Corrosion Inhibition of Mildsteel in Acid Medium by Hexadecyl Amine

By

Mangayarkarasi .S

A DISSERTATION SUBMITTED TO THE AVINASHILINGAM INSTITUTE FOR HOME SCIENCE AND HIGHER EDUCATION FOR WOMEN-DEEMED UNIVERSITY, COIMBATORE - 641 043
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MASTER OF SCIENCE IN APPLIED CHEMISTRY

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Certified as Bonafide Research Work.

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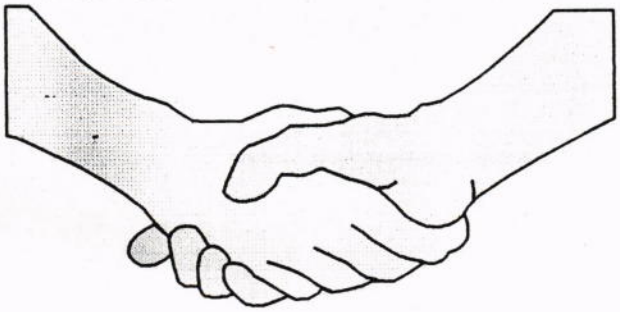
Head of the Department

Signature of the Guide



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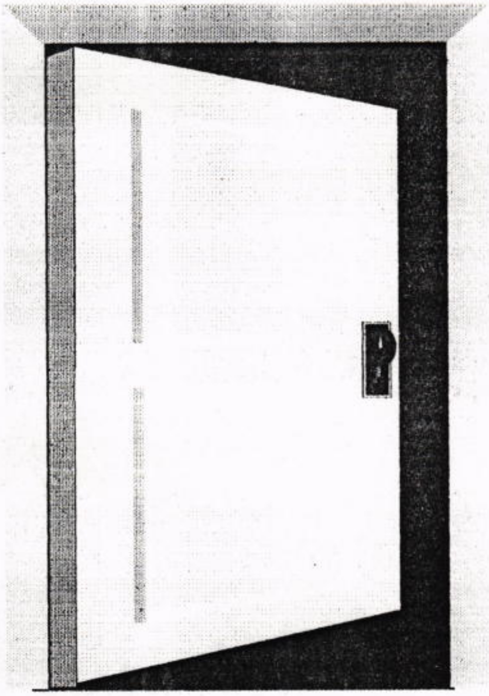

INTRODUCTION

INTRODUCTION

" As corrosion reactions are all surface reactions, the protection of the surface of the metal is the primary objective to prevent corrosion"

- Sharma, (1995).

Most of the metals except noble metals, which find extensive application in industries and domestic uses exist in nature as ores in the form of oxides, silicates, chlorides, etc. They are extracted from the ores by a series of metallurgical operations involving expenditure of energy. The pure metal thus being at a higher energy state and unstable tends to revert back to the compound form. The metals are converted into metallic compounds at the surface and these compounds wear as corrosion products. This phenomenon of deterioration of metals is known as corrosion (Shukla et al, 1977).

$$\text{Metallic Compound} \underset{\text{Corrosion}}{\overset{\text{Metallurgical operations}}{\rightleftarrows}} \text{Metal}$$

The greater the energy expended in extraction , more readily does the metal tends to corrode.

Corrosion may be defined as the loss of useful properties of a material as a result of chemical or electrochemical reaction with its environment (Raj Narayan, 1988).

Corrosion may also be defined as a process of deterioration and subsequent loss of metal through its reaction occuring at the surface with the environmental agencies (Karunanithi et al, 1993).

Rusting of iron, formation of green patina on copper roofs, tarnishing of silverware, formation of millscale on iron and steel are typical examples of corrosion.

Depth of Corrosion Problem

Corrosion is a serious problem in all fields of application of metals. The loss of metal resources whose abundance is limited is cumulative and poses a danger to conservation and serious economic problem. In the U.K., 1 tonne of steel is converted completely into rust every 90 seconds (Kenneth. R. Trethewey, 1988).

Economic loses occur due to corrosion in all countries of the world. These could be direct or indirect (Raj Narayan, 1988).

Direct losses result primarily from replacements including:

- Inability to use otherwise desirable materials
- Overdesign to allow for corrosion
- Cost of repair or replacement of the corroded component or equipment.
- Cost of painting or other anticorrosion methods.

Indirect losses could be either economical or social and workout to a much higher value. They may include:

- Contamination of the product
- Shutdown losses in the form of loss of production
- Loss of efficiency
- Safety due to possible explosions and loss of life
- Appearance

Annual cost of corrosion in different countries (S.D. Shukla et al, 1977)

Country	**Cost (Rs.)**
India	600 Crores
USA	28,000 Crores
UK	2,300 Crores

Classification of corrosion:

Corrosion may be classified based on the mechanism into 2 types namely :

1. Dry or chemical corrosion
2. Wet or electrochemical corrosion

1. Dry or Chemical Corrosion

This type of corrosion occurs mainly through the direct chemical action of the environment or atmospheric gases like oxygen, halogens, sulphur-dioxide, etc. with the metal surface in the immediate proximity. Some forms of chemical corrosion are oxidation corrosion, corrosion by gases and liquid metal corrosion.

2. Wet or Electrochemical Corrosion

Electrochemical corrosion occurs when the metal is in contact with a corroding liquid or when two dissimilar metals or alloys are immersed partially or completely in a solution. The main basis involves the formation of anodic and cathodic parts in contact with each other through the presence of a conduction electrolyte, the media. The electrochemical corrosion proceeds quickly in cases where both anodic and cathodic products formed are freely soluble in the medium (Evans, 1976).

The two main reactions in corrosion process are:

a) Anodic Reaction

Metal dissolution and actual corrosion takes place at the anode where the metal is oxidised with the liberation of electrons.

$M \rightarrow M^{n+} + ne^-$

$M + H_2O \rightarrow MO + 2H^+ + 2e^-$

M^{n+} formed dissolves in the electrolyte.

b) Cathodic Reaction

Reduction takes place at the cathode with absorption of electrons liberated from the anode. Cathodic reaction depends on the environment

$2H^+ + 2e^- \rightarrow H_2$ (acid medium)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (neutral medium)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (basic medium)

These reactions occur simultaneously on the numerous local anodes and cathodic areas of the metal at equal rates. Since the electrons produced in the anodic reaction are consumed at the cathode, a current flow exists between the anodic & cathodic areas of the metal.

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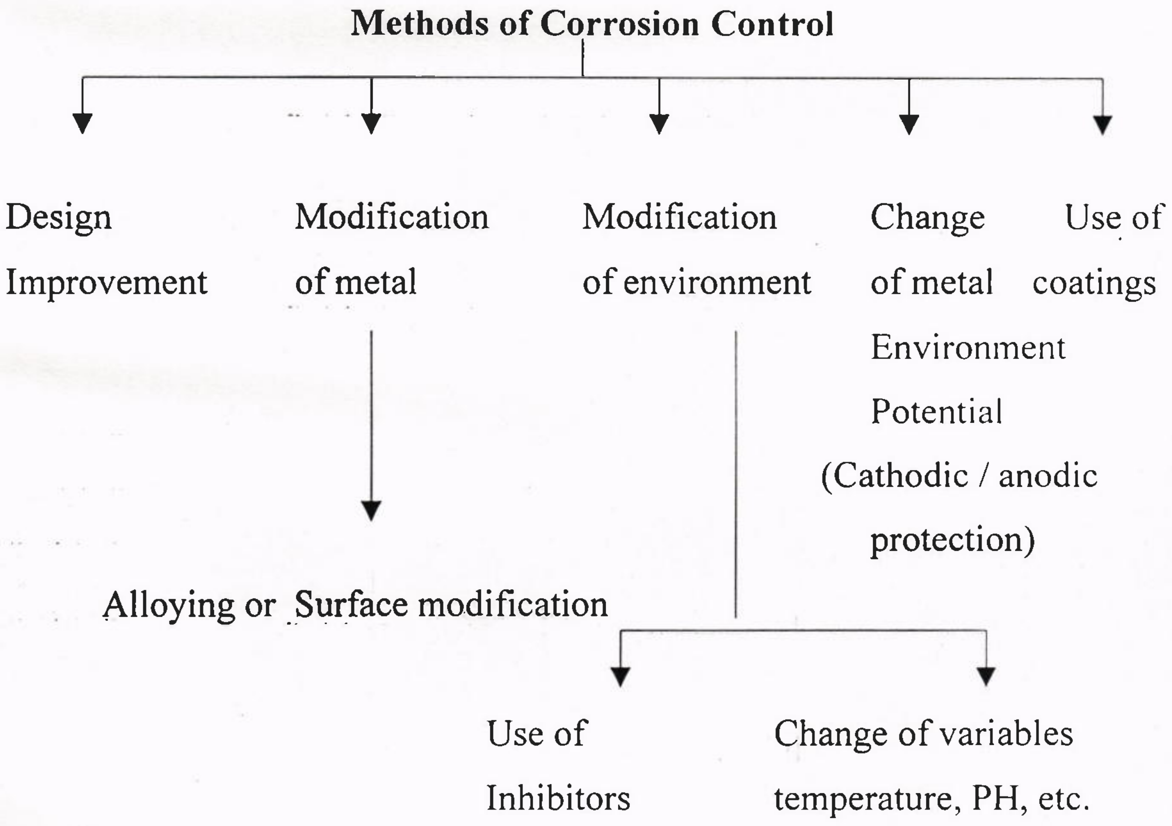
Forms of Corrosion:

Corrosion takes different forms in different environments. They include:

1) Galvanic or bimetallic corrosion
2) Stress corrosion cracking
3) Intergranular corrosion
4) Erosion corrosion
5) Pitting corrosion
6) Crevice corrosion
7) Fretting corrosion
8) Microbial corrosion
9) Concentration cell corrosion

Control of Corrosion

Corrosion is inevitable but can be minimised by adopting certain anticorrosion methods:



(a) Design Improvement:

Proper selection of the metal and designing to avoid crevices, residual moisture, sharp bends and mechanical stress minimizes corrosion rate.

a) Modification of Metal:

- Modification of composition of metal by alloying
- Surface modifications to improve corrosion resistance, wear and high temperature resistance

b) Modification of Environment:

- Using inhibitors either acidic, vapour phase, neutral or alkaline
- Deaeration
- Dehumidification

c) Cathodic / Anodic Protection:

- Lowering the potential of the metal in the negative (anode) direction in the domain of immunity. This is called cathodic protection.
- Increasing the potential of the metal in the positive (cathode) direction in the domain of passivity. This is called anodic protection.

d) Use of Coatings:

In order to separate the metal from the environment, metallic & nonmetallic coatings like ceramics, paints etc. are employed.

Protection of metals from corrosion depends largely on the environment to which the metal is exposed. Decrease in corrosivity by the addition of substance called **INHIBITORS** to the corrosive media has been very efficient (Putilova et al, 1960).

INHIBITORS

"Corrosion inhibitors are an effective means of eliminating this undesirable phenomenon" – Rozenfeld, (1981).

An inhibitor in a chemical substance which when added in small concentration to an environment, effectively checks, decreases or prevents the reaction of the metal with the environment (NACE, 1965).

An inhibitor may be defined as a substance which when added in small amounts to the corrosion environment around a metal, effectively decreases the corrosion rate (Dhara, 1992).

Corrosion inhibitors are added to many systems in acid pickling baths of metals, steam boilers, cooling systems, refinery units, chemical operations, oil and gas production units (Nathan, 1974).

Inhibitors may be classified based on certain factors as:

Basis	**Classification**
1) Environment	Acid inhibitors
	Alkali inhibitors
	Neutral inhibitors
2) Mechanism	Anodic inhibitors
	Cathodic inhibitors
	Mixed inhibitors
	Pickling inhibitors

3) Mode of protection	Chemical passivators Adsorption inhibitors Film forming inhibitors Vapour phase inhibitors

Anodic inhibitors function by forming an insoluble compound at the anodic sites of the metal surfaces. Eg: Phosphates, chromates, molydates, anodical ions of transition elements with more oxygen atoms.

Cathodic inhibitors increase the cathodic polarization and hence moves the corrosion potential in anodic direction. They are substances which decrease the rate of acid attack on metals in processes like pickling. Eg: Salts of Zn, Mg, Ni, organic inhibitors like amines, heterocyclic nitrogen compounds.

Acid corrosion inhibitors may be organic or inorganic. Inorganic inhibitors function by deposition of the metal on iron & steel by reduction and increasing the hydrogen over potential Eg: As_2O_3, Sb_2O_3, Phosphates, Carbonates, Anions like Cl^-, Bi^-, I^-, metal ions like Pb^{2+}, Mn^{2+}, Cd^{2+}. They are used in cooling systems like automobile radiators (Dhara, 1992).

Organic inhibitors containing polar groups are widely used in acidic solutions. Generally nitrogen & sulphur containing compounds with a hydrocarbon part attached to the polar group are used as inhibitors (Muralidharan et al, 1998). They form protective layer on the metal surface by adsorption. Eg: amines and its salts, thiourea, mercaptans, etc. They are used in various metal cleaning operations like pickling baths, chemical equipments , etc.

Theories of Inhibitors

Inhibitors of corrosion may be explained based on the following theories:

Adsorption Theory:

According to this theory, inhibitors are adsorbed on the metal surface forming a protective layer; which may be by physisorption or chemisorption.

Film Theory:

Effective protection may be due to formation on the metal surface of a layer of insoluble or slightly soluble corrosion products.

Need of Corrosion Prevention

- To protect various equipments, tanks, ships and bridges from corrosive attack and reduce losses.
- To conserve metallic resources associated with the production and fabrication of metal surfaces and finally decreasing the loss of valuable products.
- To improve the safety of operating equipments.
- To improve the efficiency of industrial processes
- To preserve rare and expensive metals from losses due to corrosion.

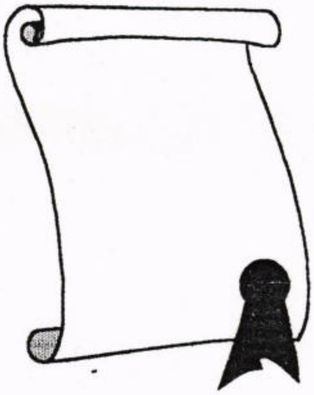
Hence expensive research work has been undertaken especially in the field of corrosion control. Corrosion protection by chemical methods has become so essential that it seems to be very effective in the presence of inhibitors (Schmitt, 1987).

It is well known that a particular inhibitor which gives a very high efficiency for a metal corrosive system may not function similarly in other systems. It therefore becomes necessary to seek different inhibitors for different systems.

OBJECTIVES:

The aim of the present study is to shed light on the role of hexadecylamine $C_{16}H_{35}N$ on corrosion of mild steel in 1M H_2SO_4 medium. Present work is taken with the following objectives:

- ♠ To study the effect of hexadecylamine on the corrosion of mild steel in 1M H_2SO_4 by weight loss method.
- ♠ To find out the open circuit potential at various concentrations of the inhibitor.
- ♠ To find the effect of hexadecylamine at higher temperatures.
- ♠ To find the effect of halide ions namely chloride, bromide and iodide ions on the corrosion inhibition of mild steel by hexadecylamine.
- ♠ To study the cost of the inhibitor incurred for maximum inhibition efficiency.



REVIEW OF LITERATURE

REVIEW OF LITERATURE

Various technological processes are inevitably associated with metals being subjected to the aggressive attack of acids. In such cases, conditions must be created so as to minimise the dissolution of the base metal and acid consumption. This can be achieved solely by the use of acid corrosion inhibitors (Shrier, 1977). Corrosion inhibitors have always had wide spread use, but in the past years, as the understanding of their function has increased, their application has become even wider (Rawal et al, 1985).

The present study

"Corrosion inhibition of mild steel in acid medium by hexadecylamine"

has been reviewed and subdivided into the following classes:

(i) Acid corrosion inhibitors
(ii) Halides as inhibitors
(iii) Amines as inhibitors
(iv) Synergistic effect of inhibitors

1) ACID CORROSION INHIBITORS:

Inhibitors of acid corrosion have been the subject of numerous studies to understand the mode of inhibition especially in acids used in pickling process (Elhosaey, 1995).

Many researchers have used a number of organic and inorganic compounds to retard the dissolution of metals and alloys in various aggressive media (Chaturvedi et al, 1994).

Knowledge of the mechanism of inhibitor effect contributes to a theorotical approach in the choice of inhibitors for a given medium and a corresponding metal (Chauhan et al, 1986).

The rate of corrosion was found to depend on concentration of the acid, the inhibitor, temperature and the potential. As the concentration of the acid, temperature and potential decreases and inhibitor concentration increases, rate of corrosion was found to be reduced (Alsuhybani et al, 1989).

It is assumed that the dissolution of a metal in an acid proceeds according to an electrochemical mechanism and thus the inhibitors can vary the dissolution rate only if they are able to affect the kinetics of the electrochemical reactions lying at the basis of the corrosion process (Rozenfeld, 1981).

Various theories of inhibitors have been suggested. Trabanelli et al (1970) have given a comprehensive treatment of the mechanism and phenomenology of the action of organic inhibitors in acid medium. Kaesche & Hackerman (1958) have proved adsorption to be the possible mode of inhibition.

Attachment of inhibitor may fulfill a double function. The nonpolar part of the inhibitor may provide a diffusion barrier preventing the inward movement of aggressive substances towards the metal and preventing dissolution of products formed from the metal (Friberg et al, 1970).

If the inhibitor form an ionisable salt with the corroding acid, there will be positive inhibitor ions formed (cations) which replace the positive iron atoms formed during corrosion. If the inhibitor is not affected or attacked by the electrolyte, it forms a protective coat. This layer is not penetrable by H^+ ions of the acid and thus the metal will be fully protected against acid corrosion. The closeness of packing ions in the covering layer will determine how efficiently the metal has been covered and whether or not H^+ ions can penetrate this layer. In case of organic inhibitors, the steric arrangement of the ion determines the projected area and packing so that the H^+ ions cannot get through and thus inhibit metal dissolution (Mann, 1936).

The degree of surface coverage is an important factor in determining the efficiency of an inhibitor (Hackerman et al, 1967). Composite film formation by the inhibitor on the metal surface is yet another mode of inhibitor in some cases (Ohi et al, 1994).

Adsorptive properties of inhibitors having great influence on metal dissolution in acid media have been proved by Betova et al (1993).

More sulphuric acid is produced than any other chemical in the world and being directly or indirectly used in nearly all industries (Fontana, 1971). Many attempts have been made to study the rate of corrosion and its inhibition in this medium.

Afanas'ev et al (1966) carried out comprehensive studies of industrial inhibitors designed for pickling metals in 20% H_2SO_4, but the mechanism is not well explained. Coal tar base fractions had a good inhibitive effect as pickling inhibitors in 2N H_2SO_4(Hudson et al, 1967).

Inhibitory effect of some ammonium halides for H_2SO_4 corrosion of mild steel were suggested by Savithiri et al, 1996. Amino benzoic acids had an inhibitive effect on hydrogen permeation through mild steel in 0.5M H_2SO_4 and 1M HCl (Muralidharan et al, 1996).

In sulphuricacid medium some amide derivatives had inhibition on corrosion of mild steel (Jha et al, 1991), benzotriazole (Gomma, 1998), benzamidazole on 12kh18N10T steel (Tatarchuko et al, 1992). Inhibitive studies in other acid media namely HCl (Quarishi et al, 1996), $HClO_4$(Masaru et al, 1992)and phosphoric acid (Mackrides, 1973) have also been reported.

The rate of corrosion reactions increase rapidly with temperature in a manner similar to that of other chemical reactions. In addition, the diffusion of oxygen and conductivity of the solution will be increased. Each of these factors cause more rapid corrosion. Temperature appears to apply a limit upon the nature of the metal and use of inhibitors. Protection by inhibitor has been found to drop off rapidly and 450°F appears to be the limit for effective inibitor usage (Bregman, 1963).

Corrosion of metals has been shown to increase 3 times when the temperature was raised from 50°C to 100°C (Lyalin, 1962). Above 70°C, the corrosion rate drops off due to adhesive nature of reaction products(Foley, 1970).

At a particular concentration, the inhibition efficiency decreases with an increase in temperature. This is due to the time lag between the process of adsorption and that of desorption of the inhibitor molecules on the surface of the metal and thus reducing the total coverage area (Rawat et al, 1987).

Inhibition of hot sulphuric acid corrosion by aromatic acids suggests that adsorption of the additive on the metal surface and formation of surface compounds act as protective films causing inhibition (Oni, 1992). The degree of surface coverage was found to be reduced at higher temperature lowering inhibition (Gomma et al, 1993).

A temperature dependent study on corrosion rates by Muralidharan et al (1985) revealed that the inhibitors used enhance the activation energy. chemisorption was the mechanism proposed for inhibition (Miskidzh'yan et al, 1970).

2) HALIDES AS INHIBITORS:

A number of mechanistic studies on the dissolution of iron and steel in halide containing media has been conducted by various scientists. Halides are found to enhance and inhibit corrosion of metals(Azim et al, 1995).Effect of chloride ions on metal dissolution is a widely studied subject. Chlorides form complexes with iron atom(Foroulis, 1996).

Anion effects can be interpretted as due to formation of halide complexes with the transition metal, iron. The surface complexes are scarcely soluble explaining that halide ions inhibit dissolution of iron (Rengamani et al, 1994). Divergent views are held regarding the aggressive or nonaggresive nature of various anions and the manner in which they operate (Traubenberg et al, 1971).

It has been determined that increase in halide concentration decreases the rate of corrosion until an optimal concentration. This concentration depends upon the radius of halide ions, increasing in the order. $Cl^- < Br^- < I^-$(Kirkov, 1973).

With increase in halide concentration from 0-900 ppm the percentage inhibition went up from 50-86 in case of chloride and bromide and 92 in case of iodide (Rawat et al, 1985).

Halide ions in general inhibit steel dissolution by a strong interaction with the steel surface through chemisorption. The halide ions adsorb specifically on the iron surface in acid solutions in the order $Cl^- < Br^- < I^-$ mainly due to electrostatic effects and covalent bonding to the metal (Hackerman et al, 1966).

The activating or passivating effect of halide ions was attributed to 2 factors; 1) deformability of the anion increases in the order $Cl^- < Br^- < I^-$. 2) ability of the anion to form soluble metal complexes which activates corrosion process. Both bromide and iodide are able to form soluble surface compounds by covalent linkages than chloride (Rudresh et al, 1979).

Hackerman et al (1967) suggested that halide ions are themselves inhibiting and that the adsorption of halide ions is electrostatic. The transformation from adsorption to film formation occurs at a higher critical concentration with chloride ion and for bromide and iodide it occurs at a lower critical concentration.

The good protective properties of iodide compounds was attributed to the heightened adsorptivity of iodide and bromide in comparison with chloride. The iron surface was assumed to be positively charged and the adsorption of cation active substances was attributed to a preliminary adsorption of halide ions reducing the positive charge on the surface (Miskhidzh'yan et al, 1970).

Jha et al (1990) studied that inhibition efficiency was in the order $Cl^- < Br^- < I^-$. Owing to the better adsorptivity of Br^- and I^- than Cl^- ion. Inhibition of corrosion in presence of Cl^- ions was studied by Murakawa et al (1968).

3) AMINES AS INHIBITORS:

Amines have been known for a number of years as effective corrosion inhibitors (Fujji et al, 1958). Their efficiency is attributed to the presence of nitrogen atom of NH_2 group acting as the active centre for the adsorption of organic molecules on the metal surface (Hackerman et al, 1995).

Several aliphatic and aromatic amines have been reported to serve as effective corrosion inhibitors for iron and steel in acid media (Rawat et al, 1987). Organic amines act as inhibitors of dissolution of iron in acid by adsorbing at metal solution surface (Ayers et al, 1963).

It is believed that there is a certain degree of inhibitor ion orientation at the cathodes on the metal surface in case of nitrogen derivatives. Amine type of inhibitors inhibit both anodic and cathodic processes for a metal corroding in acid solution. In the anodic reaction, the non protonated amine is chemisorbed on the metal surface through interaction of the lone pair of electrons on N atom with the metal atom. But in cathodic region, the onium ions formed in the acid solution adsorb on the negatively charged metal surfaces by electrostatic interaction with the metal. But cathodic inhibition being predominant (Sudbury et al, 1950).

Antropov (1967) has suggested that adsorption is an inevitable part of the process of inhibition and that the mechanism of inhibition by a given organic compound depends on the nature of corroding material and on the conditions of corrosion. Hackerman et al (1953) have pointed out that cathodic inhibition is as result of both physisorption and chemisorption. Electrostatic bonding at the cathodic areas contributes to overall inhibition. The inhibitor chemisorption takes place by formation of coordinate covalent bonds with the surface atoms of the metal, where by the inhibitor acts as an electron donor and the metal as an electron acceptor. The inhibition efficiency for each amine was found to be a linear function of the surface area masked by the amine by electron sharing between nitrogen and iron atoms (Shram et al, 1958).

A redistribution of electrons between the metal atom appears to be necessary for passivity (Roustron et al,1979). Inhibitors with amino group perform well due to formation of cationic species in acid solutions (Singh et al, 1995). The adsorptive ability was found to decide the efficiency of inhibition, that in turn depends on basicity, substituent constant and ionization potential (Kaesche et al, 1958).

Hackerman et al (1954) postulated a two step mechanism of inhibition:

(i) Diffusion of the cation to the surface where it is weakly adsorbed.

(ii) Transformation of the weakly adsorbed cation to the strongly adsorbed free amine and an equilibrium exists between these species at the surface.

Chemisorption increased with increasing chain length of organic inhibitors (Viswanathan et al, 1998). Adsorption behaviours of amines were studied extensively by Pushi et al (1994). Chlorosubstituted anilines were studied as corrosion inhibitors proving that adsorption followed langmuir isotherm (Vashi et al, 1997).

. The organic compounds used as inhibitors have both polar and nonpolar ends. The polar ends of the inhibitor molecule take part in adsorption process. Chemisorption occurs at active sites and the rest of the surface is covered by weaker physical forces. Then there exists a strong covalent bond between the polar group of the inhibitor and the surface there exists a direct relationship between the strength of the bond and effectiveness of the inhibitor. A chemical bond exists between nitrogen of the amine and iron atom and hydrogen bonds are formed between amine and oxygen atom on the surface (Lopez et al, 1993).

The function of amine functional group was studied in a detailed manner by Subramaniam et al(1998). Cyclohexylamines (Ngobeni et al, 1994), alkyl amines (Aramaki et al, 1973), hydroxyl amine (Marshakov et al, 1997), hexamethylene tetramine(Brolo et al, 1992), N-Octyl-amine (Muralidharan et al, 1994) have been successfully used as corrosion inhibitors in acid media.

Nathan (1956) has shown that branching of alkyl chain decreases inhibition efficiency as it reduces the ease of adsorption. The non polar radicals should have close interlocking. Primary amines are highly effective and for best protection C_{16} and C_{18} chain should be present Thus many factors like physisorption, chemisorption and molecular structure play vital roles in determining the overall efficiency of the metal-inhibitor system.

4) SYNERGISTIC EFFECTS:

It has been shown that two or more inhibitors acting together can produce a greater effect than would be expected when they act separately. This phenomenon is called "Synergism". Advantage of combining an anodic and cathodic inhibition is today generally realised and emphasized in various acids (Murakawa, 1968).

Synergism in corrosion inhibition is widely studied (Lazarides et al, 1979). Organic compounds pick up protons, as a result of which cations appear in solution (Trabanelli et al, 1970). It is explained that the organic cations that have greatest tendency toward covalent bonding have best corrosion inhibition. The greatest synergistic inhibition was for an anion-cation pain in which both ions have appreciable tendency towards covalent bonding (Hackerman et al, 1966).

A remarkable synergistic effect resulted in regard to inhibition of iron dissolution when inorganic halides were added to H_2SO_4 medium containing organic compounds (Hudson et al, 1970). Organic cations are not strongly adsorbed on iron surface as both are of positive charge in H_2SO_4. However, if halides are introduced, inhibition increased (Rozenfeld, 1981). Halide ions so alter the properties of the surface that adsorption of organic cations on it becomes possible (Losev et al, 1953).

The adsorption of cations, protonated inhibitors in acid media is facilitated by the halide ions which form intermediate bridges,the negative ends of the halogen-metal dipoles being oriented towards the solution. Synergistic may also be attributed to the formation of covalent bond between a non ionized molecule of the inhibitor and the adsorbed halogen. In the presence of iodide ions especially, surface charge is changed to a more negative charge by specific adsorption of these ions resulting in joint adsorption of anion with amine cation (Iofa et al, 1965). Adsorbed halide ion on the positively charged steel surface acts as a bridge between the surface and the electrolyte for adsorption of protonated inhibitor (Singh et al, 1995).

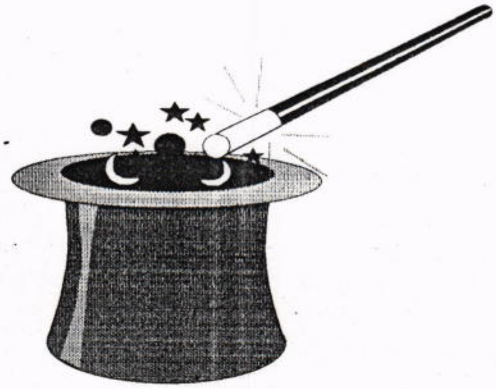
Hackerman et al, (1987) have suggested that an organic inhibitor may act in 2 ways:

1) compete with halide ions for position on the metal surface. Thus, the protonated amine loses its protons on entering the double layer and gets chemisorbed by donating a pair of electons to the metal.
2) Protonated amines can be electrostatically adsorbed on the halide covered metal surface through its H^+ ions. Both these mechanisms increase the inhibitors performance.

Synergistic adsorption can be classified as:

1) Coadsorption of anions and amines.
2) Physical overlap adsorption of amine cations over anion covered iron surface which depends on attraction force between the adsorbed anion and cation in solution (Murakawa et al, 1968).

Iodide ions were found to have higher inhibitive effect due to high adsoptivity (Hackerman et al, 1966). Synergistic effect of halides with various amine inhibitors namely N-hecyl amine (Muralidharan et al, 1997), cyclohexylamine (Li et al, 1997), dicyclohexylamine(Muralidharan et al, 1995), benzylamine (Rawat et al, 1985) have been proved successfully.



MATERIALS & METHODS

MATERIALS AND METHODS

The study of the corrosion inhibition by hexadecylamine was carried out using mild steel specimens in 1M H_2SO_4 medium using efficient methods namely, weight loss method and measurement of open circuit potential. Protection of steel equipments from corroding media by electrochemical and weight loss measurements is emerging as a useful alternative (Gaur et al, 1993).

SAMPLE SELECTION:

MILD STEEL

Mild steel was the material of choice due to its characteristics of wide application, cost and easy availability. Mild steel, being a low alloy steel softer than cast iron can be easily machined and has high tensile and impact strength. Therefore it finds a variety of applications like motor car bodies, machines, gears, pipes, tanks, etc. in most of the chemical industries. (Thankamma Jacob, 1987). It suffers from severe corrosion in aggressive environments of acids and more dissolution during pickling processes. Hence the study of corrosion inhibitors of mild steel in aggressive media is a subject of technological significance .

MEDIUM:

SULPHURIC ACID

More sulphuric acid is produced than any other chemical in the world. It is directly or indirectly used in nearly all industries and is a vital commodity in our national economy (Fontana, 1971). It is widely used for pickling, descaling and chemical cleaning processes of steel and ferrous alloys.

Hence 1M H_2SO_4 medium was selected to study the effect of hexadecylamine on corrosion of mild steel.

PARAMETERS STUDIED:

The parameters taken into consideration for the study were:

1) Determination of corrosion rate by weight loss method at
    a) Room temperature
    b) Higher temperature
2) Determination of open circuit potential by potentiometry

1) Weight Loss Method:

Weight loss tests are most commonly used for measurement of corrosion. They give more significant information than other methods.

Mild steel specimens of size 5 x 1.5 cm were used for weight loss measurements. All chemicals / reagents used were prepared from analar grade chemicals using double distilled water.

The specimens were well polished to a smooth surface using a sequence of emery papers 1/0, 2/0, 3/0, 4/0 grade and were degreased with acetone. Then the specimens were exposed to the medium at room temperature (32°C ± 0.2°C) and varying higher temperatures, 50°C ± 0.2°C (323 K), 60°C ± 0.2°C (333K) and 70°C ± 0.2°C (343K) in a thermostat.

(a) Room Temperature:

The area of the polished, clean mild steel specimens were measured and weighed accurately. The specimens were then immersed in 250ml of the following media for a constant time.

1M H_2SO_4 (a) Without the inhibitor, (blank)

(b) With varying concentrations of hexadecylamine :
10^{-3} M, 5×10^{-3} M, 10^{-4}M, 5×10^{-4}M, 10^{-5}M, 5×10^{-5}M, 10^{-6}M, 5×10^{-6}M,

(c) With varying concentrations of the inhibitor in combination with halides namely chloride, bromide and iodide. The concentrations selected to study the effect of halide with hexadecylamine on corrosion of mild steel in the acid medium are given below:

Inhibitor Concentration	Halide Concentration
10^{-6}M	10^{-2}M
10^{-6}M	5×10^{-3}M
5×10^{-6}M	10^{-2}M
5×10^{-6}M	5×10^{-3}M

They were then taken out and washed thoroughly with distilled water. The specimens were dried and reweighed. The difference in weight gives the weight loss. The experimental setup (Photo 1,2) and appearance of the specimens before and after the experiment (Photo 3) are shown .

b) Higher Temperature:

The thermostat was set to the temperaures 50°C±0.2°C(323K), 60°C±0.2°C(333K) and 70°C±0.2°C(343K) and the experiment was carried out as done at room temperature(Photo 4).

Accurately measured and weighed mild steel specimens were immersed in the following media for a constant time.

250 ml of 1MH_2SO_4

(a) Without the inhibitor

(b) With varying concentrations of the inhibitor.

(10^{-4}M, 10^{-5}M, 10^{-6}M, 5 x 10^{-6}M, 10^{-7}M,)

Since 5x 10^{-6} M concentration of hexadecylamine was used in combination with halides, it was taken for the study at higher temperatures.

Then they were washed thoroughly with distilled water, dried and reweighed.

Determination of corrosion rate:

The corrosion rate, expressed as Mils per year in every case was calculated using the formula:

$$\text{Corrosion rate in Mpy} = 534 \times W / DAT$$

W :	Weight loss in milligrams	D :	Density of the specimen in g/cc
A :	Area of the specimen in $inch^2$	T :	Exposure time in hours.

In case of mild steel, D, the density of the specimen is 7.9g/cc. Thus substituting the weight loss, area of the specimen used and exposure time, corrosion rate was calculated.

Inhibition Efficiency:

Inhibition Efficiency (%) =

$$\frac{\text{Corrosion rate without inhibitor} - \text{corrosion rate with inhibitor}}{\text{Corrosion rate without inhibitor}} \times 100$$

Determination of

(a) Activation Energy:

The activation energy at different concentrations of the inhibitor at the various temperatures used was determined by plotting log (Corrosion rate) vs 1/temperature (Fig.2). From the slope, the activation energy E_a was calculated using the formula:-

$E_a = 2.303 \times R \times \text{slope}$. R = Gas constant

(b) Change in Free Energy of Adsorption:

The change in free energy of adsorption for different higher temperatures in comparison with room temperature at various concentrations of hexadecylamine was calculated using the formula:

$$\Delta G_a = -2.303 \times R\,(T_2 - T_1) \times \text{Log}\,K_2 / K_1$$

T_2 = Higher Temperature in Kelvin

T_1 = Room Temperature in Kelvin

K_2 = Corrosion Rate at T_2

K_1 = Corrosion Rate at T_1

2) Open Circuit Potential:

The shift of open circuit potential in the presence of inhibitor permits the specification of which partial process is influenced by the inhibitor (Hackerman et al, 1958). The change in potential during corrosion is measured potentiometrically using digital potentiometer(Photo 5) with reference to standard calomel electrode connected through a salt bridge.

Iron surface attains a positive charge in aqeous acid solutions as its potential of zero charge varies from - 0.4V to –0.7V(SCE). The potential shifts in the active direction with passage of time (Singh et al, 1995).

250 ml of the same media as used in weight loss method were taken. The mild steel specimens were cleaned, polished and wound with insulation tape so as to expose an area of $1cm^2$ of the specimen to the electrolyte. They were then immersed in the media, exposed for 30 minutes. The potential was noted every minute continuously for 30 minutes. A graph was plotted between Time in minutes vs OCP.

Photo- 1
An experimental set up of weight loss method
With hexadecylamine

Photo-2
An experimental set up of weight loss method
With hexadecylamine and halides

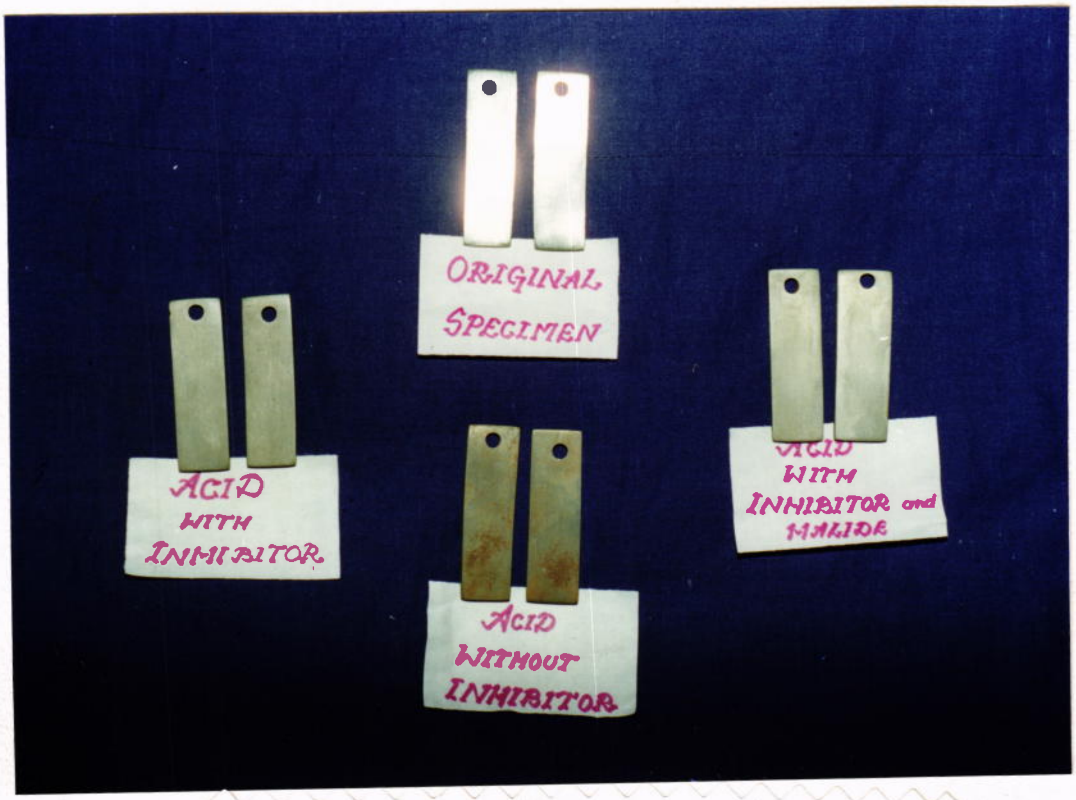


Photo-3
Appearance of the specimens before and after
Immersion in the corrodant

Photo-4
Thermostat at work

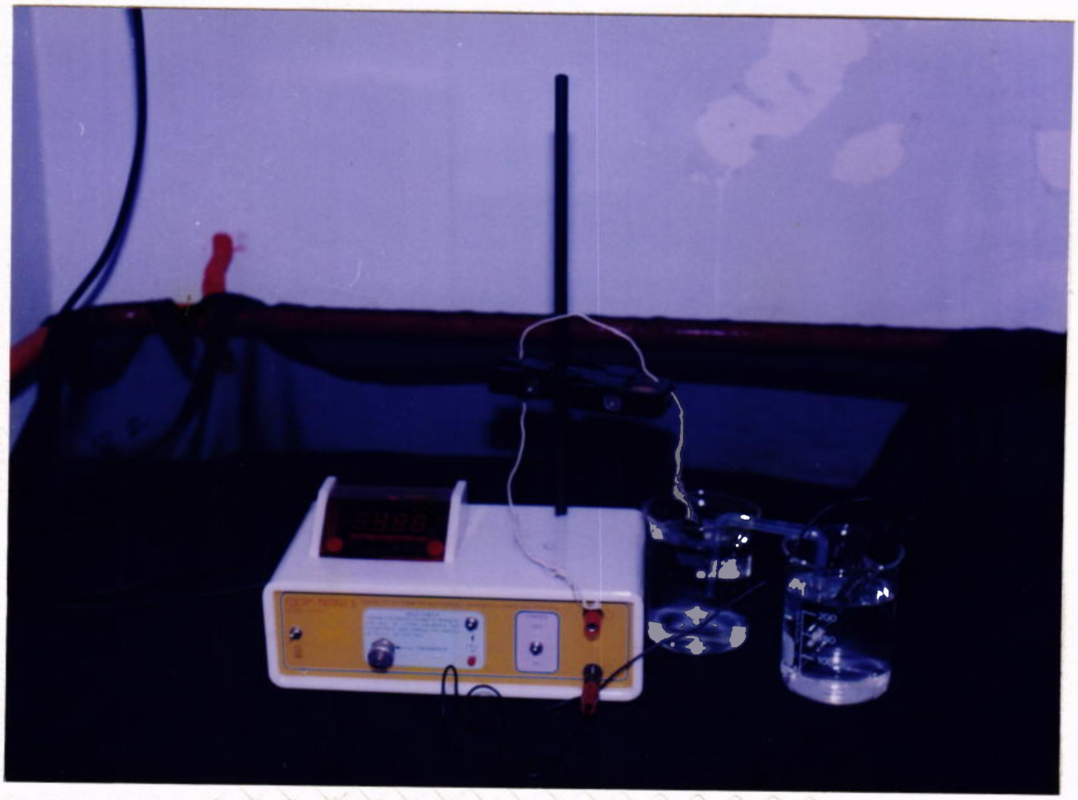
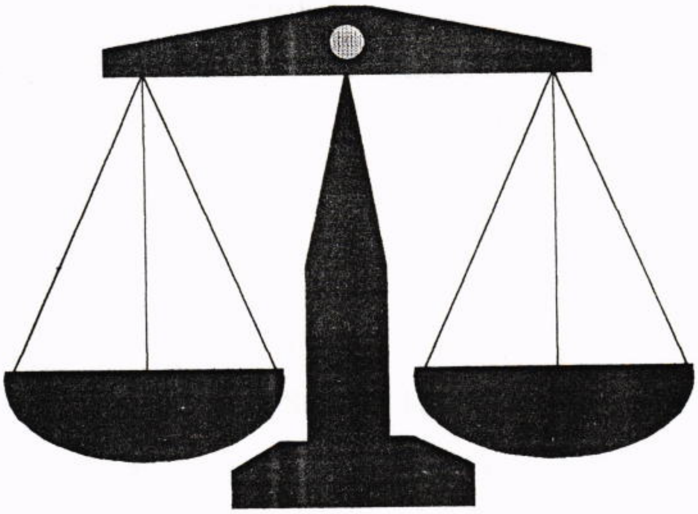


Photo-5
An experimental set up for
open circuit potential measurements



RESULTS & DISCUSSION

RESULTS AND DISCUSSION

The role of hexadecylamine on corrosion of mild steel in 1M H_2SO_4 was studied which yielded the following results.

EFFECT OF HEXADECYL AMINE:

(a) WEIGHT LOSS METHOD:

The results obtained by weight loss method at room temperature are given in table 1 and at various higher temperatures namely 50°C ± 0.2°C (table 3), 60°C ± 0.2°C (table 4) and 70°C ± 0.2°C (table 5) are presented.

Table 1

EFFECT OF HEXADECYLAMINE AT ROOM TEMPERATURE:

S . No.	Conc. of inhibitor (M)	Area (cm^2)	Weight loss (g)	Corrosion rate (Mpy)	Inhibition Efficiency (%)
1.	-	7.6842	0.0344	1902.77	-
2.	10^{-6}	8.064	0.1010	1820.73	4.31
3.	$5x10^{-6}$	7.8842	0.0980	1807.77	4.99
4.	10^{-5}	7.9442	0.0966	1767.67	7.10
5.	$5x10^{-5}$	7.688	0.0746	1410.59	25.87
6.	10^{-4}	8.0896	0.0723	1299.76	31.72
7.	$5x10^{-4}$	7.3457	0.0526	1040.94	45.29
8.	10^{-3}	7.9913	0.0078	141.89	92.54
9.	$5x10^{-3}$	7.4	0.0042	82.51	95.66

From the table it is evident that as the concentration of hexadecylamine increases, the corrosion rate decreases and the inhibition efficiency increases. The maximum efficiency that could be obtained using hexadecylamine may be 95.66% using a concentration of $5x10^{-3}$M of inhibitor.

The inhibitive effect of the amine inhibitor can be explained as due to adsorption of the inhibitor on the metal surface where the nitrogen atom of the NH_2 group may act as the active centre for adsorption (Hackerman et al, 1995) the corrosion in the media is inhibited.

A two step mechanism as proved by Hackerman et al (1954) may be the possible mode of inhibition:

(i) Diffusion of the cation to the metal surface where it is weakly adsorbed.

(ii) Transformation of the weakly adsorbed cation to the strongly adsorbed free amine exhibiting equilibrium, thus inhibiting the corrosion process.

Chemisorption may occur due to the polar group (NH_2) at the active sites and the rest of the surface may be covered by weaker physical forces as interpretted by Lopez et al (1993).

(b) OPEN CIRCUIT POTENTIAL (OCP):

On measurement of the open circuit potential (OCP) of different concentrations of hexadecylamine (HDA) with reference to the standard calomel electrode the values in table 2 were obtained.

Table 2

EFFECT OF HEXADECYL AMINE – ROOM TEMPERATURE OPEN CIRCUIT POTENTIAL MEASUREMENTS

Time (min)	1MH_2SO_4	10^{-7}M HDA	5x10^{-7}M HDA	10^{-6}M HDA	5x10^{-6}M HDA	10^{-5}M HDA	5x10^{-5}M HDA
1.	-0.389	-0.469	-0.400	-0.471	-0.473	-0.472	-0.475
2.	-0.392	-0.477	-0.402	-0.480	-0.474	-0.474	-0.478
3.	-0.393	-0.478	-0.402	-0.481	-0.475	-0.475	-0.479
4.	-0.394	-0.478	-0.402	-0.481	-0.475	-0.475	-0.479
5.	-0.395	-0.478	-0.402	-0.481	-0.476	-0.476	-0.479
6.	-0.395	-0.478	-0.402	-0.481	-0.476	-0.476	-0.478
7.	-0.396	-0.478	-0.402	-0.481	-0.476	-0.476	-0.478
8.	-0.396	-0.478	-0.402	-0.481	-0.476	-0.476	-0.477
9.	-0.397	-0.478	-0.403	-0.481	-0.476	-0.476	-0.477
10.	-0.398	-0.479	-0.403	-0.481	-0.476	-0.476	-0.477
11.	-0.399	-0.479	-0.404	-0.481	-0.476	-0.476	-0.477
12.	-0.399	-0.479	-0.404	-0.481	-0.476	-0.476	-0.477
13.	-0.400	-0.480	-0.404	-0.482	-0.477	-0.476	-0.477
14.	-0.401	-0.480	-0.404	-0.482	-0.478	-0.476	-0.477
15.	-0.402	-0.481	-0.405	-0.483	-0.478	-0.476	-0.477
16.	-0.403	-0.481	-0.406	-0.484	-0.478	-0.482	-0.477
17.	-0.404	-0.481	-0.406	-0.484	-0.478	-0.482	-0.477
18.	-0.406	-0.482	-0.407	-0.484	-0.479	-0.483	-0.476
19.	-0.407	-0.482	-0.407	-0.485	-0.479	-0.483	-0.476
20.	-0.408	-0.483	-0.407	-0.485	-0.480	-0.484	-0.475
21.	-0.410	-0.483	-0.408	-0.486	-0.480	-0.485	-0.474
22.	-0.411	-0.484	-0.408	-0.486	-0.480	-0.485	-0.473
23.	-0.413	-0.485	-0.409	-0.487	-0.481	-0.486	-0.473
24.	-0.415	-0.485	-0.409	-0.487	-0.481	-0.486	-0.472
25.	-0.416	-0.486	-0.410	-0.487	-0.482	-0.486	-0.472
26.	-0.417	-0.486	-0.410	-0.488	-0.482	-0.487	-0.471
27.	-0.418	-0.486	-0.412	-0.488	-0.482	-0.487	-0.472
28.	-0.420	-0.487	-0.412	-0.487	-0.483	-0.487	-0.472
29.	-0.421	-0.487	-0.414	-0.487	-0.483	-0.486	-0.472
30.	-0.422	-0.488	-0.415	-0.486	-0.484	-0.486	-0.471

The observations of shift of OCP in the presence of inhibitor permits the specification of which partial process is being influenced. A decrease in corrosion rate with shift in corrosion potential in anodic (negative) direction indicates increased polarization at cathode, a corresponding change in electrode potential in cathodic direction indicated increased polarization at the anode (RajNarayan, 1988).

A constant value shows maximum surface coverage by the inhibitor (Hackerman et al, 1948). The time required to obtain constant potential is found to increase at higher concentrations of the inhibitor. The weight loss measurements show a decrease in the corrosion rate with increasing concentration of the inhibitor. As the concentration of the inhibitor in the medium increases, the potential is not found to steadily increase towards any particular direction, anodic or cathodic. Hence it can be suggested that hexadecylamine acts as a mixed inhibitor.

The plot of OCP Vs time is shown in fig. 1.

50°C ± 0.2°C:

The results obtained at 50°C ± 0.2°C are presented in table 3.

Table 3

EFFECT OF HEXADECYLAMINE AT 50°C ± 0.2°C:

S. No.	Conc. of inhibitor (M)	Area (cm^2)	Weight loss (g)	Corrosion rate (Mpy)	Inhibition Efficiency (%)
1.	-	7.2618	0.0956	11482.18	-
2.	10^{-7}	7.8186	0.0916	10218.27	10.99
3.	10^{-6}	7.8156	0.0854	9530.30	16.98
4.	$5x10^{-6}$	7.6415	0.0776	8857.15	22.85
5.	10^{-5}	8.1672	0.0420	4485.26	60.93
6.	10^{-4}	8.224	0.0174	1845.34	83.93

The table clearly shows that the corrosion rate decreases and the inhibition efficiency increase with increase in concentration of the inhibitor. The maximum efficiency obtained is 83.93% using a concentration of 10^{-4}M of the inhibitor.

60°C ± 0.2°C:

The values obtained using different concentrations of the inhibitor at 60°C ± 0.2°C are shown in table 4.

Table 4

EFFECT OF HEXADECYLAMINE AT 60° C ± 0.2° C:

S. No.	Conc. of inhibitor (M)	Area (cm^2)	Weight loss (g)	Corrosion rate (Mpy)	Inhibition Efficiency (%)
1.	-	7.6725	0.1532	17425.8	-
2.	10^{-7}	8.0471	0.1484	16084.43	7.69
3.	10^{-6}	7.65	0.1352	15414.39	11.54
4.	$5x10^{-6}$	7.6406	0.1192	13606.92	21.92
5.	10^{-5}	7.134	0.1068	13057.18	25.07
6.	10^{-4}	8.1011	0.0714	7687.15	55.89

The table reveals that with increase in concentration of hexadecylamine in the acid medium, the corrosion rate decreases and the efficiency of inhibition increases to a maximum of 55.89% at a concentration of 10^{-4}M of the inhibitor.

70°C ± 0.2°C:

Table 5 shows the values obtained for different concentrations of the inhibitor at 70°C ± 0.2°C.

Table 5

EFFECT OF HEXADECYLAMINE AT 70° C ± 0.2° C:

S. No.	Conc. of inhibitor (M)	Area (cm^2)	Weight loss (g)	Corrosion rate (Mpy)	Inhibition Efficiency (%)
1.	-	7.6456	0.2208	25181.08	-
2.	10^{-7}	7.134	0.1926	23546.93	6.49
3.	10^{-6}	7.35	0.1912	22688.81	9.81
4.	$5x10^{-6}$	7.6194	0.1854	21222.67	15.72
5.	10^{-5}	7.7532	0.1760	19798.98	21.37
6.	10^{-4}	7.7616	0.1136	13889.23	44.84

The corrosion rate is found to decrease and inhibition efficiency is found to increase with increasing concentrations of the inhibitor being studied. The maximum efficiency obtained being 44.84% at a concentration of 10^{-4}M of the inhibitor.

A comparison of the inhibition efficiencies obtained using different concentrations of hexadecylamine at different temperatures are presented in table 6.

Table 6

EFFECT OF HEXADECYLAMINE AT DIFFERENT TEMPERATURES:

S. No.	Conc. of inhibitor (M)	Inhibition Efficiencies (%)		
		50°C±0.2°C	60°C±0.2°C	70°C±0.2°C
1.	10^{-7}	10.99	7.69	6.49
2.	10^{-6}	16.98	11.54	9.81
3.	$5x10^{-6}$	22.85	21.92	15.72
4.	10^{-5}	60.93	25.07	21.37
5.	10^{-4}	83.93	55.89	44.84

It is evident from the tables that the rate of corrosion rapidly increases with temperature in a similar manner as that of other chemical reactions.

Table 6 reveals that at a particular concentration, the inhibition efficiency decreases with increase in temperature. This may be due to the time lag between the process of adsorption and desorption of the inhibitor molecules on the metal surface as explained by Rawat et al (1987). The maximum efficiency that could be obtained also decreases with rise in temperature.

ACTIVATION ENERGY AND CHANGE IN FREE ENERGY OF ADSORPTION:

The activation energy and free energy change of adsorption in comparison with room temperature were calculated for different concentrations of the inhibitor at different temperatures.

The table 7 shows log(corrosion rate) for different concentrations as a function of temperature(T). log(corrosion rate) vs 1\T is plotted and from the slope, activation energy is calculated. Fig.2 shows a sample plot.

Table 7

LOG(CORROSION RATE) AT DIFFERENT TEMPERATURES

S.No.	1/T	Log (Corrosion rate)				
		Blank	10^{-6}M	5×10^{-6}M	10^{-5}M	10^{-4}M
1.	3.3	3.28	3.26	3.26	3.25	3.11
2.	3.1	4.06	3.98	3.95	3.65	3.27
3.	3.0	4.24	4.19	4.13	4.12	3.89
4.	2.9	4.40	4.36	4.33	4.29	4.14

The activation energy and change in free energy of adsorption obtained are given in Table 8.

Table 8

ACTIVATION ENERGY AND CHANGE IN FREE ENERGY OF ADSORPTION

S. No.	Conc. of inhibitor (M)	Activitation energy Ea (Kcal/mol)	Change in Free Energy of Adsorption ΔG_a(Kcal/mol)		
			50°C ±0.2°C	60°C ±0.2°C	70°C ±0.2°C
1.	-	-13.001	-71.44	-132.03	-205.31
2.	10^{-6}	-12.887	-65.79	-127.35	-200.54
3.	$5x10^{-6}$	-12.694	-63.16	-120.35	-195.80
4.	10^{-5}	-12.644	-37.01	-119.23	-192.06
5.	10^{-4}	-12.264	-20.57	-115.93	-188.35

The table shows that the corrosion process proceeds with increase in energy of activation as the concentration of the inhibitor increases. It can be explained based on a temperature dependent study by Muralidharan et al (1985). It has been proved that the inhibitors used enhance the activation energy.

The free energy of adsorption is also found to increase, a positive free energy change is observed with increase in concentration of the inhibitor. The results obtained are in close relation with the interpretation by Nathan (1987) that free energy is the driving force for corrosion. Metals with negative free energy change undergo corrosion where as, those with positive free energy possess good resistance to corrosion. Thus as E_a and ΔG_a increase inhibition efficiency increases. All the values obtained are negative proving that the reaction is feasible.

EFFECT OF HEXADECYLAMINE IN COMBINATION WITH HALIDES

The results obtained when hexadecylamine was used in combination with halides namely chloride, bromide and iodide are presented.

EFFECT OF CHLORIDE ON THE CORROSION INHIBITION OF MILD STEEL BY HEXADECYLAMINE:

(a) WEIGHT LOSS METHOD:

The values obtained using different combinations of the inhibitor with chloride are tabulated in table 9.

Table 9

EFFECT OF HEXADECYLAMINE WITH CHLORIDE:

S . No.	Conc. of inhibitor (M)	Conc. Of Chloride (M)	Area (cm^2)	Weight loss (g)	Corrosion rate (Mpy)	Inhibition Efficiency (%)
1.	-	-	7.5044	0.0400	2323.90	-
2.	10^{-6}	-	8.064	0.1010	1820.73	4.31
3.	10^{-6}	$5x10^{-3}$	7.474	0.0414	1207.82	48.06
4.	10^{-6}	10^{-2}	8.1989	0.0410	1009.39	56.61
5.	$5x10^{-6}$	-	7.8842	0.0980	1807.77	4.99
6.	$5x10^{-6}$	$5x10^{-3}$	7.2358	0.0306	922.13	60.32
7.	$5x10^{-6}$	10^{-2}	7.1359	0.0425	866.53	62.71

The corrosion rate is found to decrease and the inhibition efficiency increases with increase in concentration of both the inhibitor and chloride in the medium. The maximum efficiency is 62.71% at a concentration of $5x10^{-6}$M hexadecylamine with 10^{-2}M chloride. The combination of the inhibitor and chloride is shown to provide a higher inhibition efficiency than the inhibitor used separately.

(b) OPEN CIRCUIT POTENTIAL:

The OCP values obtained for the combinations of the inhibitor and chloride are given in table 10.

At all the combination of concentrations initially the potential is found to increase in more negative direction. Then a constant potential is attained for 7 to 10 mins which shows maximum surface coverage, followed by a decrease in the negative potential. The time required to attain constant potential initially increases and then decreases at a higher concentration. Since the shift is not steady towards anodic or cathodic direction with increasing concentration of the inhibitor, it may be explained that hexadecylamine in combination with chloride may act as mixed inhibitor.

A plot of OCP vs time measurement is shown in fig. 3.

Table 10

EFFECT OF HEXADECYL AMINE WITH CHLORIDE-OPEN CIRCUIT POTENTIAL MEASUREMENTS

Time (min)	10^{-6}M HDA + $5\text{x}10^{-3}$M Cl$^-$	10^{-6}M HDA + 10^{-2}MCl$^-$	$5\text{x}10^{-6}$M HDA + $5\text{x}10^{-3}$MCl$^-$	$5\text{x}10^{-6}$M HDA + 10^{-2}MCl$^-$	(1M H_2SO_4)
1.	-0.436	-0.455	-0.469	-0.479	-0.486
2.	-0.441	-0.457	-0.470	-0.480	-0.486
3.	-0.444	-0.458	-0.470	-0.479	-0.485
4.	-0.444	-0.458	-0.470	-0.478	-0.484
5.	-0.445	-0.458	-0.469	-0.478	-0.483
6.	-0.445	-0.458	-0.469	-0.478	-0.482
7.	-0.445	-0.458	-0.469	-0.477	-0.481
8.	-0.445	-0.457	-0.468	-0.477	-0.481
9.	-0.444	-0.457	-0.468	-0.476	-0.480
10.	-0.444	-0.457	-0.468	-0.475	-0.479
11.	-0.443	-0.457	-0.468	-0.475	-0.479
12.	-0.443	-0.456	-0.468	-0.474	-0.478
13.	-0.442	-0.456	-0.468	-0.474	-0.478
14.	-0.442	-0.456	-0.468	-0.473	-0.479
15.	-0.442	-0.456	-0.467	-0.472	-0.479
16.	-0.442	-0.456	-0.467	-0.472	-0.479
17.	-0.442	-0.456	-0.467	-0.472	-0.481
18.	-0.442	-0.456	-0.467	-0.472	-0.482
19.	-0.442	-0.455	-0.466	-0.472	-0.483
20.	-0.442	-0.455	-0.466	-0.472	-0.484
21.	-0.443	-0.455	-0.465	-0.472	-0.485
22.	-0.443	-0.455	-0.464	-0.472	-0.486
23.	-0.443	-0.455	-0.464	-0.472	-0.486
24.	-0.444	-0.455	-0.464	-0.472	-0.487
25.	-0.444	-0.455	-0.464	-0.471	-0.488
26.	-0.444	-0.455	-0.463	-0.471	-0.488
27.	-0.444	-0.455	-0.463	-0.471	-0.489
28.	-0.444	-0.455	-0.463	-0.470	-0.489
29.	-0.444	-0.455	-0.462	-0.470	-0.490
30.	-0.445	-0.455	-0.462	-0.470	-0.490

EFFECT OF BROMIDE ON THE CORROSION INHIBITION OF MILD STEEL BY HEXADECYLAMINE

(a) WEIGHT LOSS METHOD:

When the inhibitor was used in combination with varying concentrations of bromide, the following values in table 11 were obtained.

Table 11

EFFECT OF HEXADECYLAMINE WITH BROMIDE:

S . No.	Conc. of inhibitor (M)	Conc. of Bromide (M)	Area (cm^2)	Weight loss (g)	Corrosion rate (Mpy)	Inhibition Efficiency (%)
1.	-	-	7.44	0.0418	2450.11	-
2.	10^{-6}	-	8.064	0.1010	1820.73	4.31
3.	10^{-6}	$5x10^{-3}$	7.777	0.0496	927.11	62.2
4.	10^{-6}	10^{-2}	7.6304	0.0422	803.94	67
5.	$5x10^{-6}$	-	7.8842	0.0980	1807.77	4.99
6.	$5x10^{-6}$	$5x10^{-3}$	7.6859	0.0452	854.88	65
7.	$5x10^{-6}$	10^{-2}	8.2521	0.0324	570.74	77

The table shows that as the concentration of both bromide and the inhibitor increases, corrosion rate decreases and the inhibition efficiency increases to a maximum of 77% with a combination of $5x10^{-6}$M hexadecylamine and 10^{-2}M bromide.

(b) OPEN CIRCUIT POTENTIAL:

The OCP measurements using hexadecylamine with bromide are shown in table 12.

Table 12

EFFECT OF HEXADECYL AMINE WITH BROMIDE-OPEN CIRCUIT POTENTIAL MEASUREMENTS

Time (min)	10^{-6}M HDA + $5x10^{-3}$M Br^-	10^{-6}M HDA + 10^{-2}M Br^-	$5x10^{-6}$MHDA + $5x10^{-3}$M Br^-	$5x10^{-6}$MHDA + 10^{-2}M Br^-	(1M H_2SO_4)
1.	-0.480	-0.465	-0.468	-0.471	-0.486
2.	-0.483	-0.466	-0.468	-0.471	-0.486
3.	-0.483	-0.467	-0.468	-0.473	-0.485
4.	-0.483	-0.466	-0.467	-0.474	-0.484
5.	-0.483	-0.466	-0.467	-0.475	-0.483
6.	-0.482	-0.466	-0.468	-0.475	-0.482
7.	-0.482	-0.466	-0.468	-0.472	-0.481
8.	-0.482	-0.466	-0.470	-0.472	-0.481
9.	-0.480	-0.468	-0.472	-0.471	-0.480
10.	-0.479	-0.468	-0.472	-0.471	-0.479
11.	-0.479	-0.468	-0.472	-0.471	-0.479
12.	-0.478	-0.468	-0.473	-0.471	-0.478
13.	-0.478	-0.469	-0.473	-0.471	-0.478
14.	-0.478	-0.470	-0.474	-0.471	-0.479
15.	-0.478	-0.470	-0.475	-0.471	-0.479
16.	-0.478	-0.470	-0.476	-0.471	-0.479
17.	-0.478	-0.471	-0.475	-0.472	-0.481
18.	-0.477	-0.471	-0.474	-0.472	-0.482
19.	-0.477	-0.471	-0.474	-0.472	-0.483
20.	-0.480	-0.472	-0.474	-0.472	-0.484
21.	-0.481	-0.473	-0.474	-0.473	-0.485
22.	-0.482	-0.476	-0.474	-0.473	-0.486
23.	-0.483	-0.477	-0.475	-0.473	-0.487
24.	-0.485	-0.477	-0.476	-0.474	-0.487
25.	-0.486	-0.477	-0.477	-0.474	-0.488
26.	-0.487	-0.478	-0.477	-0.476	-0.488
27.	-0.488	-0.479	-0.480	-0.476	-0.489
28.	-0.489	-0.480	-0.483	-0.476	-0.489
29.	-0.490	-0.480	-0.489	-0.477	-0.490
30.	-0.491	-0.481	-0.489	-0.477	-0.490

Initially the potential is found to increase to more negative direction. This is proceeded with a decrease and attainment of a constant value. Again the potential goes on with increasing negative potential as time increases. At the constant potential, the surface is covered by the inhibitor to the maximum extent. The time required for the attainment of constant potential is found to be more at higher concentration.

With increasing concentration of the inhibitor and bromide, the potential does not steadily decrease or increase in a particular direction, it can be suggested that hexadecylamine in combination with bromide may act as mixed inhibitor.

A plot of OCP Vs Time is shown in fig. 4.

EFFECT OF IODIDE ON THE CORROSION INHIBITION OF MILD STEEL WITH HEXADECYL AMINE

(a) WEIGHT LOSS METHOD:

Different concentrations of the inhibitor and iodide when used in combination, the results in table 13 were obtained.

Table 13

EFFECT OF HEXADECYLAMINE WITH IODIDE:

S . No.	Conc. of inhibitor (M)	Conc. Of Iodide (M)	Area (cm^2)	Weight loss (g)	Corrosion rate (Mpy)	Inhibition Efficiency (%)
1.	-	-	7.6842	0.0344	1903.00	-
2.	10^{-6}	-	8.064	0.1010	1802.73	4.31
3.	10^{-6}	$5x10^{-3}$	8.3619	0.0066	114.00	94
4.	10^{-6}	10^{-2}	7.623	0.0078	148.74	92
5.	$5x10^{-6}$	-	7.8842	0.0980	1807.77	4.99
6.	$5x10^{-6}$	$5x10^{-3}$	7.545	0.0050	95.15	95
7.	$5x10^{-6}$	10^{-2}	7.6347	0.0070	134.86	93

As it is evident from the table, with increase in concentration of iodide and the inhibitor, the corrosion rate steeply decreases and inhibition efficiency increases. The maximum efficiency obtained being 95% with combination of $5x10^{-6}$M hexadecylamine with $5x10^{-3}$M iodide.

(b) OPEN CIRCUIT POTENTIAL:

Table 14 presents the values of OCP with increase in time using hexadecylamine with iodide.

Table 14

EFFECT OF HEXADECYL AMINE WITH IODIDE-OPEN CIRCUIT POTENTIAL MEASUREMENTS

Time (min)	10^{-6}M HDA + $5x10^{-3}$M I^-	10^{-6}M HDA + 10^{-2}M I^-	$5x10^{-6}$M HDA + $5x10^{-3}$M I^-	$5x10^{-6}$M HDA + 10^{-2}M I^-	(1M H_2SO_4)
1.	-0.424	-0.429	-0.424	-0.432	-0.486
2.	-0.422	-0.422	-0.423	-0.423	-0.486
3.	-0.419	-0.418	-0.420	-0.417	-0.485
4.	-0.414	-0.415	-0.417	-0.415	-0.484
5.	-0.412	-0.414	-0.415	-0.413	-0.483
6.	-0.411	-0.414	-0.414	-0.410	-0.482
7.	-0.410	-0.415	-0.413	-0.410	-0.481
8.	-0.410	-0.415	-0.413	-0.409	-0.481
9.	-0.409	-0.415	-0.412	-0.408	-0.480
10.	-0.408	-0.415	-0.412	-0.408	-0.479
11.	-0.408	-0.415	-0.411	-0.408	-0.479
12.	-0.408	-0.417	-0.411	-0.406	-0.478
13.	-0.408	-0.417	-0.411	-0.407	-0.478
14.	-0.408	-0.418	-0.411	-0.407	-0.479
15.	-0.408	-0.421	-0.410	-0.407	-0.479
16.	-0.408	-0.423	-0.410	-0.407	-0.479
17.	-0.409	-0.423	-0.410	-0.406	-0.481
18.	-0.409	-0.424	-0.411	-0.406	-0.482
19.	-0.409	-0.425	-0.411	-0.406	-0.483
20.	-0.409	-0.425	-0.411	-0.406	-0.484
21.	-0.409	-0.424	-0.411	-0.406	-0.485
22.	-0.409	-0.424	-0.411	-0.406	-0.486
23.	-0.409	-0.424	-0.410	-0.406	-0.486
24.	-0.408	-0.423	-0.410	-0.406	-0.487
25.	-0.408	-0.422	-0.411	-0.406	-0.488
26.	-0.407	-0.422	-0.411	-0.406	-0.488
27.	-0.406	-0.422	-0.411	-0.407	-0.489
28.	-0.406	-0.423	-0.411	-0.407	-0.489
29.	-0.406	-0.424	-0.411	-0.407	-0.490
30.	-0.406	-0.424	-0.411	-0.408	-0.490

The negative values of OCP decrease initially for a few minutes followed by an increase and attainment of a constant potential for some time which shows maximum surface coverage by the inhibitor. It takes a longer time to attain the constant value at higher concentrations of the inhibitor. The potential is not found to proceed constantly in anodic or cathodic direction with increasing concentration of the inhibitor. Therefore, hexadecylamine in combination with iodide may act as mixed inhibitor.

A plot of OCP Vs time is shown in fig 5.

In general, the inhibition efficiency of hexadecylamine was found to increase when halides were used in combination with the inhibitor. This combined effect is known as "**synergistic effect**". Thus a synergistic effect of halides and hexadecylamine has been efficient in the inhibition of the corrosion of mild steel in 1M H_2SO_4 medium.

This effect can be explained as due to:

(i) Coadsorption of halies and the amine on the metal surface as proved by (Murakawa et al, 1968)

(ii) The halide ions forming intermediate bridges between the surface and the electrolyte facilitating adsorption of the protonated amine to the metal surface as suggested by Singh et (1995). This forms a protective layer on the surface preventing the attack by H^+ ions in the medium and thus inhibiting corrosion and loss of the metal.

The synergistic effect can also be attributed as due to the increased adsorption of organic cations in the presence of halide ions because of the change in the nature of interaction between the adsorbed particles of the inhibitor. In combined adsorption vanderwaals forces and coloumbic forces are found to predominate over coloumbic repulsion resulting in increased inhibition as suggested by Antropov (1973).

The maximum inhibition efficiency obtained with chloride has been found to be 62.71%, with bromide the maximum efficiency obtained was found to be 77% and that in case of iodide it was 95%.

The passivating effect of halide ions can be attributed to 2 factors:

(i) Deformability of the anion increases in the order $Cl^- < Br^- < I^-$

(ii) Ability of the anion to form soluble metal complexes. Both bromide and iodide are found to form soluble surface compounds by covalent linkages than the highly electro negative chloride as explained by Rudresh et al (1979).

(iii) Adsorptivity of Br^- and I^- have been predicted to be better than Cl^-, the best being I^- ions. Thus the inhibition efficiencies have been proved to be in the order $Cl^- < Br^- < I^-$ as shown by Jha et al (1990).

The higher efficiency of iodide ions are explained as due to:

(a) its larger ionic size

(b) stronger adsorption due to easy polarisibility of its electron shells and

(c) possible formation of surface layer on the metal with the amine

Thus hexadecylamine proves to be a good inhibitor for the corrosion of mild steel in 1M sulphuric acid. It also inhibits the corrosion process at higher temperatures. Halides namely chloride, bromide and iodide ions have a synergistic influence on the inhibition.

COST INCURRED FOR MAXIMUM INHIBITION EFFICIENCY

Table 15 depicts the cost that may be incurred for the inhibitor to obtain maximum inhibition efficiency.

Table 15

COST INCURRED:

Maximum inhibition efficiency (%)	Concentration of Inhibitor (M)	Amount of Inhibitor /250 ml (g)	Amount of Inhibitor /litre (g)	Cost of inhibitor /litre (Rs.)
95.66	$5x10^{-3}$	0.3019	1.2075	11.81

The maximum inhibition efficiency attained was 95.66% using $5x10^{-3}$M of the inhibitor in 1M sulphuric acid. 1.2075 g of hexadecylamine is required for 1 litre of the acid costing Rs. 11.81 per litre. Therefore, if the pickling bath contains 1000 litres of the acid, the cost incurred may amount to Rs. 11, 810 to obtain maximum inhibition efficiency.

Fig 1 Effect of Hexadecylamine

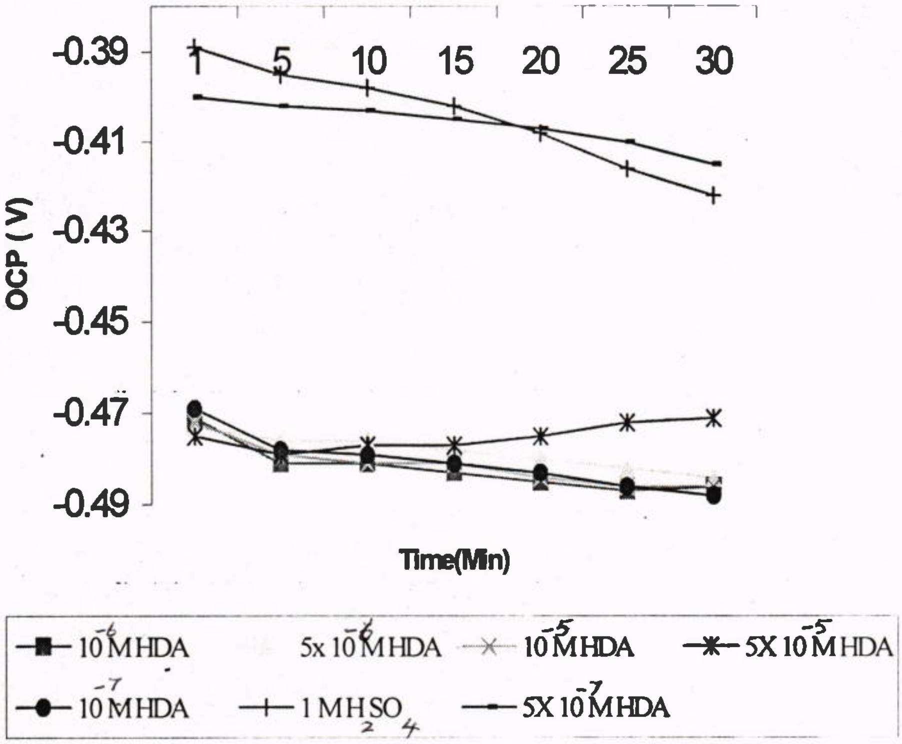


Fig 2

1/T vs Log(Corrosion Rate)

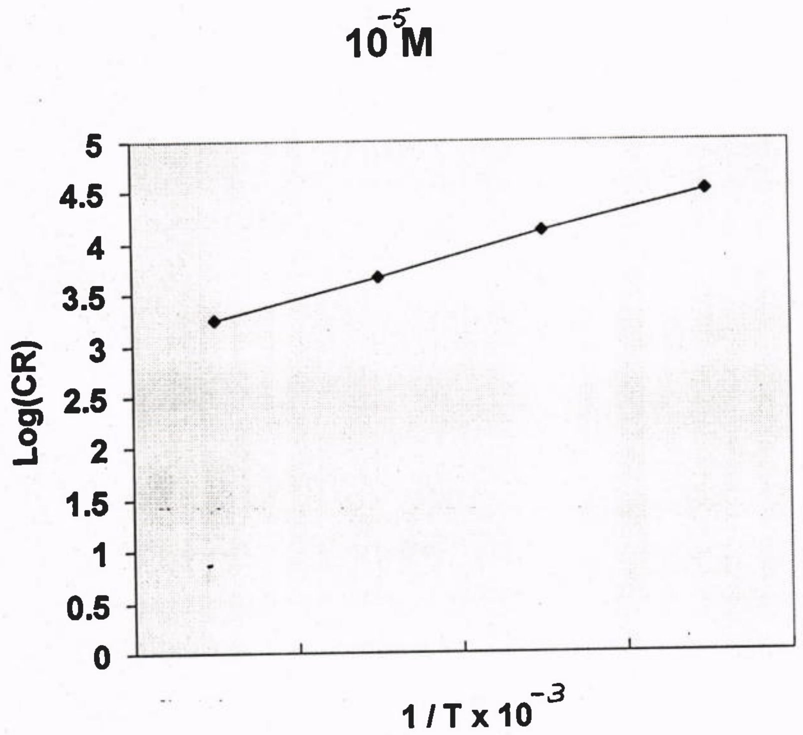


Fig 3 Effect of Hexadecylamine with Chloride

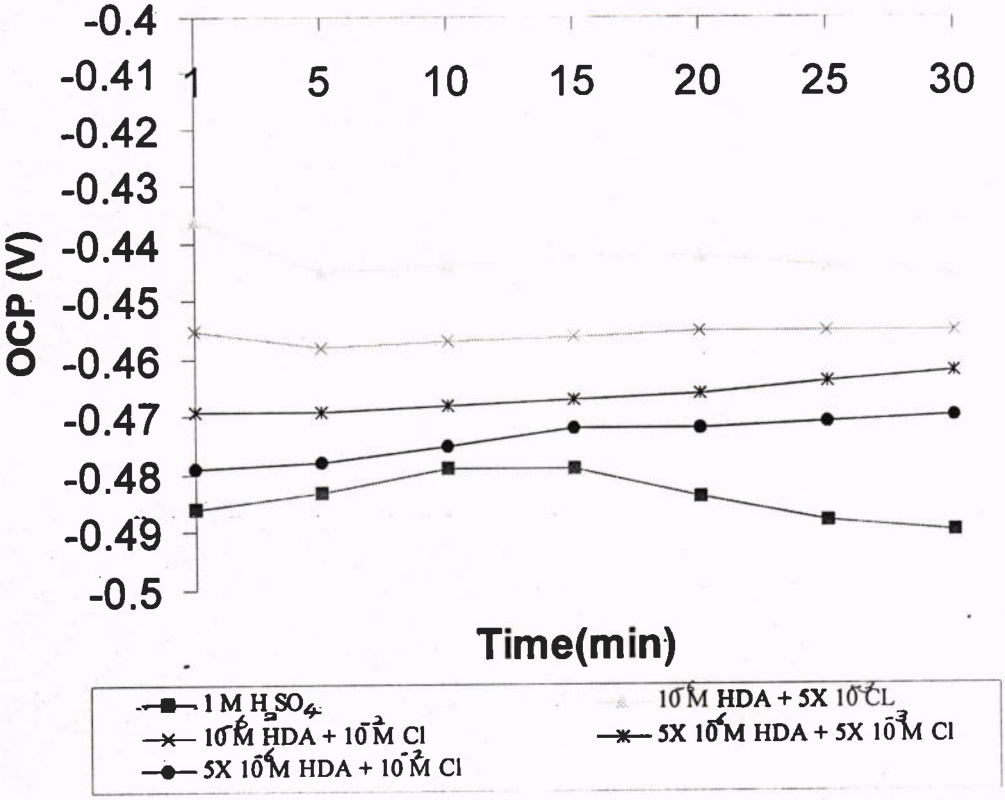
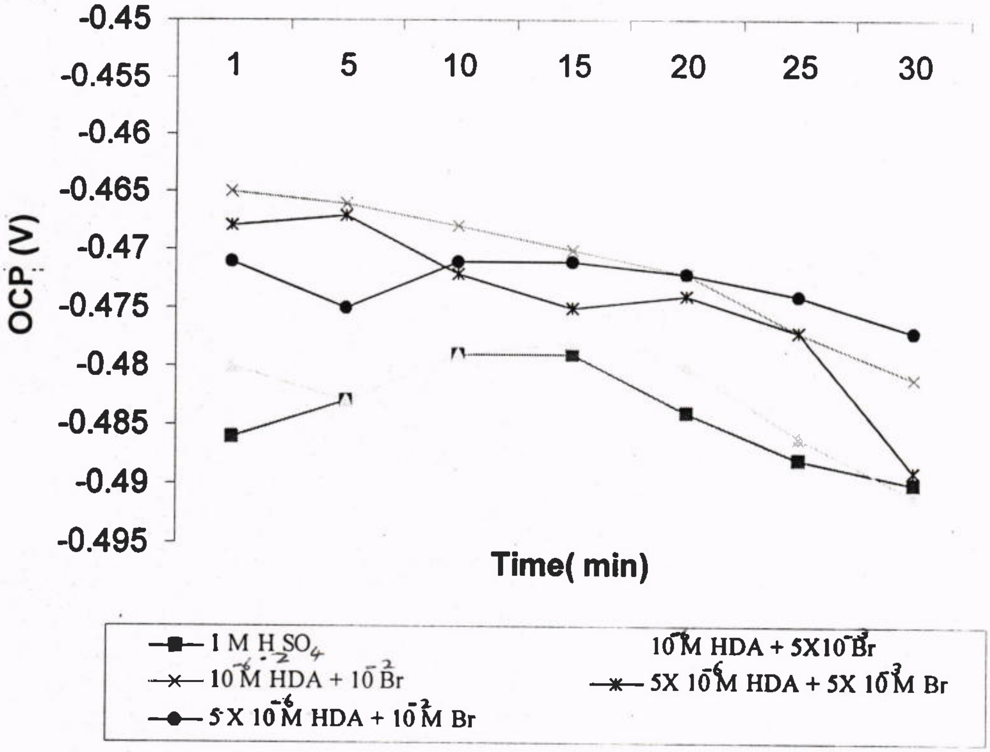


Fig 4 Effect of Hexadecylamine with Bromide



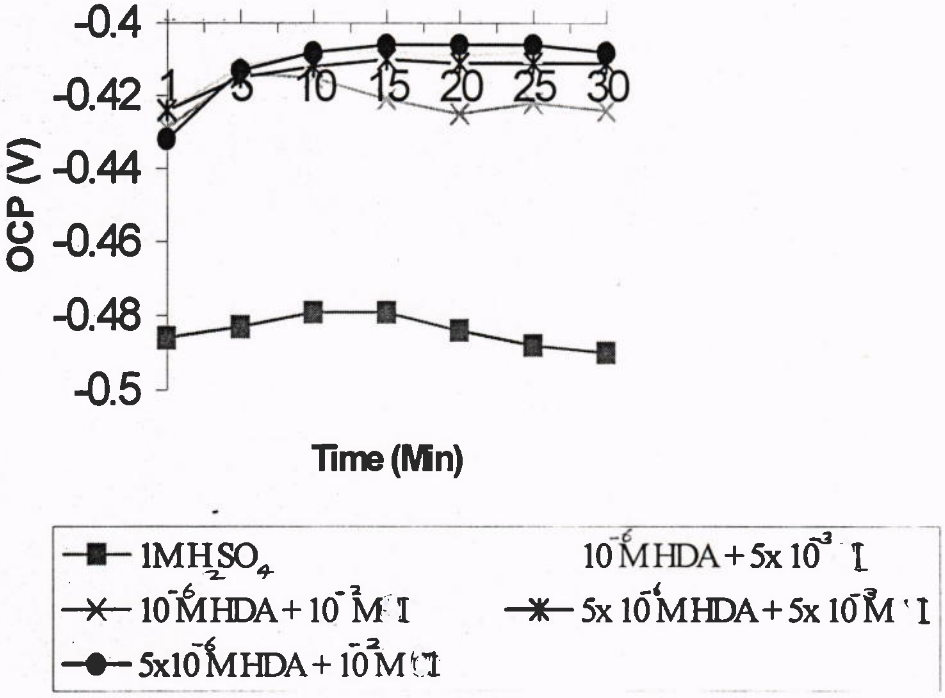
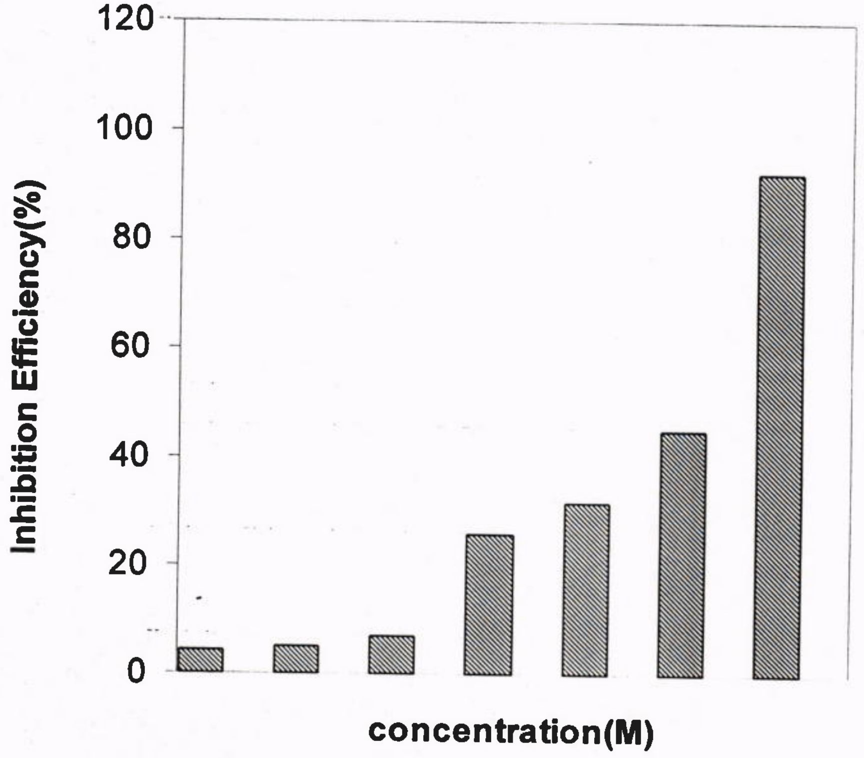
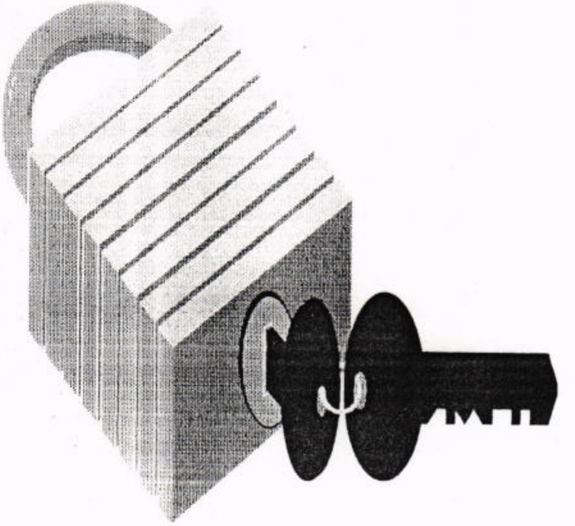


Fig. 5 Effect of Hexadecylamine with Iodide

Fig.6 Effect of Hexadecylamine at room temperature





SUMMARY & CONCLUSION

SUMMARY AND CONCLUSION

The following conclusions could be drawn based on the present study.

- ♣ Hexadecylamine is found to act as an inhibitor for the corrosion of mild steel in 1M H_2SO_4.
- ♣ The amine also inhibits the corrosion at higher temperatures, but the inhibition efficiency is found to be less.
- ♣ Increase in activation energy and positive free energy change with increase in concentration of hexadecylamine also confirm inhibition.
- ♣ When halides namely chloride, bromide and iodide are used in combination with hexadecylamine, a synergistic influence on the inhibition which increases the efficiency of inhibition is observed.
- ♣ Among the halides, iodides have the maximum synergistic influence and a maximum inhibition efficiency of 95% could be achieved.
- ♣ The open circuit potential measurements reveal that hexadecylamine functions as mixed inhibitor.
- ♣ The cost of hexadecylamine to be used in 1 litre of the acid to obtain maximum inhibition efficiency may be Rs. 11.81.

In summary, hexadecylamine inhibits the corrosion of mild steel in 1M H_2SO_4 and the inhibition efficiency is increased when halides are used in combination

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