INTRODUCTION

CHAPTER 1

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Preliminary consideration:

An inhibitor is a chemical substance which, when added in small concentration to an environment, effectively checks, decreases, or even prevents the reaction of the metal with the environment.

Inhibitors fall into several classes (1), which include passivator's precipitators, vapour phase, cathodic, anodic, neutralizing and adsorbents inhibitors.

Corrosion can be defined in many ways, the one most preferred in literature (2) is the loss of useful properties of a material as a result of chemical or electrochemical reaction with environment. Corrosion is a heterogeneous reaction, which is often diffusion controlled. There are three necessary conditions, which must be met simultaneously to proceed the reaction electrochemically. There must be a potential difference, mechanisms for charge transfer between electronic and electrolytic conductors existing, and a continuous path which must be available.

A corrosion cell consists of anode, cathode and, electrolyte for electrical connection. The absence of one parameter prevents corrosion to occur. The most common types of corrosion are galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, and selective leaching corrosion and stress corrosion cracking . There are numerous methods for measuring the corrosion rates and comparing the efficiency of the inhibition by additives. These include weight-loss, hydrogen evolution,thermometric (3),electrode potential measurement (4) construction of electro - capillary curves

(5), depression of polarographic maxima (6), determination of electrode reaction parameters (7), linear polarization measurements (8), and improved electrochemical methods including electrode impedance technique and cyclic voltammetry. However, the work in the present thesis is concerned with corrosion inhibitors for C-steel applying the weight loss and polarization measurements.

Types of inhibitors (9) :

Corrosion inhibitors are substances which when added to the corrosive medium lower the corrosion rate of the metal. Inhibition can result from the retardation of the anodic process, the cathodic process or both. Inhibitors can be classified into:

(I) Anodic inhibitors (10) :

These are very effective and are widely used. These are anions, which migrate to the anode sites of the metal and lead to passivation of the metal surface under favourable conditions. When the anion alone is capable of passivating the metal, the agent has oxidizing properties e.g. nitrite, nitrate and chromate which were named passivators.

(II) Cathodic inhibitors (11) :

Unlike anodic inhibitor, cathodic inhibitors are safe, these are cations which migrate towards the cathodic areas of the surface and precipitated either chemically or electrochemically on the surface. Examples of cathodic inhibitors are the natural contents of $Ca(HCO_3)_2$ in hard water. The cathodic reaction of the corrosion in natural aerated solution is the reduction of oxygen , the resulting OH^- ions will interact with the inhibitor to precipitate $CaCO_3$.

(III) Vapour phase inhibitors (12):

These are used for the temporary protection of the metals in corrosive atmospheres. These are compounds, which have low, but significant vapour pressure about (0.1–1.0 mm Hg) and has corrosion inhibition properties. They are essentially soluble, filming inhibitors and include nitrate, benzoate and or chromate anions attached to a suitable heavy organic cation. eg. dicyclohexayl ammonium nitrate, which is one of the most effective inhibitor of this type.

(IV) Adsorption inhibitors (13):

They are mainly organic compounds containing nitrogen, oxygen or sulfur atoms through which they can be adsorbed, usually by chemisorption on the metal surface (14). Chemisorption usually occurs through donation of electrons from N, S or O functional atoms to the metal atoms on the surface. Inhibitors can bound to the metal surface to form a coordinate type of link. This process is favourd by the presence of vacant orbitals with low energy on the metal atom, as in the case of the transition metals. Electron transfer from the adsorbed species is favoured by the existence of relatively loosely bound electrons, such as those in anions and neutral organic molecules containing lone pair of electrons or π-electrons system associated with multiple, especially triple bonds or aromatic rings.

In organic compounds, suitable lone pair of electrons for coordinate bonding occurs in functional group containing elements of group V and VI of the periodic table. The tendency to stronger coordinate bond formation (and hence stronger adsorption) by these elements increases by decreasing electronegativity in the order O< N< S (15-17), and depends also on the nature of the functional groups containing these elements.

The degree of inhibition of anodic and cathodic inhibitors depends on the chemical structure of the inhibitor, potential of the metal, and size of the molecule.

Kirkov (18), postulated that inhibition efficiency of surface-active compounds appeared to include both" chemical " and " electrochemical " factors . The chemical factors influenced formation of the protective surface layer at the metal corrosive medium interface. The electrochemical factor influenced the equilibrium potential on the metal surface and consequently, directed the charge transfer process. Kirkov (18), showed also that the double layer capacity on the metal and oxide surface solution interface, in the presence and absence of inhibitors, depends to a great extent on the nature of the adsorbed layer and on the compactness of the oxide surface,

Hoar (19, 20), concluded that adsorption of inhibitor molecules reduced the formation of electrode reaction sites and inhibition by a monolayer formation predominates, where the surface is covered with a monolayer film.

(V) Precipitation inhibitors:

These are inhibitors, which interfere with anodic and cathodic reactions and are film forming compounds over the metal surface. Examples for these inhibitors are phosphates and silicates.

Corrosion prevention:

Methods of preventing corrosion have been conveniently summarized as follow:

(I) Prevention based on the environment:

1- By addition of corrosion inhibitor
2- By decreasing the electrical conductance, electrolytic corrosion can be reduced
3- By purification of or de-humdifications of air
4- By raising the pH value , the acidity of solution can be eliminated
5- By deaeration using an inert gas or use of an oxygen scavenger e.g. hydrazine and Na_2SO_3, oxygen reduction of differential aeration can be stopped.

(II) **Prevention based on the metal:**

1- By addition of alloying element which increases corrosion resistance. e.g. steel-containing chromium is more resistant than normal steel.
2- By raising purity of metals, impure metals corrode at much faster rates than pure metals.
3- By heat treatment, this reduces the probabilities of stress corrosion cracking
4- By plating with a less reactive metal like copper on normal steel that can make surface coating.

(III) **Prevention based on protective coating:**

1- Metal coating
2- Organic coating (paints, resins, atc.)
3- Inorganic coating (cements)
4- Coating by reaction product (electrochemical or chemical treatment of metal surface).
5- Temporary protection

(IV) Prevention based on electrochemistry:

The corrosion in aqueous solution is electrochemical in nature, so the prevention is achieved by preventing the cathodic reaction, the anodic reaction or both :

(a) Anodic protection: the prevention occurs by interfering with the anodic reaction which is based on changing the potential on the corroding metal in the positive direction to the extent of passing the domain of metal dissolution and bringing the metal into the region of passivity. This is achieved by oxidizing inhibitor e.g. chromate, nitrite and nitrate.

(b) **Cathodic protection**: the prevention occurs by interfering with the cathodic reaction, which is based on changing the potential of the corroding metal towards negative direction to an extent whereby the dissolution reaction $M = M^{+n} + ne^-$ becomes no more feasible.

The limitations and uses of inhibitors:

Inhibitors have been used for many years to protect metals whose mechanical and physical properties must be considered before deciding their use (22).

1-Inhibitors, which contaminate the environment and are often toxic. Theses cannot be used in food industries or in any system, which could indirectly allow the consumption of inhibitors by humans.

2- They are most useful in closed system where the corrosive environment is either retained for long period or recycled.

3- Inhibitors generally lose their effectiveness as the concentration of the corrosive material and temperature are increased. This can be remedied by Keeping the concentration of the inhibitors at a level, which` h exceeds the optimum value, necessary for protection.

4- Inhibitors can offer a cheap, easy to apply and highly effective method for corrosion control when certain consideration are taken.

Correlation between inhibition and stability of organic compounds:

The factors which are responsible for inhibition of corrosion by organic compounds depend on the nature of the corroding metal, the composition of the corrosive medium and the conditions under which the corrosion process occurs; added to these the chemical properties and structure of organic compounds.

An organic substance can effectively protect a given metal under certain conditions or with other metals. If different kinds of inhibitors are considered separately, the factors responsible for inhibitive action of the organic compound could be understood better.

(A)Inhibition by chemically stable surface active organic compounds:

In many cases the stability and the ability of organic compounds to be adsorbed depends on the nature of the corroding metal. It is very difficult indeed to find compounds, which do not undergo any chemical changes in solution during the course of corrosion process(23) . For a given solution the adsorption of inhibitors depends (24) . First of all on the charge on the metal and on the potential of the metal (Q) . In solution, the charge on the metal is relative to the zero charge potential. Q potential controls the electrostatic interaction of the metal with dipoles in adsorbed neutral molecules and hence the orientation of the dipole and the adsorbed molecule. Thus, as the Q potential becomes more positive the adsorption of the anions is favoured and as the Q potential becomes more negative the adsorption of the cation is favoured.

(B) Inhibition by Surface active chemically unstable organic compounds:

The inhibition efficiency-concentration relationship had been considered and the probability of maxima or minima had been noted. As a result of interaction with the cathodic hydrogen, the significance of the chemical change in the nature of additives was realized. The following three cases have been discussed (25):

(i) Surface active additives reducible to surface inactive compounds.
(ii) Surface inactive additives reducible to surface-active compounds.
(iii) Surface active reducible to new surface-active compounds.

The types of chemical transformation are: -

(a) protonation

Antropov (24,25). in discussing electro-organic reduction process considered the following points as being important with regard to protonation reaction .

(i) It occurs usually on the surface of a metal and can under definite conditions be a rate-determining step of the overall reaction.
(ii) Its rate depends on the surface concentration of the organic substance and therefore on the charge on the surface (its Q- potential).
(iii) As a result of the opposite effect of electric field and the charge of a metal, the rate of reduction (protonation) can reach maximum value.

(b) Reduction :

The reduction of organic inhibitor could take place only if the corrosion potential is sufficiently negative. If this condition is fulfilled, the main principles of the theory of electroreduction of organic compounds (24-26) .could be applied to that particular case of organic electrochemistry. Thus, the selective reduction of inhibitors on various metals should be expected.

(c) Polymerization:

Cathodic reduction under certain conditions may lead to the formation of dimmer and polymers. If polymerization is a surface process, and the formation of copolymer between the inhibitors and corroding metal is possible, the degree of protection should be increased (27).

Adsorption isotherm:

Four types of adsorption may take place in the inhibiting phenomena involving organic molecules at the metal solution interface namely: -

(i) Electrostatic attraction between charged molecules and the charged metal.
(ii) Interaction of electron pairs in the molecule with the metal.
(iii) Interaction of electron with the metal
(iv) A combination of the above(28).

Interpretation may be found in the easier polarization and lower electronegativity of the elements. The adsorption of an adsorbate on the surface of a metal is regarded as a substitution adsorption process between the organic compound on the aqueous phase , Org. $_{aq,}$ and the water molecule adsorbed on the electrode surface (29).

$$\mathrm{Org}_{aq} + x\,\mathrm{H_2O}_{(s)} = \mathrm{org}_{(s)} + X\,\mathrm{H_2O}_{aq} \qquad \mathbf{(1.1)}$$

where x is the size ratio which is the number of water molecules.

The inhibition efficiency of homologous series of organic substance, containing different heteroatoms increases in the order (S > N > O). Equilibrium is reached when the chemical potential on the left side is equal to that of the right side of the equation.

One may obtain different expressions for the adsorption isotherm, the mostly used are:

Frumkin (30). $$[\theta / 1-\theta]\ \mathrm{exp.}^{[-2a\theta]} = k.\ C \qquad (1.2)$$

where (a) is a molecular interaction parameter depending on the molecular interaction in the adsorption layer and on the degree of heterogeneity of the surface; it is a measure of steepness of adsorption isotherm. The more positive the value of (a) the steeper the adsorption isotherm, θ is the degree of surface coverage. The more positive the value of (a) the steeper the adsorption isotherm. This has been interpreted (31). To imply that interaction between molecules with positive values which cause an increase in adsorption energy with increase of θ, C is the inhibitor concentration in the bulk of solution, k is the equilibrium constant of the adsorption reaction.

Hill de Boer (32) $[\theta /1-\theta] \exp^{[\theta /1-\theta][-2a\theta]} = k. C.$ (1.3)

Parsons (33) $[\theta/1-\theta] \exp^{[-2a\theta/1-\theta][-2a\theta]} = k. C.$ (1.4)

Timken (34) $a\theta = \ln k.C.$ (1.5)

Flory Huggins(35) $\theta/x\ (1-\theta)^X = K.C.$ (1.6)

where x is a number of water molecules replaced by one molecule of the organic adsorbate.

Dhar- Flory-Huggins $\theta/e^{(x-1)}(1-\theta)^x = k.C.$ (1.7)

Bokris-swinkels(36) $[\theta/(1-\theta)^x]^{[\ \theta+x(1-\theta)\ x-1]}\ x^x = k.C.$ (1.8)

Basically,all above isotherms are(37)

$$(\theta,x) \exp.^{-a\theta} = k.C. \qquad (1.9)$$

where F (θ,x) is the configuration factor which depends essentially on the physical model and assumption's underlying derivation of the isotherm(38) .k is the equilibrium constant of the adsorption processes and is related to the standard free energy of adsorption $\Delta G°$ by

$$k = 1 / 55.5 \exp^{-(-\Delta G_{ads} /RT)} \qquad (1.10)$$

Equation (1.9 and 1.10) are used to evaluate the most suitable isotherm describing the adsorption of inhibitors on the electrode surface .

Langmuir (39) $C / \theta = 1 / k + C$ (1.11)

where k is the equilibrium constant of adsorption.

EFFECT OF MOLECULAR STRUCTURE ON CORROSION INHIBITOR

The inhibition attributable to the initial compound is called, "primary inhibition and that brought about by the reduction products "secondary inhibition" (40,41) .The inhibition efficiencies calculated for different homologeous series of organic compounds have sometimes underlined the difficulty of attributing the variation in inhibition within a series mono functional substances to a single molecular property such as electron density.

It is necessary to know the possible steric effect including molecular size and mode of interaction, which may provide a screening action on the reaction center for the adsorption of the molecule at the metal surface (42). Complexation between the organic molecule and the metal and the stability constants of the resulting complexes was taken in consideration.

Kinetic and equilibrium processes in organic chemistry have been found to an empirical equation proposed by Hammett (43) and discussed and extended by Jaffe(58) .and Taft (45) .The family of relationships thus obtained is a form of linear free energy relationship (LFER) usually designated as the Hammett relation and is given by

$$\log k/k_o \text{ or } \log K/K_o = \rho_\sigma \qquad (1.12)$$

where k's = rate constants, or K's = equilibrium constants. The zero subscripts σ refer to parent or reference compounds, ρ = reaction constant and σ = substitution constant. By setting the reaction constant equal unity, for the substituted benzoic acid, the reaction further simplified to yield:

$$\log k/k_o = (pk_a\text{-}pk) = \log K/K_o = \sigma \qquad (1.13)$$

This equation is then taken as the definition of the substituent constant σ i.e. a substituent is given a numerical value which is dependent on its effect on the pk of the substituted benzoic acid compared to benzoic acid. From this definition, hydrogen has a σ of zero. Substituents which increase ionization (i.e. weaken the O-H bond) have positive value of σ and those which decrease ionization (i.e. strengthen the O-H bond) have negative values. Therefore, σ is a measure of the electron density or distribution on an atom. This measure of the electron density or distribution at a specific atom in the molecule is justified on the basis of quantum- mechanical calculations of electron charge density of individual atom within a molecular orbital structure (46). Steric effect have not been considered since Hammett correlated only meta and para substituent and aliphatic systems caused Tafel to develop σ scale (46). In general, this leads to rate or equilibrium equations, which are due to polar effects resulting from structural changes.

A comprehensive approach to corrosion inhibition was suggested by Fouda (47). According to this approach metallic corrosion inhibition depends not only on the polar effect or the electron charge density of functional groups or adsorption active centers in the molecule, but also on the molecular size of the inhibitor, its mode of adsorption on the metal surface, its heat of hydrogenation, and its ability to form insoluble metallic complexes that can be incorporated in the oxide layer thus reinforcing it or soluble ones that enhance dissolution.

CORROSION INHIBITION OF IRON AND ITS ALLOYS

As known that the economic power of any country is determined by its output of steel, since progress in the principal economic branches such as mining, transporting, manufacturing engineering or agriculture is unthinkable without steel. So, studies of steel properties in general and especially electrochemical, have been received a great attention. In such aspect, the corrosion and corrosion inhibition of steel in the different media become very interesting and important owing to its wide applicability in industry and domestic life. Numerous studies on iron and steel were done including the corrosion nature and its mechanism in different media. Corrosion inhibition using different inhibitors and the various factors affecting on it were studied by many authors (48, 69) .In the following a concise literature survey on the metallic corrosion and its inhibition by some related organic compounds in acidic medium.

Oftedal (70) studied the anodic dissolution and film growth on Armco iron in acid chloride solutions. He assumed that imperfections of the iron surface serve as active sites. When pairs of sites are combined with OH^-ions, two surface complexes, denoted $FeOHFe.H_2O$ and $FeOFe.H_2O$ are formed by two different mechanisms. The former, $FeOHFe.H_2O$, serves as nuclei for formation of film when $pH > 1.5$. The film stabilizes the nuclei. Atkinson and Marshall (71) showed that addition of decylamine to acidic chloride solutions reduced the rate of the dissolution reaction of iron, but the form of the polarization curves and the mechanism of dissolution remained unchanged.

The influence of chloride ions on the kinetics of iron dissolution was investigated by McCafferty and Hackerman (72), and Darwish *et al* (73). The dissolution mechanism of iron changes, if the concentrations of hydrogen ions and chloride ions are increased to a certain level. The electrochemical reaction order related to each of H^+ and Cl^- ions are +1.1 and+0.6, respectively. The correlation to known mechanisms is discussed.

Laengle and Hackerman (74) studied the corrosion inhibition of iron in HC1 solutions by aliphatic and aromatic oximes and quinclidine using galvanostatic anodic and cathodic potential measurements. Inhibition of both the anodic iron dissolution and the cathodic H_2-evolution by oximes and quinuclidine was caused by adsorption of the organic molecules on the metal surface. Also, the presence of nitriles in acid chloride solutions gave about the same inhibition of both the anodic and cathodic processes (75).

Corrosion inhibition by bis-n-butyl-sulphinylmethane, bis-n-butyl-sulphonylmethane and ethylene oxide condensed of 2,2'-dihydroxy-n-hexylsulphide on iron in HC1 and H_2SO_4 acid solutions was measured by Matsuda *et al.* using electrochemical methods (76). These compounds were found to be excellent acidic inhibitors for iron and inhibited both cathodic and anodic corrosion reactions.

Thiourea and its derivatives were used extensively as corrosion inhibitors for iron in acidic solutions by many workers (77-83). Results showed that guanylthiourea has a strong inhibiting effect for the corrosion of iron in both H_2S0_4 and HCl solutions (79) The inhibition efficiency of this compound was related to the properties of the polar groups and the size of N-substituted groups (80). S-substituted derivatives exert increasing anodic polarization with increasing concentration (81,82). Surface of the corroded specimens in HCl solutions with hexamethylenetetramine was much smoother than that with thiourea, regardless of the corrosion rate (83).

The effect of electronic delocalization in organic groups of thiocarbamoyl (R-CS-NH_2) and related compounds on inhibition efficiency of iron in 1.0 M HCl solutions was studied by Donnelly *et al* (84) .The inhibition efficiency of the compound was found to be related qualitatively to the electronic resonance in the R group.

Inhibitive effect of naturally occurring substance, tobacco, on the dissolution of mild steel in HCl solutions was investigated by Kumkum and Poonan (85). Tobacco polarizes both the anode and cathode areas, the extent of polarization increases with inhibitor concentration. The results proved that the alkaloids, nicotine and papaverin, contained in natural products such as tobacco leaves and black papper act as excellent inhibitors. The mechanism of inhibition is one of chemisorption.

Epoxidized fatty materials modified with aliphatic and aromatic amines as new corrosion inhibitors for mild steel in 0.05N HCl solutions at 70°C were used by Abdul Azim *el al.*(86). It has been shown that the efficiency of these compounds in the gaseous environment increased with branching of the inhibitor molecule and with increasing in the length of the chain attached to the functional group. In the liquid environment branching lowered the efficiency of the inhibitor. A ranking of the compounds according to percentage inhibition agreed with the order of increasing electron density on the nitrogen atom in these compounds.

Frignani *et al*(87) tested the corrosion inhibition of iron in H_2SO_4 and HC1 acid media at 25°C and 70°C using N-decyl-pyridinium derivatives (DP). The efficiency of the DP ion can be improved by the introduction of suitable substituents in the 3-position of the aromatic ring. These derivatives act mainly by physical adsorption between the organic cations and the anions, Cl^- or Br^-, pre-adsorbed at the metal surface of the electrode. The organic cations inhibit mainly the H^+ ion discharge, but when present in higher concentrations they also inhibit the iron dissolution reaction.

Recently, the inhibiting action of some benzimidazole derivatives on iron corrosion in HC1 solutions was studied by Ushakov *et al*(88) .The distribution of the π-electron density on the reaction centres of the inhibitor molecules was compared with the electrochemical characteristics of the corrosion process and the adsorption properties of the molecules. The protective effect of the inhibitors is caused by the chemisorption of molecules on the metal surface and depends substantially on the polar properties of the molecules. Also, the effect of benzothiazole derivatives as inhibitors for corrosion of steel in HCl solutions was investigated by Makovei *et al* (89). Carbonyl compounds were used as corrosion inhibitors for mild steel in HC1 solutions (90). Galvanostatic polarization data indicate that all carbonyl compounds are predominantly cathodic inhibitors. Schiff bases have been examined as corrosion inhibitors of mild sleel in 1.0-6.0N HC1solution by Desai et al (91). It was found, also that these schiff bases are cathodic inhibitors.

Szklarska and Dus (92) studied the effect of some organic phosphorous compounds on the corrosion of low carbon steel in HC1 solutions of various concentrations and at different temperatures. Results showed adsorption of inhibitors followed the isotherm of Freundlich and that the adsorption process was influenced by adsorption strength and resistance hindering diffusion of inhibitor molecules. Compounds containing selenium were more effective than those containing sulphur. The role of phosphates in inhibiting pitting corrosion of commercial mild steel in chloride containing media was investigated by Awad and Hoar (93). Also, the corrosion inhibition properties of disodium monoalkyl phosphates and phosphonates on corrosion of steel in chloride media was studied by Derbali et *al* (94).

The inhibition of cathodic and anodic processes of iron corrosion as a result of dimethylphenylbenzyl arsonium bromide ($R_3AsR'Br$) adsorption in 1M HC1 solutions was investigated by Reshetnikov *et al* (95). The product of the decomposition of $R_3AsR'Br$, i.e. R_3As, together with Br^-, is adsorbed in the inner layer (called secondary adsorption), and the inhibition properties of the R_3As are much higher than those of R_3AsR'. In the outer layer, also, the R_3AsR' cation as an ionic pairs with Br^- is adsorbed.

Bockris *et* al(96) .studied the absorption of chloride ion on iron in borate buffer solutions using a radiotracer technique. The adsorption of chloride ion on bare iron and passive layer surfaces follows the Temkin type of isotherm. Also, the sorption of (37) labeled Cl^- by the layer of corrosion products adhered to the surface of corrosion steel samples in chloride media was studied using radiotracer method by Karva et al*(97)*.

The oxide layers formed on steel in chromate solutions in presence of chloride ion were found to be thicker by an order of magnitude than those formed in the absence of oxide (98) .The oxide layer is subdivided into small regions behaving superparamagnetically. This heterogeneity of the layer is ascribed to the attack of the chloride ions.

Temperature effect on pitting corrosion of mild steel in deaerated sodium bicarbonate-chloride solutions was studied by Jelinek and Neufeld (99). Raising the temperature up to 90°C restricts or completely prevents the breakdown of the passive film at chloride concentrations up to about 130 ppm. At concentrations above this level the temperature effect is reversed and raising the temperature facilitates film breakdown. The two phenomena are explained in terms of two competing processes concurrently occurring at the passive film surface: reduced adsorption of Cl^- ions and reduced stability and/or increased solubility of an Fe-Cl complex at enhanced temperatures.

Majda (100) studied the corrosion inhibition of nitrogen containing compounds in aqueous acidic chloride solutions at high temperatures for preventing corrosion of steel pipes. Evaluation of corrosion inhibitors in concentrated HC1 solutions at high temperatures was also investigated (71). A corrosion inhibition mechanism is proposed as a model explaining the behaviour of weight loss to linear polarization rate ratio in terms of water diffusion across a hydrophobic inhibitor barrier.

The use of some phenoxy acetamide derivatives as corrosion inhibitors for iron in 3N nitric acid was studied by thermometric and weight loss measurements (101). The additives caused a decrease in the maximum reaction temperature and a corresponding reduction in the reaction number (RN). The results indicated that the additives reduce the corrosion rate by adsorption through the carbonyl group, while the atomic nucleus lies flat on the surface of the corroding metal. The inhibitory character of these compounds depends upon the concentration of the inhibitor as well as its chemical composition.

Fouda *et al* (102) studied the corrosion inhibition of iron in 2M $HN0_3$ by thiophene and some of its derivatives using both electrochemical polarization and weight loss measurements. The results showed that the inhibitors under consideration, influencing both the cathodic and anodic processes, are adsorbed on the metal surface in their molecular form. They do not change the mechanism of the reaction between iron and nitric acid, but decrease its rate. This effect is controlled by the values of their dipole moments. The weight loss technique also gave the same order of inhibition efficiency of the tested inhibitors.

Some quaternary ammonium compounds were prepared from cycloaliphatic amines and have been tested as corrosion inhibitors for mild steel in 50% H_3PO_4 by weight loss and polarization techniques (103). Both the two techniques gave the same order of inhibition. It is suggested that these heterocyclic quaternary ammonium compounds act mainly as cathodic inhibitors of the acid corrosion of mild steel. The degree of coverage of electrode surface was calculated from the corrosion rate with and without inhibitor. Also thermodynamic parameters for the adsorption process were calculated and discussed.

Dissolution of mild steel in sulfuric acid was studied in the presence and absence of magnetic field, with and without inhibitor, under various conditions (104). The magnetic field reduced the dissolution of the steel, the effect being greater at lower concentrations of acid and in the absence of inhibitor. The steel was protected to a greater extent at longer immersion times.

An ellipsometric study has been made on the effect of indole , thiosemicarbazide , and thioacetamide on the surface of mild steel in HCl (105) . The ellipsometric results for most solutions of the inhibitors tested showed that during the first few minutes of immersion stimulation of corrosion took place. Evidence for this was also found from weight loss and electrochemical data as well as from microscopic observation. The presence of indole up to 5 nm on the metal surface was detected during cathodic polarization, much of which desorbs when the polarization is removed.

Weight loss measurements were performed in 20% and 28% hydrochloric acid at 90°C on carbon steel, 22 Cr 5Ni duplex stainless steel, and two-superaustematic steel-27Cr31Ni3Mo and 19Cr25Ni4Mo in organic substances used singly or mixed (106). The organic substances examined were quaternary ammonium salts (l,4-pyridyl)-pyridinium chloride hydrochloride, dodecylpyridinium chloride,benzyldimethylstearyl ammonium chloride, and dodecyltrimethylammonium bromide, alkynols (l-octyn-3-ol, propargyl alcohol) and trans-cinnamaidehyde. The Synergistic effect of potassium iodide on the inhibitive efficiency of the organic substances was studied. The variation of corrosion rate during the test time (normally six hours) were recorded by means of polarization resistance measurements. Polarization curves were also recorded. The corrosion rates of the four steels examined can be reduced to less than 1 mg/cm^2.

The effect of 2-ferrocenylvinyl-1 -n-butylpyridinium iodide (FVBPI) and 2-phenylvinly-1-ethyl-pyridium iodide (PVEPI) on the corrosion of carbon steel in acids have been investigated (107). Corrosion rates were determined by weight loss of steel samples; coefficients of corrosion retardation of steel, and the degree of protection, were determined in acid solutions.

The effect of benzuoaxazole, 2-benzoxazolone, 2-methyl benzoxazole, and 2-mercaptobenzoxazol on corrosion of carbon steel in hydrochloric acid were studied (108). The effects investigated were the protection characteristic, the activation energies of the corrosion process, the polarization curves, the kinetics of cathodic hydrogen evolution, anodic iron dissolution, and the adsorption characteristics of the benzoxazole derivatives.

To ascertain the effect of the ferrocene nucleus on the inhibitor properties of organic compounds, ferrocene derivatives and their benzene analogies as corrosion inhibitors of carbon steel in 2M HCl were investigated (109) .The corrosion rate of steel was determined, and the corrosion - braking factor of the steel and the degree of protection for inhibitor concentrations were calculated. It was found that ferrocene compounds are more effective inhibitors than their benzene analogies.

Hettiarachchi *et al* *(110)* studied the effectiveness of phthalocyanines as acid corrosion inhibitors for steel. It was found that water soluble tetrasulfophthalocyanines are very poor corrosion inhibitors. Water insoluble tetraaminophthalocyanines serve as better corrosion inhibitors than the water soluble ones when the metal surface is coated with an adsorbed layer of the phthalocyanine. Water insoluble polymeric phthalocyanine coatings based on Fe(III) centers gave inhibitor efficiencies as high as 82% as confirmed by both slow potentiodynamic technique and the ac impedance analysis. Polymerization was achieved by simple dip coating followed by heat treatment of the coated surface at 450°C in an inert atmosphere. The resulting coating is adherent and electrically conducting, thereby providing a unique set of conducting polymer inhibitors that can be used in acid environments.

The effect of 1,10-phenanthroline (Phen) has been examined as a corrosion inhibitor for mild sleel in 1 N sulphuric acid by weight loss and gasometric methods (111). Studies have also been made in 1N HC1 solution to compare the efficiency of the inhibitor in both acids. Activation energy in the presence and absence of the inhibitor has also been evaluated. Galvanostatic polarization data indicate that the compound is predominantly a cathodic inhibitor. Cathodic polarization curves for mild steel in 1N H_2SO_4 and 1N HC1 containing various concentrations of thiourea (TU) (1-25 mM) and thiosemicarbazide (TSC) (0.2-25 mM) were measured in the temperature range $20\text{-}25^0C^{(112)}$. The apparent activation energy for corrosion (ΔE) was calculated from log Icorr. Vs. 1/T and R_p/T vs. 1/T relations, ΔE is virtually constant by changing TU concentrations (55-57 KJ/mol in H_2S0_4). An interpretation for the loss of inhibition efficiency of TU in acid solution is given based on the decomposition of TU to ammonium thiocyanate.

The protective effect of quaternary salts of ammonium, phosphonium and arsonium with the composition $[C_5H_6CH_3.2XR]^{+2}\ Br_2^{2-}$, where X is N, P, As, R is C_3H_5, C_3H_7 on the corrosion of iron in 0.5M H_2SO_4 was studied(113) .The formation of the products of chemical transformation of the inhibitors on the surface of metals does not always lead to inhibition. For this purpose, the chemisorption of these products or formation products of polymerization in the case of unsaturated compounds are essential.

The inhibitive action of thiourea, allylthiourea and n-phenylthiourea on the corrosion behaviour of martensitic 410 stainless steel in 1N H_2SO_4 was investigated using weight loss measurements, potnetiodynamic polarization and scanning electron microscope (114). All these inhibitors reduced the corrosion rate of 410 stainless steel. Adsorption followed the Langmuir adsorption isotherm, with n-phenylthiourea showing the highest surface coverage. The steel became more noble on addition of n-phenylthiourea and allylthiourea to the acid while thiourea made it more active. All the three organic compounds reduced the rate of hydrogen evolution reaction. Inhibition action of various azoles on the corrosion of mild steel in sulfuric acid was studied (115) .For all the azole compounds studied the inhibitive efficiency increases with temperature from 30-50°C. This efficiency may be due to two reasons. Higher activation energy is available for adsorption at higher temperatures; and surface coverage is enhanced at higher temperatures by the inhibitor molecules.

The effect of propagyl alcohol (2-propyn-l-ol) on the corrosion of carbon steel was studied in hydrochloric acid solutions of various concentrations (l, 2,5%) at 40°C and 60°C (116) .The rate of corrosion was measured electrochemically using a polarization technique. The results obtained showed that the rate of dissolution of carbon steel is considerably decreased by propagyl alcohol in aqueous hydrochloric acid solutions at 40°C and 60°C. Capacitance measurements indicated that the inhibitor species are adsorbed on the steel solution interface to a greater extent in the range of negative polarization. On the basis of impedance spectroscopy measurements the characteristics of the adsorption were separated from those of the electron transfer process.

Fouda *et al* (117) studied the inhibitive effect of some substituted phenyl N-phenylcarbamates on the corrosion of iron in 2N HC1 using galvanostatic polarization measurements. Studies carried out with different concentrations of the inhibitor indicate that the compounds act as mixed type inhibitors. The results indicate that the additives reduce the corrosion rate by away of adsorption through the oxygen atom of phenoxy group and nitrogen atom of NH group. The inhibitory character of the compounds depends upon the concentration of the inhibitor as well as its chemical composition. The results of electrocapillary measurements are consistent with the electrochemical measurements.

The degree of protection of methyl, ethyl and butyl ethers of 4,5-dihydroxyimidazolidine thione-2 of steel was studied$^{(118)}$. Corrosion tests of three parallel samples of steel were carried out at 20°C in sulfuric acid solution with 4,5-dialkoxyimidazolidine thione-2 added in amounts of 0.05, 0.10, 0.25 and 0.50 g/liter. After exposure of the samples to acid they were carefully washed with distilled water, dried and weighted. The more concentrated acid and the longer exposure time, the stronger is the protective action of each inhibitor. Thus when 0.50 g/liter of 4,5-diethoxyimidazolidinethione-2 was added, the average extent of protection in 1 M H_2S0_4 is 98% after 50 h, and 98.6% after 100 h.

An inhibiting effect of octylamine derivatives has been experimentally tested on St3 steel specimens in 1M H_2S0_4, 1M HC1 and 1M H_2S0_4 + 5M NaI at $20^0C^{(119)}$. Steady-state corrosion is studied by weight loss and potentiodynamic measurements using a rotating disk electrode. Comparison of polarization curves showed that for solutions under study a discharge is the cathodic process-limiting step. It is This step that is retarded by amines, which may be explained by contraction of surfaces carrying the discharge: surfaces are partially suppressed due to interaction with amine thus decreasing the hydrogen ions (discharge rate). A conclusion is drawn that synergism results from transition to a blocking mechanism of the corrosion inhibition by amines and soft anions.

The effect of n-dimethylaminophenylferocenylcarbinol (DFC); its-methyl derivatives (MDFC) and their mixture with KI and KSCN on the steel St3 corrosion was studied in acid solutions$^{(120)}$. It is shown that both reactants inhibit corrosion in nonoxidized acids (HC1, H_2SO_4, and H_3P0_4), and promote it in oxidized acid (HNO_3). The latter point is due to the capacity of ferrocene derivatives to oxidate to ferrocene - cation under these conditions. Mixtures of MDFC and DFC with known anion - active additions are efficient inhibitors in H_2S0_4 solutions. The highest synergistic effect was observed with the carbinol – salt ratio of 1:3.

A study has been made for corrosion resistance of one carbon steel and two low alloy steels in 2M HC1 solutions at temperature between 60°C and 90°C and of the effectiveness of some organic compounds used as corrosion inhibitor under the same experimental conditions (121) . Weight loss results spectrophotometric analysis for the determination of the Fe^{2+} ion concentration, and electrochemical data suggest that the level of inhibition and the various effects of the examined inhibitors on the behaviour of carbon and low alloy steel can be explained by the specific mechanisms of the action of each inhibitor.

The inhibition effect of potassium iodide on the corrosion of stainless steel has been examined using weight loss and electrochemical measurements (122). Potassium iodide was found to be an excellent inhibitor for stainless steel types 316, 430 and 440 (more than 95% efficiency), and moderate for the type 304. The corrosion rates in 1M HC1 and in presence of potassium iodide fit the Arrhenius equation. The presence of potassium iodide lowers both the activation energy and the rate of corrosion. Polarization measurements indicated that potassium iodide acts as cathodic inhibitor at lower concentrations.

The efficiency of 12 pyrazolone derivatives as corrosion inhibitors has been tested on 05 K_p steel at 200°C in 1M sulphuric and hydrochloric acids by weight loss method (123). It is shown that their protective action in sulphate solutions is inferior to that in chloride solutions. Di- (l-hexyl-5-hydroxy-3-methyl-4-pyrazolyle) methane derivatives are highly attractive, stable and low toxic inhibitors which are readily synthesized from reactants available.

The effect of some phosphonic acid derivatives on the corrosion behaviour of carbon steel has been investigated in hydrochloric acid solutions by gravimetric and electrochemical methods (124). Some phosphonic acids were found to have inhibitive effects. These effects depend on the molecular structure, the number of nitrogen atoms and phosphono groups, but mainly on their position in the molecules, as shown by the differences in corrosion rates in the presence of various phosphonic acids. The variation of polarization resistance with time suggests that the inhibitive action of diethylenetriaminepentamethylenephosphonic acid depends mainly on the protective film formed on the surface of the steel and is independent of changes in solution composition with time.

Muralidharan *et al* (125) studied the inhibiting action of polyamino-benzoquinone (PAQ) on corrosion of mild steel in 1N H_2SO_4) / and 1 N HCl. PAQ is found to behave better in 1N H_2S0_4 than 1N HCl. Potentiodynamic polarization studies revealed the fact that PAQ is a mixed-type inhibitor. PAQ is able to reduce considerably the permeation current through the steel surface in both acids. Changes in impedance parameters (R_{ct} and C_{dl}) are indicative of adsorption of PAQ on the metal surface leading to the formation of a protective film, which grows, with increasing exposure time. The adsorption of the inhibitor was also found to obey Temkin's adsorption isotherm in both acids, thereby indicating that the main process of inhibition is by adsorption. UV spectral studies were also carried out to establish the actual mechanism of inhibition of corrosion.

An inhibiting effect of 2-mercapto-benz-imidazol derivatives was investigated for the annealed St 20 specimens in hydrochloric acid (pH 0-2) (126). Electrochemical, weight loss and gasometric technique were applied to estimate the inhibiting effect. Physicomechanical tests were also performed to determine a fraction of oxygen depolarization and a coefficient of hydrogen absorption suppression. It was found that the molecule hydrophobization favours a chelating activity, increasing chelate film stability, and inhibiting effect improving.

The effect of some hydrazone oxime derivatives on the corrosion of iron in 2M HCl have been studied by polarization and weight loss techniques (127). It was found that the compounds under consideration are adsorbed on the iron surface according to the Temkin isotherm. The Tafel slope is approximately constant independent of the concentration of the inhibitor. The results of polarization indicated that all compounds tested were of a mixed type, but the cathode is more preferentially polarized.

Moretti *et al.*(128-130) studied the inhibiting effect of indole (IN), 5-hydroxyindole(HIN),5-aminoindole(AIN),5-chlorindole(CIN)and 5-nitroindole (NIN) on the corrosion of mild steel in sulphuric acid. Potentiodynamic polarization experiments showed that in the temperature range from 25 to 55°C, the inhibiting effect of IN and its derivatives is more pronounced on the anodic rather than on the cathodic process. For a given temperature the corrosion rates were decreased as inhibitor concentration was increased but as the temperature is increased higher corrosion rates resulted. These experimental data fit Frumkin (for IN, AIN, CIN and NIN) and Temkin (for HIN) isotherms. The best inhibiting effect was obtained at the highest concentrations (0.005-0.0075M) of IN and CIN up to 23-35 °C. This is probably due to the fact that these two molecules can form oligomers on the electrode surface.

Kangelov and Mircheva (131) studied the corrosion rate of mild steel in 1M H_2SO_4 containing (tetramethyldithio-oxamide TMDTO) with or without addition of Fe (II), Co (II), Ni (II) and Sn(II) over a temperature range 20-80°C. Invariably, the rate of corrosion in media, with only oxamide, was 1.2-1.8- fold lower than that in media to which metal ions had been introduced.

This fact was proved to be the result of the formation of coordination complex $M_2[TMDTO]_2$.

The influence of three isomers of aminobenzoic acids on the corrosion of mild steel in 1M HCl and 0.5M H_2SO_4 has been studied using weight loss, gasometric measurements and various electrochemical techniques (132). All the three isomers of aminobenzoic acid inhibit the corrosion of mild steel in both HCl and H_2SO_4 according to the order ortho greater than meta greater than para. It was observed that the inhibition is greater in HCl than in H_2SO_4. The predominant behaviour is the cathodic inhibitor mode. These compounds reduce the permeation current in 1M HCl and enhance it in 0.5M H_2SO_4. The adsorption of these compounds on mild steel in 1M HCl and 0.5M H_2SO_4 obeys Langmuir's adsorption isotherm.

The effect of some benzene sulphonyl hydrazone derivatives on the corrosion of iron in 1 M HCl solution at 303 K was investigated using polarization and weight loss techniques (133). A significant decrease in the corrosion rate of iron was observed by the presence of traces of these compounds. The corrosion rate ($I_{corr.}$) was found to be a function of the nature, concentration of the inhibitor and temperature of the medium .The degree of surface coverage calculated was used to evaluate the free energy of adsorption ($\Delta G^{\circ}_{ads.}$) of the inhibitors. The observed experimental data indicated that all compounds tested are of mixed type, but the cathodic is more preferentially polarized.

The effect of pyridoxal (P), 4-methylthiosemicarbazide (4MTS), pyridoxal-(4)-methylthiosemicarbazone) (P4MTS) and Zn(II)-pyridoxal-(4-methylthiosemicarbazone) (ZnP4MTS) on steel corrosion in hydrochloric acid has been studied (134). Weight loss and hydrogen evolution measurements revealed that ZnP4MTS exhibit a higher inhibition efficiency than P4TS, PHC and 4MTS. Generally, inhibition was found to increase with increasing inhibitor concentration, half-life, activation energy and with decrease in the first order rate constants at 30 and 40°C. Physical adsorption mechanism has been proposed for the inhibitors and the difference in the inhibition behaviour of the compounds has been explained in terms of the difference in their molecular weights (size).

Bastidas *et al* (135) studied the influence of the butyl groups as substituent in n-butylamine used as a mild steel corrosion inhibitor in hydrochloric acid solution. An inhibition mechanism was proposed for n-butylamine, dibutylamine and tributylamine in the concentration range from $1x10^{-4}$ to 1M and at temperature range from 278-308 K using electrochemical, gravimetric and surface roughness techniques. It was found that the three inhibitors are adsorbed on mild steel surface according to a Frumkin isotherm.

The inhibitive effects of alanine, valine, phalanine, serine and threonine. amino acids on the corrosion of steel in 2M H_2S0_4 have been investigated by weight and gasometric techniques at 25^0C(136). The inhibition efficiency depended on the type of amino acid. and ranged from 42% to 91%.

The dissolution of carbon steel was studied in HC1 solution as a function of acid and inhibitor concentrations as well as of temperature (137). The inhibition efficiency of some ethoxylated fatty amines having the general formula R-NH- (CH_2CH_20) n-H, as detected from polarization measurements and weight loss experiments, was found to increase, with increasing inhibitor concentrations and or decreasing temperature . Inhibition was explained by adsorption on the metal surface through their ethoxy groups while the hydrocarbon parts protrude brush-like into the solution. These compounds act as mixed inhibitors.

The inhibitory effect of quinazole-4-one derivatives on the corrosion of iron in hydrochloric acid was investigated (138). Polarization curves indicated that these compounds act as mixed type inhibitors, but the cathode is more preferentially polarized. The effect of structure change of these compounds on their inhibition efficiency has been studied. The inhibitor appear to obey general adsorption following the Langmuir adsorption isotherv v m. Results indicate that the rate of corrosion of iron increases with increasing temperature over the range 27-50 °C both in absence and presence of inhibitor.

N-benzylidine phenylamine-N-oxide (nitrone) and eight of its derivatives with subsitutents in the para position of the alpha phenyl group were synthesized and their inhibition of the corrosion of mild steel in 1 M HCl was investigated by weight loss, potentiodynamic polarization, hydrogen permeation, and impedance measurements (139). Determination of inhibition efficiency in the presence of these compounds at different temperature indicated that the dimethyl derivatives shows the best performance even at temperature as high as 70 °C. Potentiodynamic polarization studies, revealed the fact that nitrone and its derivatives act as mixed type inhibitors. All of these compounds are found to reduce the permeation of hydrogen through mild steel in 1 M HCl solutions. The adsorption of these compounds on the mild steel surface obeys Temkin's adsorption isotherm.

Macrocyclic compounds constitute potential class of corrosion inhibitors. In an attempt to develop effective corrosion inhibitors we have synthesized four macrocyclic compounds were synthesized by condensing o-ethylene diamine and o-phenylene diamine with ethylacetoacetate and succinic acid (140). Their inhibiting action was evaluated on corrosion of mild steel in 1 M HCl and H_2SO_4 by weight loss and potentiodynamic polarization methods. A macrocyclic compound derived by condensing o-phenylene diamine with ethylacetoacetate exhibited best performance by giving IE of 98 % at 500-ppm concentration. The potentiodynamic polarization studies revealed that the tested compounds are either mixed type or predominantly cathodic inhibitors. IE of all the investigated compounds increased significantly on addition of small concentration of KI in both acids due to synergism.

The inhibiting effect of cationic surfactant N, N, N-dimethyl 4-methylbenzyl dodecyl ammonium chloride on mild steel in HCl solutions was investigated by surface and thermodynamic measurements, weight loss tests, polarization measurements and EDS Techniques (141). The data obtained from surface and thermodynamic measurements in presence of the inhibitor indicate that the area per molecule slightly increases with increasing temperature and both adsorption and micellization processes are spontaneous. Weight loss measurements showed that inhibition efficiencies increased with increasing surfactant concentration and attained a maximum around their critical micelle concentration. Polarization studies revealed that the inhibitor behaves as a mixed type in HCl solutions and acted on the cathodic reaction without modifying the mechanism of the hydrogen evaluation reaction. EDS measurements showed high coverage of surfactant on the mild steel surface.

4-aminodimethylamino-benzylidene-3-propyl - 5 - mercapto - 1, 2, 4-triazole (ADPMT), have been synthesized. Their inhibiting action on the corrosion of mild steel in 15% HCl under boiling conditions has been studied by weight loss method (142). With the exception of ADPMT, all the triazole derivatives tested showed an inhibiting efficiency greater than 98%. Triazole compounds ACPMT and ASPMT showed an efficiency greater than 99%. Their efficiency has been found to be comparable with that of proprgyl alcohol, the standard corrosion inhibitor for mild steel in boiling HCl. Potentio-dynamic polarization studies revealed that all the triazoles investigated are mixed type inhibitors inhibiting the corrosion of mild steel by blocking the active sites of the metal surface. The adsorption of these compounds on mild steel from 15% HCl has been found to obey Temkin 's adsorption isotherm

The effect of Schiff base- metallocomplexes on the corrosion of mild steel were investigated by weight loss, electrochemical measurements and surface analyses in various aqueous solutions such as HCl solutions and pseudo cooling water (143). The maximum value of inhibition efficiency on the corrosion of mild steel in 1 mol / dm ^{3} HCl acid solution was about 95.8 % on the case of indium (III) left brace N, N, prime - bis (salicylaldehyde)-1, 12-diaminododecane right brace complex. The molecules of Schiff base-metallocomplexes adsorbed on the surfaces of the mild steel depress the corrosion.

The corrosion behaviour of steel (0.05% C) in 0.5 M sulphuric acid solutions in the presence of pyrazole- halide mixture was studied (144). The increase in surface coverage values in the order of I^- greater than Br^- greater than Cl^- seems to indicate that the radii and the electronegativity of halides play an important role in the adsorption process. The inhibition efficiency (P %) increases with increasing concentration of pyrazole. The addition of halides enhances the inhibition efficiency to a considerable extent. Increase of temperature increases the corrosion rate in the range 30-85 °C in the presence and absence of inhibitors. The apparent activation energy is 12.4 Kcal / mol. The synergistic effect of pyrazole and halide ions is discussed from the viewpoint of adsorption models.

The corrosion behaviour of low-carbon steel using different concentrations ($1X10^{-3}$ to $9X10^{-3}$ M) of benzotriazole (BTA) in 1 M H_2SO_4 has been studied by potentiodynamic polarization measurements at a scan rate of 0.166-mVs^{-1} (145). It was found that passivation current, corrosion potential, passive potential and polarization resistance increase with increasing benzotriazole concentrations, while critical current, corrosion current and corrosion rate decrease. It was also, established that the corrosion rate depends on the concentration of inhibitor and chloride ions along with the sweep rate of polarization. Maximum inhibition efficiency (98.5%) was obtained at $9X10^{-4}$M BTA. Thermodynamic pramters for adsorption of BTA are calculated.

The influence of thiophenol on the corrosion and hydrogen permeation in 1 M HCl and 0.5 M H_2SO_4 has been studied using weight loss measurements ,gasometric studies and another electrochemical technique (146). Thiophenol inhibits the corrosion of mild steel in both the acids, but it is found to be more effective in H_2SO_4. It behaves predominantly as a cathodic inhibitor. It brings down the permeation current in both the acids, but is more effective in H_2SO_4.The adsorption of thiophenol on the mild steel surface from both the acids obey Temkin 's adsorption isotherm.

Methyl red has been investigated as inhibitor for corrosion of mild steel in 1.0 M sulfuric and perchloric acid solutions (147). The inhibition efficiency increases with increasing the concentration of the inhibitor and decreases with increasing temperature. Methyl red is physically adsorbed on the surface of mild steel and acts as a mixed inhibitor. The inhibition follows Langmuir adsorption isotherm and adsorption is physically in nature. Activation energy values for inhibited system are higher than those of uninhibited system.

Corrosion of mild steel in stagnant 1.0N HCl solution at 28± 2 °C was studied by (linear) polarization resistance and Tafel intercept (log) methods in absence and presence of the acid extract of Eugenia Jambolans (EJ)(148). From the change in these electrochemical parameters, it was calculated that the inhibition increased with increase in the concentration of the additive. This work aimed at developing cheap, eco-frindly and biodegradable acid corrosion inhibitors.

A preliminary laboratory study on corrosion protection of mild steel in 15%HCl and 3% HF used in acidization of oil well by some N-containing organic compound were carried out (149). Inhibition efficiencies were evaluated by metal loss and potentiostatic polarization methods. The corrosion rate of mild steel decreased appreciably even in the presence of traces of the compounds. The extent of decrease in the corrosion rate was found to depend on the nature of the inhibitor and its concentration. Results of testing the additives in preventing corrosion of mild steel by the acid solution at different temperature (30 to 70 °C) and exposure time (6 - 36 hrs.) at a fixed inhibiting concentration are also reported. Thermodynamic parameters like heat of adsorption and activation energies have been calculated in the absence and presence of these organic additives. The nature of the film formed on the metal surface was analyzed by infrared (IR) spectrum and relationship between structure of the organic compounds and inhibition efficiencies has been explained.

The influence of pyridinium chloride (PC) and n-hexa decyl pyridinium chloride (HDPC) on the corrosion of mild steel in 5 N HCl and 5N H_2SO_4 has been studied using weight loss, gasometric, potentiodynamic polarization, linear polarization studies and small amplitude cyclic voltameric techniques (150). It was found that HDPC is more inhibitive than PC and both the compounds perform better inhibition in H_2SO_4. Polarization studies revealed that PC behaves as an anodic inhibitor in H_2SO_4 and as a mixed inhibitor in HCl. Measurements of polarization resistance (R_p) and double layer capacitance (C_{dl}) in the presence of these compounds also reveal the better performance of HDPC in both acids and it was found to obey Temkin's adsorption isotherm.

Corrosion inhibitors represent the most effective and flexible means of controlling internal corrosion associated with oil and gas production (151). Tests were carried out to demonstrate the structure / effect relationship which are effective in controlling the inhibition efficiency. To illustrate this approach, the effect at the para position of 1(Benzyl) 1-H-4,5-Dibenzoyl-1,2,3 -Triazole (BDBT) on corrosion inhibition has been investigated. Mild steel rotating cylinder electrode in acid media was used in conjunction with Tafel polarization technique, ac impedance measurements and continuous linear polarization resistance method .The nitro group was found to cause a considerable decrease in the corrosion inhibition of the parent compound BDBT. Owing to the induction effects of Br^- on the aromatic ring the bromo derivative has better inhibition protection than the methyl derivative. The corrosion rate profiles obtained from on-line polarization technique showed that the inhibition capacity of the studied substituents at the para- position increases as follows: NO_2 less than CH_3 less than Br less than H.

Corrosion of mild steel in both stagnant 0.1 N HCl and H_2SO_4 solutions at 28 ± 2 °C was studied by linear polarization resistance and Tafel intercept methods using potentio- galvno-scan, Model PGS-81 (152). The values of open circuit potential, polarization resistance, corrosion current density and Tafel constants were obtained in the absence and presence of 0.5, 0.375 and 0.25% acid extracts of Lawsonia Inermis.It was observed that the inhibition increases with the increase in the concentration of the additive's extracts in both the acids. The inhibition efficiencies calculated from polarization resistance and corrosion current densities have shown in fair agreement. Probable mechanisms of the acid corrosion and its inhibition are proposed.

The inhibitive effect of benzyl triethanol ammonium chloride (BTAC) and ethoxylated benzyl triethanol ammonium chloride (EBTAC) on the corrosion of carbon steel in sulfuric acid solution was measured by the weight loss method (153). The adsorption of these compounds (surfactants) leads to the formation of a monolayer on the metal surface. The relationships between the concentration of these inhibitors and their surface properties, thermodynamic properties, surface coverage (θ) and inhibiting efficiency have been investigated. The results indicated that EBTAC is superior to BTAC.

The inhibiting action of linear and cyclic thiocarbamides on mild steel corrosion in 1 M HCl was examined (154). It was found that their inhibiting effect grows with the increase of temperature of the corrosion medium. Their presence in the solution decreases the apparent activation energy of the hydrogen evolution reaction. Inhibitor chemisorption on the metal surface is described by the Temkin adsorption isotherm. The thiocarbamides studied are adsorbed through the S-atom which is the adsorption center, forming a doner-acceptor bond between the unpaired electrons of the S-atom and the positive active centers of the metal surface.

The inhibition efficiency of formaldehyde have been studied at different concentrations on the corrosion of mild steel in 5% HCl at 303 K and 363 K using potentiostatic and gravemetric techniques and the results are compared (155). The inhibition efficiency increased with increasing concentration of the inhibitor and decreased with increasing temperature. The surface coverage, activation energy and the type of adsorption of the inhibitor have also been studied.

The synergistic influence caused by iodide ions on the inhibition of corrosion of mild steel in 0.5M H_2SO_4in the presence of n-hexyl amine (n-HA) has been studied using potentiodynamic polarization, linear polarization and a.c. impedance techniqueS (156). n-HA accelerates the corrosion of mild steel at lower concentrations but inhibits the corrosion at higher concentrations. The addition of iodide ions enhances the inhibition efficiency to a considerable extent. The adsorption of this compound is found to obey Temkin's adsorption isotherm. The increase of surface coverage in the presence of iodide ions indicates that iodide ions enhance the adsorption of n-HA on the metal surface. Defines and evaluates synergism parameter (S_I). Values of the parameter which are more than unity indicate the fact that the enhanced inhibition efficiency in the presence of iodide ions is only due to synergism and there is a definite contribution from the inhibitor molecule. n-HA is then adsorbed by coulombic interaction on the metal surface , where iodide ions are already adsorbed and thus reduce the corrosion rate.

Compounds such as 2- aminobenzothiazole (ABT), 2-amino-6-Chlorobenzothiazole (ACLBT),2-amino-6-methy benzothiazole (AMEBT), and 2-amino-6-methoxy benzothiazole (AMEOBT), have been synthesized and their inhibitive action on the corrosion of mild steel in 1M HCl has been evaluated using weight loss , potentiodynamic polarization and hydrogen permeation measurements⁽¹⁵⁷⁾. Determination of inhibition efficiency in the presence of these compounds at different temperatures indicated that ACLBT have the best performance, even at a temperatures as high as 60 °C. Potentiodynamic polarization studies reveal the fact that ABT and its derivatives act as cathodic inhibitors. It was found that all these compounds reduce the permeation of hydrogen through mild steel in 1M HCl solution. The adsorption of these compounds on the mild steel from HCl solutions obeys Temkin's adsorption isotherm. The adsorption of 2- amino benzothiazole on the mild steel has been substantiated by Auger electron spectroscopy.

Four n-alkyl amines (6,8,10 and 12 carbon atoms) were investigated as corrosion inhibitors for mild steel in 2 M HCl solution using gravimetric and polarization techniques. The influence of temperature (278-308 K) and inhibitor concentration (10^{-1}-10^{-6} M) were studied (159). Protection efficiency improved when the inhibitor concentration and the length of the alkyl chain were increased. The four amines tested were adsorbed on the mild steel surface according to a Frumkin isotherm.

Aim and Scope of the Present Work

Although the corrosion and corrosion inhibition of iron and iron alloys, in general, and steel in particular, have been received a great attention in different media with and without various types of inhibitors. The corrosion inhibition of such metals becomes of such interest to do. Such growing point of work comes from the great progress in synthesis of new organic compounds according to the suitable designing of inhibitor molecules.

The inhibitors molecules used were selected from a large number of recently prepared organic compounds. Their molecules contain different substituted groups located in various positions with respect to the active inhibition centers. Also, the acid chloride media are the most important ones owing to its dangerous effect on iron and its alloys. C-steel is one of widely applicable in industry and domestic life.

Our aim was to study the corrosion and corrosion inhibition of C-steel in acid chloride solutions, the effect of inhibitor molecule on the inhibition efficiency. In this respect, the inhibition mechanism will be proposed. Also, the effect of different substituted groups, whether the electron donating or withdrawing, on the corrosion inhibition will be studied. The correlation between the type of the substituted and its position, i.e , para, meta or ortho, and inhibition efficiency was also investigated . Finally, the effect of temperature on the inhibition process was studied.

فرع بنها
كليـــة العلوم
الدراسات العليا والبحوث

السيد أمين مكتبة / علــوم بنها

تحية طيبة وبعد/٠٠

قادم لسيادتكم السيد /صلاح سالم زهران محمد

وذلك لتسليمكم نسخة من رسالة الماجستير / ~~الدكتوراه~~ حيث أنه قد تم منحه الدرجة

برجاء التكرم بموافاتنا بما يوفيد إستلامكم النسخ

وتفضلوا بقبول فائق الاحترام ،،،،

أمين الكليـــــة

(حسن زين العابديـــــن)

رانيا انتصار

CHAPTER (II)

EXPERMINTAL

2.1 Chemical composition of the investigated materials

Carbon steel used in this investigation has the following chemical composition:

Table (2.1): Carbon steel

Element	C	Mn	P	Si	Fe
Analysis (weight %)	0.200	0.350	0.024	0.003	rest

2.2 Test specimens and treatment

2.2.1 For weight loss measurements

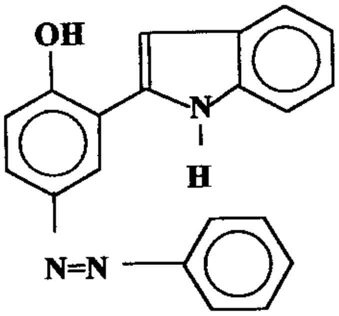
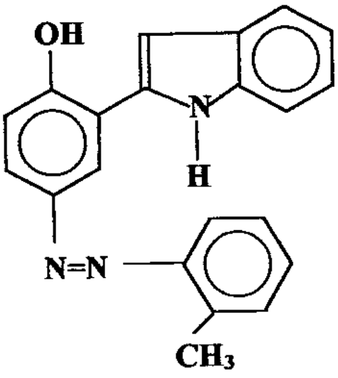
The test specimens used were in the form of sheets of dimensions1.5x1.5x0.4 cm, and of ≈ 11 gm average weight. The specimens were polished by emery papers of different grades, degreased with acetone (117), then washed with double distilled water, and finally dried between two filter papers. Such treatment was carried out immediately before each measurement

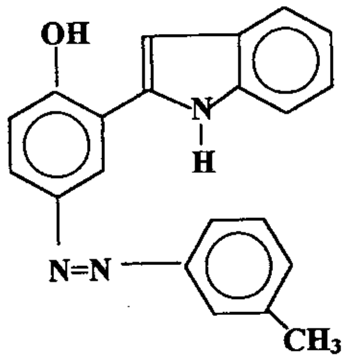
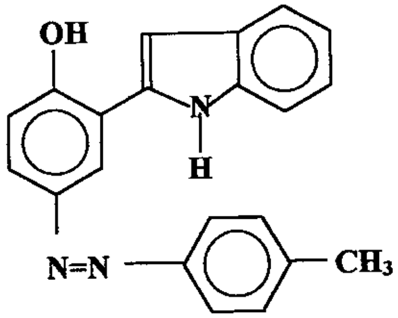
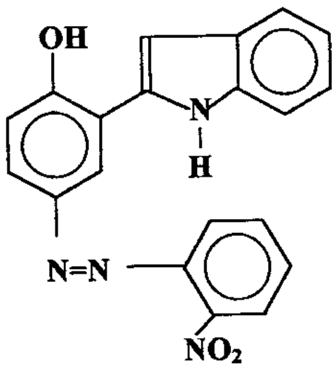
2.2.2 Galvanostatic polarization measurements

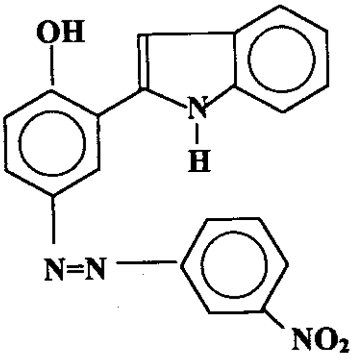
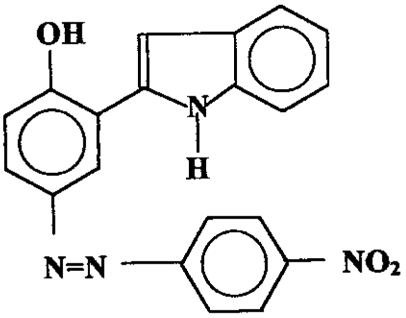
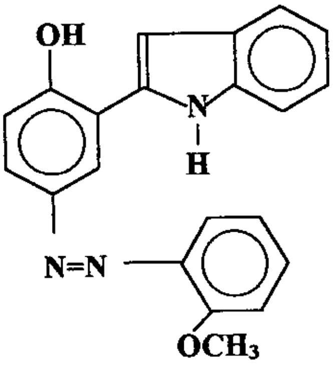
The electrodes used for such experiments having dimensions 1.5x2 x0.4cm were cut from a sheet of carbon steel. The carbon steel sheet was fixed at one end by mechanical way, and the electrode was fixed into a Pyrex glass tubing of appropriate diameter by means of araldite (Ciba- Geigy- Switzerland) leaving the exposed length, 10 mm, to contact the solution. In all measurements the preparation of electrodes was made as in case of weight loss measurements. Electrodes treated in this way were found to give reproducible results.

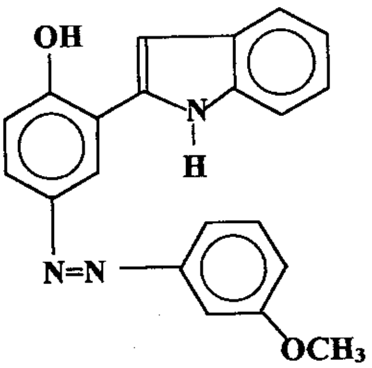
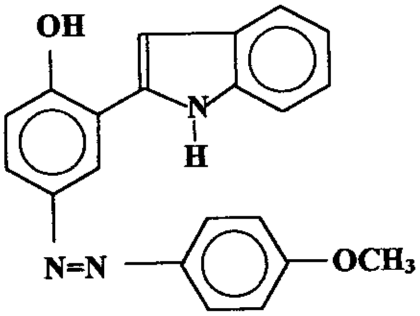
2.3 Material and solutions

2.3.1 Inhibitors. The inhibitors tested in this study were selected from indole derivatives, listed in the following Table :

Inhibitor	**Structure**	**Name**
(1)		4-phenylazo-2-(indol-2̄-yl) phenol
(II-a)		4-(2-methylphenylazo)-2-(indoi-2̄-yl) phenol

(II-b)		4-(3-methylphenylazo)-2-(indol-2̄-yl) phenol
(II-c)		4-(4-methylphenylazo)-2-(indol-2̄-yl) phenol
(III-a)		4-(2-nitrophenylazo)-2-(indol-2̃-yl) phenol

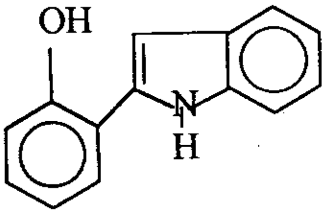
(III-b)		4-(3-nitrophenylazo)-2-(indol-2̄-yl) phenol
(III-c)		4-(4-nitrolphenylazo)-2-(indol-2̄-yl) phenol
(IV-a)		4-(2-methoxyphenylazo)-2-(indol-2̄-yl) phenol

(IV-b)		4-(3-methoxyphenylazo)-2-(indol-2̄-yl) phenol
(IV-c)		4-(4-methoxyphenylazo)-2-(indol-2̄-yl) phenol

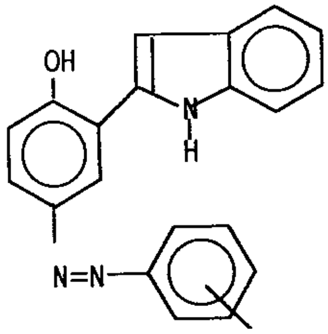
Preparation of inhibitors used:

(a) Synthesis of 2-(indol-2̄-yl) phenol (I)

A mixture of 2- hydroxyacetophenone, phenylhydrazine (0.04 mol) and polyphosphoric acid (60 gm, prepared from 40 gm phosphorous pentamid and 20 gm ortho phosphoric acid) was heated on an oil bath at 120 °C for one hr. and left to stand over night at room temperature . The reaction mixture was poured into an ice cold water. The precipitated product was filtrated, washed with water and dried. It was crystallized from methanol to yield 5.0 gm (68 %) of the named compound, m.p. 162-164 °C, I R: (KBr) 3445,3440 cm^{-1} (OH and NH, respectively).



(I)



(IIa---IV)

R= $-CH_3$ or $-NO_2$ or $-OCH_3$ in (o-,m-,p- position)

(b) (Synthesis of 4-arylazo-2-(indol-2-yl) phenol (IIa--IV)

A well stirred solution of each appropriate arylamine (0.2 mol) in 2 N HCl (125 ml) was cooled in an ice bath diazodized with 0.1 N nitrite solution (100 ml) and the mixture was stirred at 0.0 – 5 °C for one hour. The cooled diazonium solution was added dropwise to a well-stirred cold solution of 2-(indol-2-yl) phenol in sodium hydroxide solution (5%, 30ml). The reaction mixture was stirred for 2-3 hrs. until coupling was complete. The solid precipitate was filtrated, washed with water, dried and crystallized from aqueous ethanol to give the 4-arylazo-2-(indol-2-yl) phenol (IIa ---IV)

2.3.2 Test solutions

(i) Hydrochloric acid

Approximately 5 N hydrochloric acid solution was prepared by diluting the appropriate volume of the concentrated chemically pure grade acid with distilled water. The concentration of the acid was checked by titration of an appropriately diluted portion with standard solution of sodium carbonate. From this stock concentration solution, exactly 1M hydrochloric acid solution was prepared by dilution with distilled water.

(ii) Inhibitor solutions.

50 ml stock solutions (10^{-3} M) of compounds I, II and III were prepared by dissolving an accurately weighed quantity of each material in the appropriate volume of absolute ethanol, then the required concentrations are prepared by dilution with distilled water.

2.4 Procedure used for corrosion measurements

2.4.1 Weight loss measurements.

The specimen of the given metal prepared as described before (total surface area ≈ 6.3 cm) was dipped in 50 ml of the test solutions at 30 °C. This was carried out in a covered beaker to prevent contact with air and allow the escape of evolved gases. After the required immersion time, the test specimen was removed, washed with double distilled water, precautions were always made to avoid scratching of the specimen during washing after exposure, dried by a jet of air and finally weighed. The weight loss was recorded to the nearest 0.0001 g. and, the weight loss per unit area was calculated as:

$$\Delta W = W_1 - W_2 \qquad (2.1)$$

where W_1 and W_2 are the weights of the specimen before and after reaction, respectively. The percent inhibition I % was computed by the equation:

$$I\% = \frac{\Delta w_{free} - \Delta w_{inh.}}{\Delta w_{free}} x100 \qquad (2.2)$$

where ΔW_{free} and $\Delta W_{inh.}$ are the weight loss per unit area in the absence and presence of the additive, respectively.

2.4.2 Galvanostatic polarization measurements

The electrode was immersed in the test solution, and its potential was measured until a constant value was obtained ($E_{corr.}$.) The polarization was then started in cathodic direction followed by the anodic one. The potential of the electrode was measured against a saturated calomel electrode (SCE) and using the cell described below, Fig. (2.1). The electrode potential was recorded with the aid of multimeter (ABB Metrawatt GmbH, W. Germany). The current was supplied using AMEL type model 549 galvanostst. The electrical circuit for polarization measurements is shown in Fig. (2.2).

2.4.3.The corrosion cell

The cell used for polarization measurements is shown in Fig. (2.1). It was made of Pyrex glass with the dimensions illustrated, a ground glass joint, B, served for mounting the test electrode and fixing it inside the cell in such a manner that the electrode surface facing directly the lugging capillary tube. M_1 is a small side compartment to support the saturated calomel electrode (reference electrode L), M_2, is another side compartment to hold a platenized electrode, X, serving as an auxiliary electrode. Trap, T, containing bi-distilled water served as gas outlet. All measurements were carried out in a double walled electrically controlled air thermostat at the required temperature.

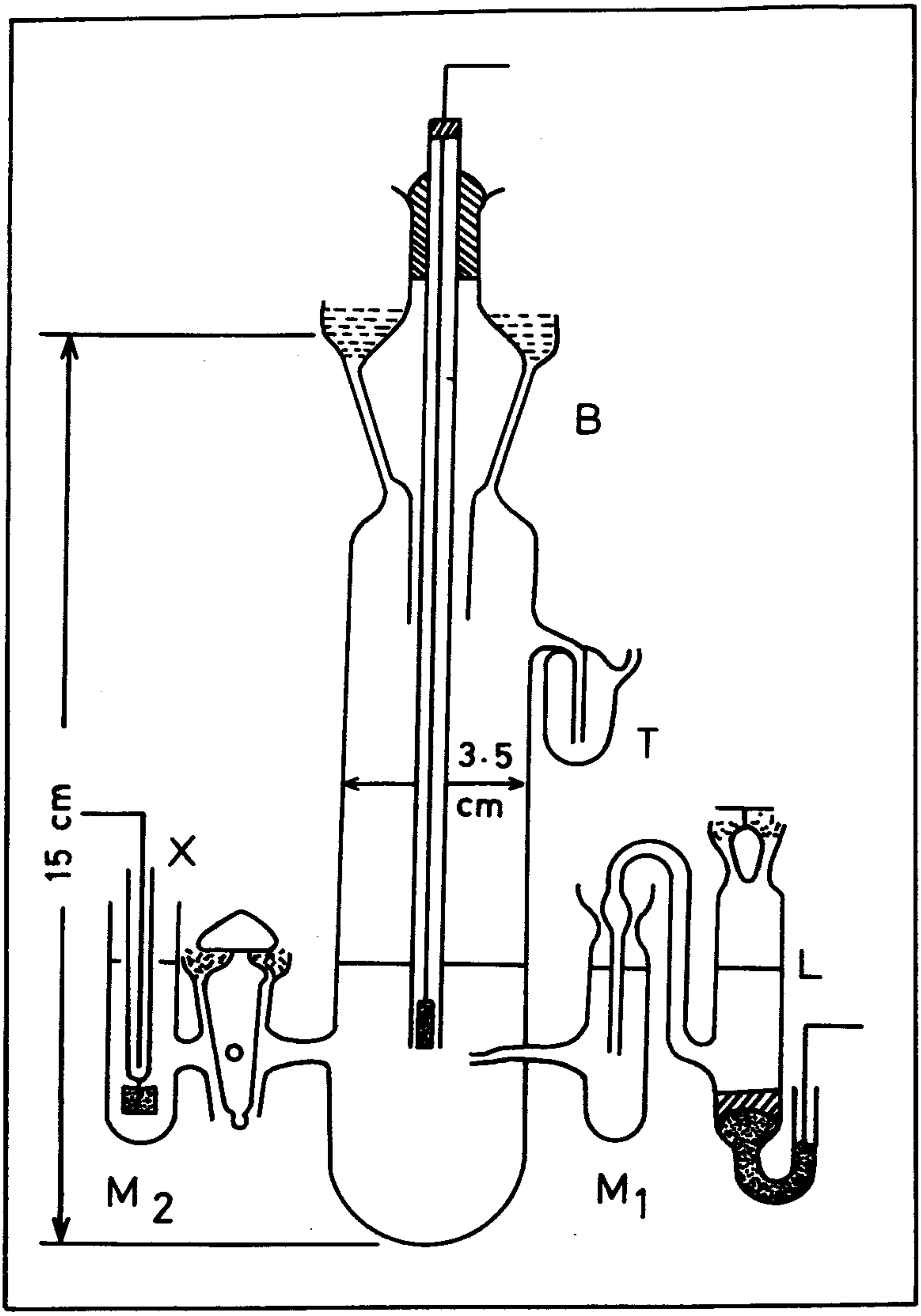
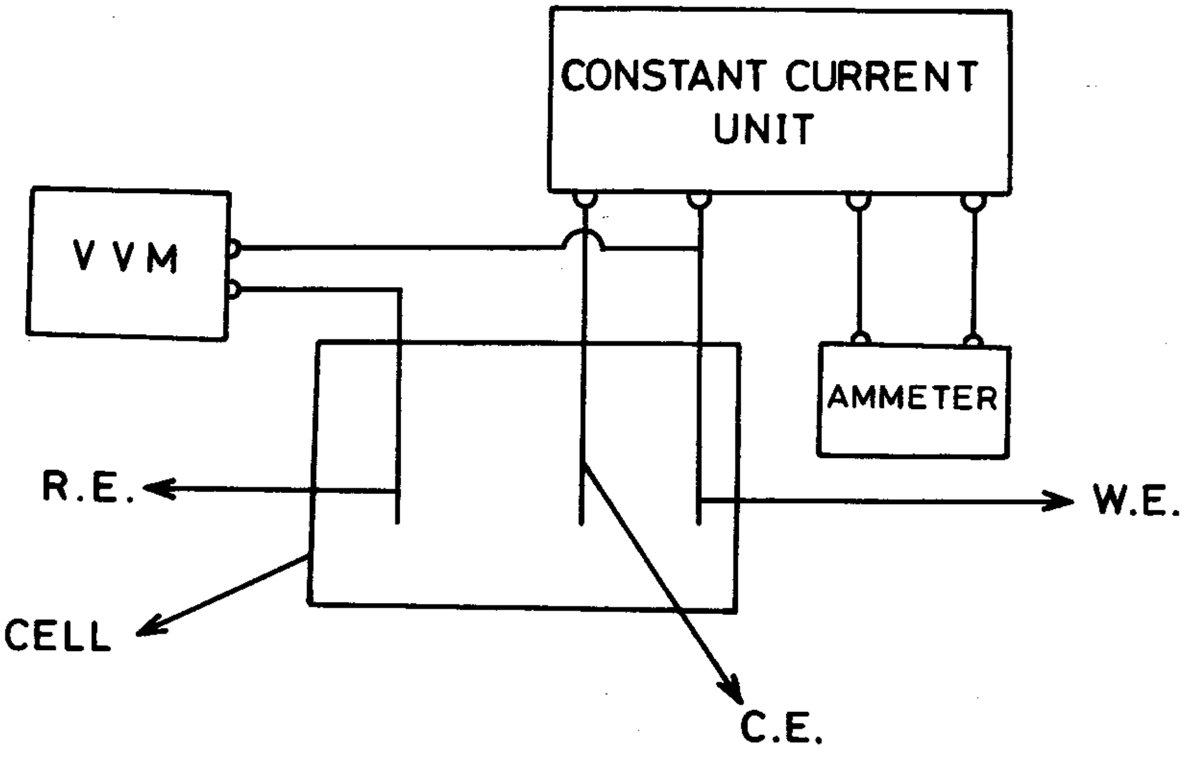


Fig.(2.1): The cell



ig.(2.2):Schematic diagram of the galvanostatic polarization circuit.