the compound acted as a cathodic inhibitor and adsorbed on the pure iron surface according to Frumkin adsorption isotherm model **(Chetouani *et al.,* 2003).**

Corrosion inhibition of mild steel in sulphuric acid solution using polyethylene glycol methyl ether (PEGME) was reported using electrochemical polarization (galvanostatic and potentiostatic) techniques **(Dubey *et al.,* 2007)**. It was found that PEGME acted as a very effective corrosion inhibitor for mild steel in acidic medium. Inhibition efficiency increased with increase in the concentration of PEGME but almost remained the same with increasing temperature. Adsorption of PEGME was found to follow Langmiur adsorption isotherm. PEGME was also found to function as an inhibitor of mixed type acting by blocking the active sites on the cathodic and anodic regions

Yurt *et al.*, (2007) studied the inhibitive performance of novel synthesized water soluble triblock copolymers-2-(diethylamino)ethyl methacrylate block-2-(dimethylamino)ethyl methacrylate-block-2-(N-morpholino)ethyl methacrylate [PDEA-PDMA-PMEMA] and 2-(diisopropylamino)ethyl methacrylate-block-2-(dimethylamino) ethyl methacrylate-block-2-(N-morpholino)ethyl methacrylate [PDPA-PDMA-PMEMA] of two different molecular weight on the corrosion behaviour of mild steel in 0.5 M HCl using potentiodynamic polarization, electrochemical impedance spectroscopy and linear polarization methods. Polarization methods indicate that all studied copolymers acted as mixed type inhibitors. Inhibition efficiencies increased with increase in inhibitor concentration. Adsorption of the inhibitors was followed Langmuir adsorption isotherm. The correlation between the inhibition efficiencies of the studied copolymers and their molecular structures based on quantum chemical calculations indicate that adsorption of the triblock copolymers depend on the charge density of adsorption centres and dipole moments.

The copolymers from different feed ratios of N-(methacryloyloxymethyl) benzotriazole (MMBT) and methyl methacrylate (MMA) were synthesised using free radical solution polymerization technique and characterized using FT-IR and ^{13}C NMR spectroscopy. The thermal stability of the polymers was studied by using thermogravimetric analysis (TGA). The corrosion behaviours of mild steel specimens dip coated with different composition of copolymers by potentiodynamic polarization and electrochemical impedance spectroscopic (EIS) method in 0.1 M HCl medium. The polarization and impedance measurements showed different corrosion protection efficiency with change in composition of the copolymers. It was observed that the copolymer obtained from 1:1 mole ratio of MMBT and MMA exhibited better protection efficiency than other combinations (**Srikanth *et al.,* 2006).**

The inhibitive action of synthesised polyvinyl alcohol–sulphanilic acid (PVASA) composite on the corrosion of commercial mild steel in 1 M HCl medium was investigated by weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopic methods. Characterization of PVASA composite was carried out using Fourier transform infrared spectroscopy (FTIR). Experimental results reveal that PVASA composite act as an effective inhibitor in the acid environment. The inhibition efficiency increased with an increase in the concentration of the inhibitor. Maximum inhibition efficiency of PVASA composite was found to be 84% at 6000 ppm. Electrochemical measurement reveal that PVASA composite acted as a mixed inhibitor and the adsorption was found to follow Langmuir adsorption isotherm **(Srimathi *et al*., 2011).**

The inhibitive nature of polyvinyl alcohol-anthranilic acid (PVAAA) on the corrosion of mild steel in 1 M HCl solution under various conditions was investigated by means of weight loss, potentiodynamic polarization and AC impedance methods. The studies show that polyvinyl alcohol-anthranilic acid exhibited excellent inhibition property. The potentiodynamic polarization studies reveal that the polyvinyl alcohol-anthranilic acid acted as a mixed type inhibitor. The adsorption of the polymer on the mild steel surface was found to obey Langmuir and Temkin adsorption isotherms (**Srimathi *et al*., 2010**).

Research on non toxic inhibitors is of considerable interest in investigations to the replacement of hazardous classical molecules. Thorough analysis of the literature survey reveals that polyvinyl alcohol-selected amino acid composites derivatives **PVAALA, PVAVAL, PVAGLU, PVAGLN, PAVTYR and PVATRP** composite have not yet been reported as corrosion inhibitors for mild steel in acid medium. The methodology adopted in this investigation is clearly presented in the **Chapter III.**