Effect Of Aliphatic Amines On The Corrosion Of Aluminium In Acid Medium

By

BHUVANESWARI. P.

A dissertation submitted to the Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore - 641 043.

In partial fulfilment of the requirements for the Degree of

MASTER OF SCIENCE IN APPLIED CHEMISTRY

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Certified as Bonafide Research work

S. Sivakamasundari 12/5/99
Signature of Head of the Department

S. Subhashini 12/5/99
Signature of Guide

Acknowledgement

ACKNOWLEDGEMENT

The author is grateful to **Padmashri Hon. Col. Dr. (Tmt). Rajammal P. Devadas**, M.A., M.Sc.,Ph. D., (Ohio State)., Hon. D.Sc(C.Azad University, Kanpur), Chancellor, Avinashilingam Institute for Home Science and Higher Education for Women (Deemed University), Coimbatore, for the facilities provided to her by the institution, to make this study possible.

She owes her special thanks to **Dr. (Tmt.) Lakshmi Santa Rajagopal,** M.S.c., (Tannesse), Ph.D., (Madras), Vice-Chancellor, Avinashilingam Institute for Home Science and Higher Education for Home Science and Higher Education for Women (Deemed University), Coimbatore, for providing all facilities necessary for the study.

Her special debt of gratitude goes to **Dr. (Tmt) Saroja Prabakaran,** M.A. Dip. in Ed. Ph.D.,(Madras), Ph.d., Mother Terasa), Registrar, Avinashilingam Institute for Home Science and Higher Education for women (Deemed University), Coimbatore, for providing adequate help required to carry out the work.

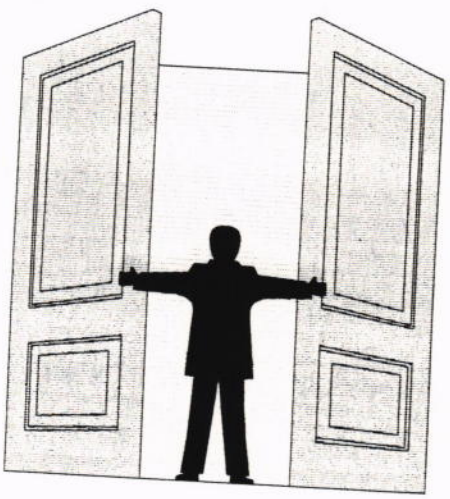
The author avails this opportunity to owe infinite reverence to **Dr. (Mrs.) S. Sivakamasundari**, M.Sc. (Annamalai), M.Phil., Ph.D, Madras) dean, faculty of science and Head Department of Chemistry Avinashilingam Institute for Home science and Higher Education for Women (Deemed University), Coimbatore, for her valued moral support, motivation and encouragement throughout the period

She is equally indebted to thank her guide **Tmt. S. Subhashini, M.Sc., M.H.Ed (Annaimalai), M.Phil, (Bharathiar),** Lecturer of the Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for women (Deemed University), Coimbatore for her constant guidance, expert suggestion, patience, help, encouragement, support and motivation right from the selection of the topic to the completion of this work.

She also wishes to thanks all the **staff** of the Chemistry Department, Avinashilingam Institute for home science and Higher education for Women (Deemed University), Coimbatore who rendered their help whenever required.

Her overwhelming gratitude goes to her **parents and friends** for their untiring help through the study.

Above all she thanks the **God Almighty** for his grace to complete her study successfully.



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Introduction

INTRODUCTION

All metals are Thermodynamically unstable and tend to react with their environment to produce compounds such as oxides or carbonates. This reaction involves the movement of electrons and is called electrochemical reaction. The readiness with which electrons are lost varies from metal to metal and the greater the readiness, the more reactive is the metal. These reactions may be regarded as a form of corrosion, since they involve the loss of electrons from the metal. Platinum, silver and gold are known as noble metals because of their low reactivity (Roger Pludek, 1977).

Metals like aluminium, magnesium, manganese, iron, nickel, tin, copper are easily susceptible to corrosion. Hence the corrosion studies of these metals are important (Carl G. Johnson, 1971).

Corrosion of metals is influenced by their environment. The degree of this influence is relative to physical state of the environment, electrolytic conductivity in environment, availability of oxidising agent in the environment and metals electronic conductivity, temperature, concentration and working conditions such as time of exposure, osmosis, effect of cycling. Corrosion of metals is also influenced by their metallurgical composition and micro structure.

The extent of corrosion reaction between dissimilar metals depends on a) electromotive force, the potential difference between the metals (b) The distance between them (c) their relative areas and (d) the electrolyte. (ROGER PLUDEK, 1977)

1.1 DEFINITION

Roger Pludek (1977) defines corrosion as "Corrosion involves loss of electrons from the metal to the environment (usually water and oxygen) and the formation of corrosion products such as oxides". Since the corrosion products are usually insoluble and may from a protective skin on the metal, the rate of corrosion may not be rapid as would be expected from the reactivity characteristic of the metal, particularly in the case of aluminium and stainless steel. But the corrosion product of mild steel is loose and non-adherent and therefore the corrosion continues.

1.1.1 IMPORTANCE OF CORROSION

In 1977, it was estimated that the financial loss in United Kingdom alone caused by corrosion is approximately 600 million ($I, 450 million) (DLAMANT, 1971).

The cost of corrosion has been estimated at $20 billion per year in United States. Corrosion in automobiles costs over $100 million per year

(Joseph. Bosich, 1970). The annual cost of corrosion in India was estimated as 600 crores in 1977. (Shukla etal, 1977).

Aside from the cost in dollars, corrosion is a serious problem because it directly and definitely contributes to the depletion of our natural resources. For example steel is made from iron ore and our reserves of iron ore are diminishing. In addition, approximately four tones of coal will eventually be consumed too. Our copper reserves are dwindling and copper is one of the elements used in the production of some classes of corrosion resistant alloys. (Joseph. Bosich, 1970).

Due to corrosion in marine and naval engineering cracking of parts which are made of aluminium magnesium alloys and stainless steel occurs. The parts of steam boiler which are made of copper base alloys, low carbon and low alloys steels are damaged due to corrosion. This leads to mechanical failure in marine engineering. (Shapino, 1962).

Corrosion takes place in the pipes of rails at the joints. Corrosion arises in lead covered cables buried in the ground and condenser (steam) tubes. (Indulkar, Thiruvengadam, 1977).

Aluminium base materials are used for electrical purposes, but corrosion or excessive deterioration of electrical and electronic parts can change the electrical properties of equipment and affect its performance and also the safety of operating equipment. (Charles, Crane, 1989 and

Roger Pludek, 1977). Drinking waters when carried through aluminium pipes were contaminated and lead to various harmful effect due to corrosion. (Diamant, 1971). Aluminium equipments when attacked by any chlorinated hydrocarbons like chloroform are corroded and the reactions could be quite dangerous. (Diamant, 1971).

The aluminium brass tube used in condensers decreased in efficiency and failed occasionally due to corrosion. The valuable parts of ship building, radial compressors which contains aluminium – alloys are affected due to corrosion (Charles, Crane, 1989).

Corrosion caused wastage of materials, expensive failure of capital equipment as well as high maintenance costs. Often it is the failure of quite small components which make a large capital installation useless; a modern equivalent to the old saga of the bottle that was lost due to the lack of a horse shoe nail. (DIAMANT, 1971). Hence corrosion has to be prevented in one way or other.

1.1.2 IMPORTANCE OF ALUMINIUM

Aluminium is a light metal and is now the second most widely used metals with specific gravity 2.7×10^3 kg/m^3 and weight for weight it is a better electrical conductor than copper. (Moss, 1971). It is ductile and can readily cost and machined. (Kenneth, Budinski, 1983). It also has

high reflectivity for light which is very much useful in pyrotechniques. (Douglas, Miner and John Seastone, 1955). Aluminium has high electronegative potential – 1.67v.

Aluminium and its alloys are widely used in various industrial and space operations. Due to its light weight it has been associated with the aerospace industries. (Polmear, 1980). It also finds application in radial compressors, jet engines and electrical purposes. (Charles, Crane, 1989). Aluminium is said to possess an excellent corrosion resistance. This is due to presence of compact, adherent, protective film of aluminium oxide which isolates aluminium from its environment. (Hugh. Godard, 1967).

Aluminium has excellent resistance to most organic acids such as fatty acids, acetic acids, nitric acid with concentration in excess of 80% at temperature below 50^0 c; ammonia any concentration both hot and cold; sulphur, hydrogen sulphide and mercaptans; fluorinated refrigerant, gases such as freons and distilled water. (Diamant, 1971).

1.1.3 ALUMINIUM CORROSION

High purity aluminium has the best resistance to corrosion. Its liability to corrode is markedly increased when other metals are in contact with it, since virtually all other common metals except magnesium are strongly cathodic to aluminium thereby increasing the rate of corrosion.

The rate of corrosion of aluminium at room temperature is high below P^H 5.5 and above P^H 8.5.

Aluminium is attacked by strong inorganic acids such as hydrochloric acid, sulphuric acid, hydrofluoric acid and phosphoric acid. It also reacts with some of the stronger organic acids such as formic, trichloro acetic acid and oxalic acid. Hydrochloric acid is particularly harmful because it causes intergranular attack which very much weakens the structure of the metal and makes it liable to stress cracking. (Diamant, 1971).

1.1.4 OBJECTIVE OF PRESENT STUDY

1) To determine the corrosion rate of aluminium in hydrochloric acid by weight loss method.
2) To find the inhibiting action of hexadecylamine and octadecylamine on the corrosion of aluminium in hydrochloric acid solution by weight loss method and open circuit potential method.
3) To evaluate the inhibitor efficiency of hexadecylamine and octadecylamine in the above experimental condition.
4) To find corrosion rate of aluminium in hydrochloric acid without inhibitor and with octadecylamine and hexadecylamine as inhibitor.

5) To calculate percentage inhibitor efficiency and surface coverage of octadecylamine and hexadecylamine on the corrosion of aluminium–1100 in 1.5M hydrochloric acid.

6) To compare the inhibitors action of hexadecylamine and octadecylamine.

7) To suggest a mechanism for the inhibitive action of amines.

1.2 INTRODUCTION TO CORROSION:

The corrosion reaction is dictated by the chemical nature of the environment and the effective concentration of the species, whether major or minor. In some cases of corrosion by acids, the presence of oxygen is required and the degree of aeration of the system (i.e) the oxygen concentration can be controlled in determining whether corrosion will occur or not.

Corrosion is sometimes considered only in the context of metallic materials in the more general sense of deterioration of materials through reaction with an environment. It also includes the behaviour of glasses, ionic solids, polymers, concrete etc, in a range of environments including the electrolytes and non-electrolytes, molten metals and gases. (Charles and Crane, 1989)

1.3 SOME DEFINITION OF CORROSION

According to Robert. Leigholl 1942, corrosion is the destruction of metals and alloys by chemical attack and it is contrast to erosion which means destruction by mechanical agencies.

Menzier (1965) defines corrosion as an electrochemical process. The deteriorating of corroding metal leaves the metallic state at anodic

areas as metallic cations which dissolve in the solution or the metal is anodically converted to a solid compound.

"Corrosion is the conversion of a metal into metallic compound. This means that the essential metallic qualities of strength, elasticity, ductility are lost and instead substances are being produced which are extremely poor with regard to these properties". This was the explanation given for corrosion by the author Diamant (1971).

The electrochemical mechanism of aqueous corrosion is outlined and it is demonstrated by Ashworth (1984) as "The process corrosion depends upon a complex interaction between the material and its environment given the particular circumstances of exposure".

Corrosive attack is the result of chemical reaction at the interface between the material and the associated environment. It can be regarded in terms of a normal bulk reaction, with the free energy for the reaction and the thermodynamic activity (i.e. effective concentration) of the reactants providing the driving force for the process (i.e.) determining the stability of the system. (Charles and Crane, 1989).

The author William Smith (1993) says that "Corrosion may be defined as the deterioration of a material resulting from chemical attack by its environment. Most corrosion of materials involves the chemical attack of metals by electrochemical cells".

According to Srivastava and Srinivasan, "Metals are found to occur in nature in a combined state, very often as oxides. Thus the combined state is more stable state and pure metals tend to attain such a state. This leads to corrosion.

1.4 CLASSIFICATION OF CORROSION

It is difficult to classify the various types of corrosive attack. Traditionally broad division into (i) wet and (ii) dry corrosion reactions have been employed. A more rational classification has been given as follows.

1.4.1 Film free chemical interaction in which there is direct chemical reaction of a metal with its environment. The metal remains film-free and there is no transport of charge. (Charles, Crane, 1989).

1.4.2 ELECTRICITY SYSTEMS

1.4.2.a. WET CORROSION

Wet corrosion occurs when liquids are present and at temperatures below the due point. An example is the corrosion of steel by water.

1.4.2.b. DRY CORROSION

Dry corrosion occurs in the absence of liquids or above the dew point. Vapours and gases are usually the corroding environment. Dry corrosion is usually associated with high temperature. An example would be the corrosion of steel by furnace gases. (Joseph Bosich, 1970).

1.4.3. FORMS OF CORROSION, CAUSES AND ITS PREVENTIVE MEASURES

In additional to general classification of corrosion, it is broadly classified depending on the appearance of corroded metal. Forms of corrosion, their causes and its preventive measures are given in the table – A.

TABLE - 1
FORMS OF CORROSION; CAUSES; PREVENTIVE MEASURES

S.No.	FORMS OF CORROSION	DEFINITIONS	CAUSES	PREVENTIVE MEASURES
1	Cavitation damage	Damage of material associated with collapse of cavities in the liquid at a solid liquid interface	Sever deformation and fracture of metal surface, creation of low pressure region, physical damage to protective films.	Vibration transfer reduction, use of cathodic protection selecting resistant material. Preventing ingress of dispersed air.
2	Concentration cells	A galvanic cell in which the e.m.f. is due to the difference in the concentration of one or more reactive constituents of the electrolyte solution.	The low oxygen areas are anodic and thus corrosion prone. When the solution over a metal contains more metal ions at one point than another, metal goes into solution where ion concentration is low.	Reducing crevices, avoiding sharp corners and stagnant areas, providing uniform environment, using welded butt joints, avoiding fibrous (or) absorbent packings.
3.	Corrosion – Erosion	A corrosion reaction accelerated by velocity and abrasion. Usually accelerated also by presence of solid particles.	Caused by an impinging water stream breaking through corrosion scale and dissolving the metal.	Minimising abrupt changes in flow direction, aligning pipe sections, stream lining inlets and outlets.
4.	Corrosion fatigue	Failure by cracking by alternating stress in the presence of a corrosive environment.	Results in metal failure occuring below the fatigue limit for non-corrosive conditions. Cyclic loads combine with corrosion and cause corrosion fatigue.	Increasing size, bulk or local strength of critical sections. Balancing stress and strength throughout the component.

5	Fretting corrosion	Localised deterioration at the interface between two contacting surfaces, accelerated by relative motion of sufficient amplitude between them to produce slip.	Differences in elastic strain between surfaces may be sufficient to cause fretting corrosion. Local attack may start fatigue cracks, mating areas are pitted.	Selecting compatible metals, suitable lubricant, isolating moving components, introducing barrier between metals.
6	Galvanic corrosion	Corrosion associated with the current resulting from the coupling of dissimilar electrodes in an electrolyte.	Caused when two dissimilar metals exposed to an electrically conductive environment are in direct contact, electrically connected by a conductor or by conductive medium.	Selecting insulation for suitable and effective materials, extending distance between dissimilar metals in conductive medium, and using cathodic protection.
7	High temperature corrosion	Corrosion associated with the effect of atmospheric conditions, various gases, molten metals and salts at high temperatures.	Caused by high temperatures and depends on the composition of the basic metals, composition of environment and salts deposited on metals.	Selecting stable material adjusting temperatures and environment and regulating duration of adverse contact.
8	Hydrogen damage	Reduction of the load carrying capability by the admission of hydrogen into the metal.	Mechanical damage of a metal caused by the presence of or interaction with hydrogen. The origin of hydrogen can be found in the cleaning, pickling, cathodic protection and welding operation.	Selecting a clean metal metallising with resistant metal, avoiding anodic metallic coatings, removing hydrogen from metal by baking.

9	Intergranular corrosion	Preferential corrosion at grain boundaries of a metal or alloy	Occurs due to a selective attack and intercrystalline cracking along the metals grain boundaries. Corrosion attack chrome-starved areas.	Selecting materials not susceptible to grain boundary depletion, selecting suitable heat treatment, avoiding welding.
10	Microbial corrosion	Deterioration of materials caused directly or indirectly by bacteria, moulds or fungi singly or in combination.	Caused by chemical attack of metals, microbial attack of organic materials, depassivation of metal surfaces and attack due to a combination of bacteria.	Providing accessibility for frequent cleaning, using cathodic protection, adding germicide, selecting suitable resistant material.
11	Pitting corrosion	Localised corrosion in which appreciable penetration into the metal occurs, resulting in the formation of cavities.	When protective film or layers of corrosion product break down, localised corrosion occurs. The pits form starting points for stress corrosion.	Secure formation of continuous and sound protective film, using protective coating, adjusting thickness of material and selecting suitable geometry of metal.
12	Leaching-selective attack	The process of extraction of a soluble component from an alloy with an insoluble component, by percolation of the alloy with a solvent – usually water.	One element of a metal (or) alloy is singled out for corrosion attack.. Common types are dezincification dealuminification and graphite corrosion.	Reducing aggressiveness of environment, selecting resistant material and use of cathodic protection.

13	Stray current corrosion-electrolysis	Corrosion resulting usually from direct current flow through paths other than the intended circuit.	Electrolytic corrosion due to uncontrolled electrical currents from extraneous sources through unintended paths such as bad earth, return on electrical equipment giving rise to leakage of current through metal structures.	Designing electrical circuits and equipments, insulating electrical cables, using non-conducting fluid and bonding metallic structures.
14	Stress corrosion cracking	Premature crocking of metals produced by the continued action of corrosion and surface tensile strength.	Caused due to a combination of high tensile stress and a corrosive environment as in sea water wedding fluxes and lubricants.	Increasing size of critical sections, reducing stress concentration, avoiding misalignment of sections and minimising applied tensile stresses.
15	Thermo galvanic corrosion	Corrosion resulting from a galvanic cell caused by a thermal gradient.	When a metal is subjected to a thermal gradient by uneven heating or dissipation of heat. This has a similar effect on the metal as galvanic corrosion.	Avoiding uneven heating, cooling and formation of hot spots, and providing insulation (or) lining.
16	Uniform corrosion (or) General corrosion	Corrosion in which no distinguishable area of the metal surface is solely anodic or cathodic.	This corrosion is indicated by a general wasting away of the surface and will normally be found where a metal is in contact with an acid or solution.	Changing or inhibiting environment, using anodic protection and selecting resistant material.

(Pludek, 1977)

1.5 FACTORS INFLUENCING CORROSION OF ALUMINIUM

1.5.1 WATER

Except in case of high temperature oxidation and gas-metal reactions, which are encountered only in special industries, there is no corrosion of aluminium unless water is present. In general also the water must contain oxygen or air; if oxygen is removed corrosion ceases.

Aluminium exposed to a aggressive marine (or) industrial atmosphere will lost longer if it is rained on frequently, since the water dilutes and washes away corrosive residues (or) salt (or) soot. In certain organic chemicals, such as phenol, traces of water prevent corrosion that would otherwise occur.

1.5.2 TEMPERATURE

An increase in temperature has strong accelerating effect on corrosion of aluminium. In the atmosphere heat can be beneficial, because it increases the rate of drying and thus reduces the period of wetness. The temperatures above 40^0C tend to reduce the rate of pitting of aluminium in water.

1.5.3 MOVEMENT

Movement of a corrosive liquid (or) gas in contact with aluminium usually accelerates the rate of corrosion. However where water is in motion in aluminium equipment, velocities greater that about 8 fpm are beneficial and may prevent pitting that might otherwise occur in a moving liquid may accelerate corrosion by eroding away or otherwise protective film.

1.5.4 SURFACE TO VOLUME RATIO

The surface to volume ratio of a metal object has a marked influence on its corrosion life. If the ratio is high, the metal deteriorates more rapidly than it does when the ratio is low. The rate of loss of tensile strength of fine wires exposed to the atmosphere increases as the diameter of the wire is reduced, since the loss of a given thickness of the metal is a larger percentage of the original thickness for fine wires that for wires of greater diameter.

1.5.5 HEAT CAPACITY OF THE SURFACE

The heat capacity of a metal surface has an influence on the corrosion rate. This may be due to the thickness of the metal itself, or to the heart capacity of other objects to which the metal is affixed. If an

unpainted aluminium – skinned aircraft is poorly maintained, pitting may develop and will be most pronounced on the underside of the wings. This is due to the large mass of wing structure, together with gasoline tanks, which causes the under surface of the wings to have a low rate of heating and cooling.

1.5.6 IMPURITIES IN THE ENVIRONMENT

Eventhough aluminium may have proved itself an excellent material for handling a specific chemicals, it is wise to check the corrosivity of a new source of this chemical, for it may contain impurities which although not affecting its quality, may lead to corrosion of aluminium vessels.

1.5.7 SURFACE FINISH

Surface finish has also effect on the corrosion of aluminium. (Hugh Godard, Jepson, Bothwell, Robert Kane, 1967)

1.6 NEED FOR PREVENTION OF ALUMINIUM CORROSION

Today aluminium is being used on an increasing scale in many items of chemical plant equipment, including heat exchangers, pressure

vessels, condensers, rotary dryers, tanks, portable containers, valves and piping.

The application of aluminium in the chemical industry dates back to the 1920's when new and more economic methods for the production of nitric acid, acetic acid and hydrogen peroxide created a demand for bulk storage and transport of these important chemicals.

Aluminium foil have increasing use in cryogenic field for the bulk transport and storage of liquefied industrial gases notably oxygen, nitrogen, argon and methane. (Hugh Godard; Bothwell; Jepson; Robert Kane, 1967).

Aluminium being rolled into sheets is used in the manufacture of furniture, airplanes, railroad and trolley cars, automobile bodies and pistons, electric cables and bus bars, rigid conduits, rivets, utensils. In the finely divided flake form aluminium is employed as a pigment in paint. (Robert Leighou, 1942).

Aluminium power head powder cables which operate above atmospheric temperature usually last indefinitely. The mechanical properties of aluminium will be lost due to corrosion. Hence there is need for prevention of corrosion. (Hugh Godard; Jepson; Bothwell; Robert Kane, 1967).

1.7 METHODS (OR) WAYS OF CONTROLLING CORROSION

Corrosion (or) the conversion of a metal back into its oxide is a surface chemical reaction only and is very expensive to eliminate completely. But there are number of ways to limit its action by slowing down (or) stopping their reaction.

The most common method of preventing corrosion is the selection of proper metal (or) alloy for a particular corrosive medium. Corrosion can be controlled by preventing corrosion reactions taking places on the metal surface. This method depends on the nature of the environment to which the metal is exposed. That is why the metal surfaces are degreased and descaled. (John Wiley and Sons, 1959)

Corrosion is also prevented by choosing a material is which galvanic attack is unlikely, by use of protective coatings, avoidance of potential crevices and use of galvanic protections. (Raymond Higgins, 1977).

In addition to these, alteration of the environment such as lowering the temperature, decreasing the velocity of the flowing fluids, removing oxidisers, changing the concentration plays a major role in the corrosion prevention. (Indulkar, Thiruvengadam, 1977).

Electrochemical techniques such as cathodic and anodic protection may also be employed to preserve metal structures especially the

underground pipelines. Stray current effects are to be considered while impressing cathodic current on the buried pipelines.

Inhibitors can be used to inhibit the corrosion rate. An inhibitor is a substance that when added in small concentration to an environment, decreases the corrosion rate. Different types of inhibitors such as oxidisers, hydrogen evolution poisons, scavengers (Na_2So_3), adsorption type inhibitors, vapour phase inhibitors are available for preventing corrosion at suitable levels.

1.8 INHIBITORS FOR CONTROLLING CORROSION OF ALUMINIUM

An inhibitor is a substance which reduces the rate of corrosion. It does not actually prevent corrosion and so protection is temporary. (Rozenfeld, 1981). The use of inhibitors to prevent the corrosion of aluminium by Mears and Eldredge and more recently by Haygood and Minford and Roebuck and Pritchett.

Inhibitors that reduce the anodic reaction are termed anodic inhibitors (e.g) chromates, whereas those that reduce the cathodic reaction are termed cathodic inhibitors (e.g.) zinc sulfate.

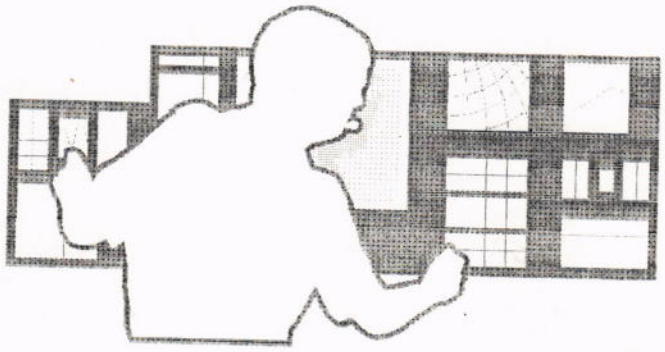
Chromates (in the form of sodium or potassium chromate (or) dichromate) the most commonly used inhibitors for aluminium is the

anodic type. 500 ppm sodium chromate is effective to prevent the pitting of aluminium in water brine solutions and for sufficient to protect aluminium in brine solutions, and for calcium chloride the level should be 3500 ppm.

Phosphates silicates, nitrates, fluorides, benzoates, soluble oil, and certain other chemicals have been recommended alone or in combination to inhibit the pitting of aluminium in aggressive waters.

In mixed-metal systems which also contain copper, sodium mercaptobenzothiazole has been found to be an effective ingredient. Neumann reported that a mixed chromate-polyphosphatedianodic inhibitor is effective at much lower concentration. (Hugh Godard, Jepson, Bothwell; Robert Kane, 1967). Inhibitors such as chromates, per-manganates react with aluminium to replace the oxide film with a more impervious salt; others may be absorbed on the surface of the metal and hinders the access of the corroding medium; others may reduce the rate of one (or) more of the corroding reactions. (Mondolfo, 1976).

Chapter - II



Review of Literature

REVIEW OF LITERATURE

Among metallurgical topics, those associated with the corrosion of metals and its prevention are of great significance in engineering. [Glikman, 1962]. Corrosion is the passage of the metal in to the chemically combined state [Ashworth, 1984]. The rate of corrosion may not be rapid as would be expected from the reactivity characteristic of the metal, particularly in the case of aluminium and stainless steel. But the corrosion products of mild steel is loose and non adherent and therefore the corrosion continues [Roger Pludek, 1977].

Many investigations were carried out on the corrosion of aluminium in different medium using various inhibitors. The literature survey was based on the following headings.

2.1 CORROSION OF ALUMINIUM IN ALKALI MEDIUM

The influence of some aldehydes on the corrosion and anodic behaviour of aluminium in sodium hydroxide solution was carried out by Krishnan and Subramanyam in the year 1977.

Sherif and Narayan (1986) had done an impedence study about corrosion of aluminium in 1M-sodium chloride solution. Similarly corrosion of aluminium in 1 H-sodium chloride solution. Similarly

corrosion of Aluminium in alkaline and water - glycerol solutions was performed by Baabd-el-Nabey, Awad Ahmed on 1988.

A report on impedence spectra for aluminium 7075 during the early stages of immersion in sodium chloride solution was given by Fernandes, Mansfeld in the year 1993. In the following year corrosion behaviour of aluminium in molten sodium was reported. [Zhang, Kuyama, Nomura, Matsumaru, 1994]

The corrosion and anodic behaviour of different grades of aluminium in alkaline media was carried out by Gnana Sahaya Rosilda, Ganesan, Anbu Kulandai, Nathan and Kapali in the year 1994. Again in 1995, the corrosion of aluminium in sodium hydroxide solution and effect of inhibitor rubeanic acid on the same was done by Sarkar, Dasgupta., Kurmaiah and electrochemical dissolution of aluminium in alkaline electrolyte was reported. [Romanenkov, Gryzlov, 1995]

Aluminium corrosion in alkaline solution and the influence of alloying elements were done. [Korolevea, Thompson, Hollrigl, Bloeck, 1995] growth of corrosion pits on pure aluminium in 1M-sodium chloride was viewed by Buzzza, Alkira, in the year 1995. Recently the electrochemical behaviour of pure aluminium in aqueous sodiumhydroxide solution was studied (Koan Emregul, Gulaybayramgles and Abb Akbwt, 1998)

2.2 ALUMINIUM CORROSION IN DIFFERENT ACID MEDIUM:

The effect of halo acetic acids on corrosion of aluminium in nitric acid was done in the year 1984 by Subramanyam and Mayanna. Corrosion of aluminium in chloro acetic acid was reported by Hesham mansour, Moustafa, Abuel-wafa and Gaber Noubi in 1986. Two years later the corrosion of aluminium in phosphoric acid and influence of some inorganic additives was performed (Hasham Mansour, 1988)

In 1993 Yadav, Wadhwani, studied the corrosion of 3003-aluminium in acidic chloride solution. Also the dissolution behaviour of aluminium in solution containing both chloride and fluoride ions were reported. (Carol, Murphy, Breslin, 1993). The electrochemical behaviour of aluminium-indium alloy in chloride solution was studied in 1993 by Bessone, Garcia. Saidman, Drazzic, Popic observed the corrosion potential of aluminium in acid chloride solutions in September 1993. Incorporation of chloride by aluminium at potentials below the pitting potential was observed Natishan, Mccafferty, in the year 1994.

In 1994, electrochemical behaviour and corrosion of aluminium in chloride media was done by Brett, Gomer, Martins. In the same year, corrosion of aluminium in acidic methanol, ethanol and acetonitrite water [AL-Abdallah, 1994). Studies on the passivation of aluminium in chromate and molybdate solutions were carried out. [Breslin, Trealy,

Carrell, 1994]. Corrosion of aluminium on ortho phosphoric acid and to control it by pyridine derivatives [Dubey, Upadhaya, Chaudhary, 1994] were carried out.

Aluminium corrosion in nitric acid and the effect of chloride on it was done by Kharafi, Badawy, in 1994. Tomashova, Chekavtsev, Davydov carried out the experiment on electrochemical behaviour of aluminium in chloride solution and the effect of cathodic incorporation of alkaline media in the year 1995 March.

Corrosion and passivation of aluminium and aluminium-silicon alloys in nitric acid solutions was reported.[Al-Kharafi, Badaway, 1995]. Also, Bjorgum, Sigurdson, Nisancioglu reported the studies based on the corrosion of commercially pure aluminium in chloride solution containing carbon-di-oxide, bicarbonate and copper ions in the year 1995.

In the same year, corrosion of aluminium and aluminium-silicon alloys behaviour in nitric acid solutions (Badeway, Al-Kharaf, 1995); electrochemical behaviour of aluminium based alloys in the presence of chloride ions [Babic, Metikos-Hukovic, Omanon, Grubec, Brinic, 1995); Induced corrosion of aluminium surfaces in sulphuric acid [Dai, Freedman, Robison [1995] were reported.

Corrosion characteristics of some aluminium alloys in oxalic acid was performed by Singh and Archana Gupta in 1996. In the following

year, effect of some anions on corrosion behaviour of 1060, 1100 and 5052 aluminium alloys in orthophosphoric acid were studied. [Indian.J. Chem.Technol, 1997]

2.3 CORROSION OF ALUMINIUM IN HYDROCHLORIC ACID MEDIUM WITH INHIBITORS

The effect of some hydrazine derivatives on the corrosion of aluminium in hydrochloric acid solutions was carried out by Moussa, Taha, Gouda and Singab in 1976.

Again the experiment on anilines as corrosion inhibitors for an aluminium-copper alloy in phosphoric acid was done. [Taltai and Pandya 1976]. Inhibition of corrosion of aluminium - 51s in hydrochloric acid solution was reported. [Desai Thakar, Chaaya and Gandhi, 1976]. The inhibitive behaviour of cadmium sulphate on corrosion of aluminium in hydrochloric acid solution was carried out by Cai, Shan, Lu.Bi Yyan, in 1993.

Pyridine derivative as corrosion inhibitors for 3003 aluminium in very dilute hydrochloric acid was done in 1993. (Yadav, Wadhwani, 1993].

Corrosion of aluminium in hydrochloric acid and its inhibitive effect by schiff bases was analysed. [Gomma, Wahdan, 1995]. Also the

inhibition of corrosion of aluminium in hydrochloric acid by cobalt tetrasulphopthalocyanine was carried out by Sivasankara Pillai, Thomas, Harkumar [1995].

2.4 STUDY OF ALUMINIUM CORROSION IN OTHER ACIDS WITH AMINE INHIBITORS

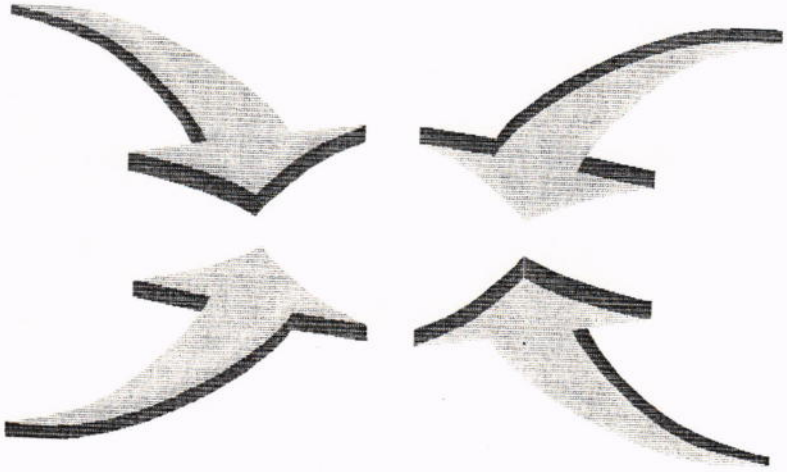
Taltai and Pandya reported the work of amines as corrosion inhibitor for B26s aluminium in phosphoric acid in 1974. Effect of chloride ion on the inhibition of aluminium in sulphuric acid by ethanolamine was reported. [Lakhan Jha and Gurmeet Singh, 1990].

2.5 CORROSION OF ALUMINIUM IN NEUTRAL MEDIUM

The electrochemical behaviour of aluminium in sodium acetate buffers was analysed by Valand and Nilsson in 1976. Corrosion of aluminium pigments in aqueous media and the effect of saccharides derivatives on the above was reported. [Muller, Kurfess, 1993].

The effect of propargyl alcohol on the corrosion of pure aluminium and aluminium alloys in aqueous solution was studied by Aksut, Bayramogly, in the year 1993. In the year 1995 Muller, Franze, studied the effect of aminomethylene phosphoric acid as corrosion inhibitors for aluminium pigments in aqueous media.

Chapter - III



Materials and Methods

MATERIALS AND METHODS

3.1 SELECTION OF SAMPLE

Aluminium and its alloys are widely used in various industrial and space operations. Aluminium alloyed with other metals, is employed in the manufacture of furniture, airplanes, railroads, automobile bodies, electric cables, kitchen utensils and also collapsible tubes for pastes. Hence aluminium was selected to study its corrosion and their protection.

Aluminium sheet of grade 1100 of composition 0.13% silica; 0.32% iron; 0.07% manganese; 0.02% magnesium, 0.01% copper and remaining aluminium was used for the present work.

3.2 SELECTION OF ACID

The acid medium chosen for this study was hydrochloric acid. Aluminium is attacked by strong inorganic acids such as hydrochloric acid, sulphuric acid, hydro fluoric acid and phosphoric acid. Hydrochloric acid is particularly harmful because it causes intergranular attack which very much weakens the structure of the metal and makes it liable to stress cracking. Hence hydrochloric acid was selected for the study.

3.3 SELECTION OF INHIBITORS

The aliphatic amines octadecylamine and hexadecylamine was used as inhibitors and its effect on the corrosion of aluminium was studied.

The inhibitor solution was prepared as follows

Octadecylamine solution of 10^{-4} concentration was prepared by dissolving 0.02695 g of octadecylamine in one litre of 1.5M hydrochloric acid. From this various concentrations were prepared.

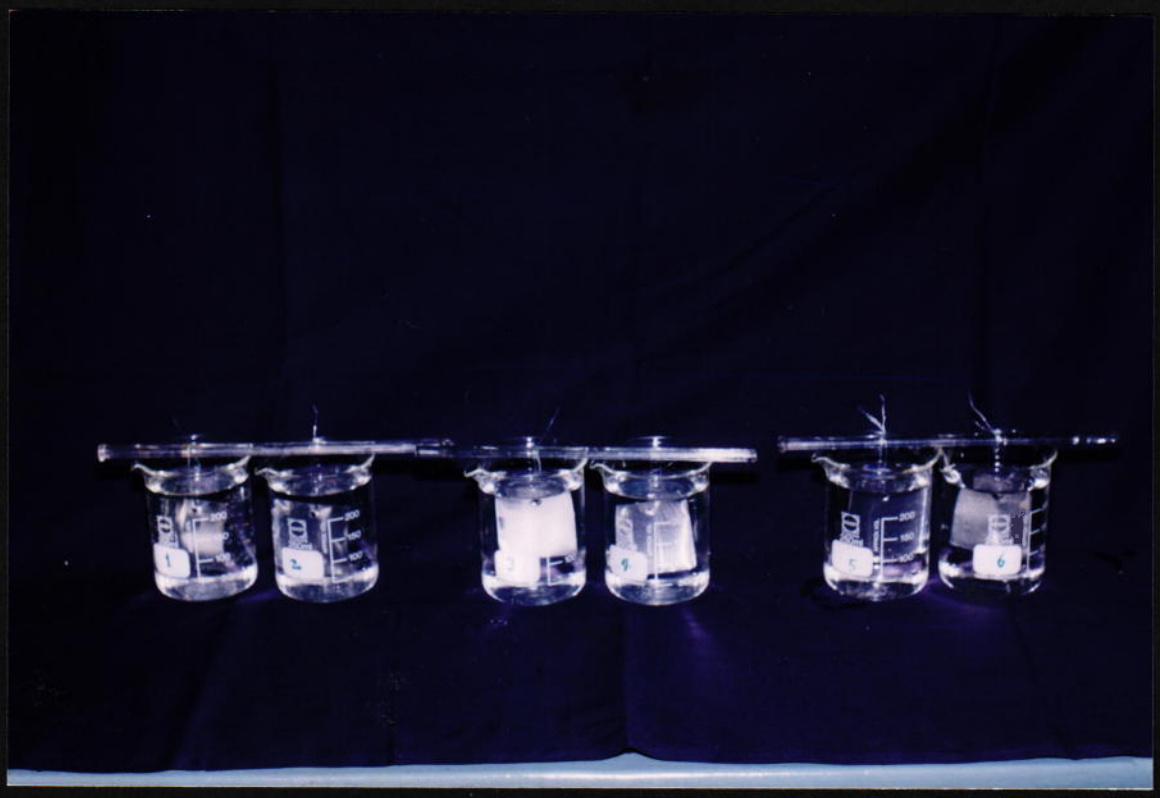
Hexadecylamine inhibitor of 10^{-4} concentration was prepared by dissolving 0.02415g of amine in one litre of 1.5M hydrochloric acid. From this various concentrations were diluted. The chemicals used were of A. R. grade.

3.4 WEIGHT LOSS METHOD

0.5M hydrochloric acid was taken in 250 ml beaker and the previously weighed aluminium sheet of size 5x4 cm and 0.15 mm thickness were suspended in the solution using glass hooks. Care was taken to the complete immersion of the specimen. After one hour the specimen was removed, washed with water, dried and weighed using physical balance to the accuracy of fourth decimal. This was done for 4 consecutive hours. From the initial and final weights of the specimen, the

PLATE - I

WEIGHT LOSS MEASUREMENT



loss in weight was calculated. The experiment was repeated with 0.75 M, 1.0M, 1.25M and 1.5M concentrations of hydrochloric acid.

250 ml of 10^{-5} concentration of octadecylamine (inhibitor prepared with 1.5M hydrochloric acid) was taken in a beaker and the experiment was repeated in the above manner and weight loss was calculated. The experiment was also done for 10^{-6}, 10^{-7}, 10^{-8}, $5x10^{-5}$, $5x10^{-6}$, $5x10^{-7}$ and 10^{-8} M concentrations of octadecylamine

Similarly experiment was carried out using hexadecylamine as inhibitor solution. A duplicate was performed for all the experiments mentioned above.

3.5 CALCULATIONS

3.5.1 CORROSION RATE

The corrosion rate was calculated using the formula in miles per year units.

$$R = KW / ATD$$

Where

R - The corrosion rate

K - Constant

W - Weight loss in grams

T - Time of exposure in hours

D - Density in g /cu. cm.

The K value is 1.00×10^4 D

The density of aluminium is 2.70 gm/Cu cm.

3.5.2 PERCENTAGE OF INHIBITION EFFICIENCY

$$\%p = \left(\frac{W_0 - W}{W_0} \right) X\ 100$$

%p - Percentage inhibitor efficiency

W_0 - Weight loss without inhibitor

W - Weight loss with inhibitor

By using the above formula %p was calculated.

3.5.3 SURFACE COVERAGE (θ)

$$\theta = 1 - \frac{W}{W_O}$$

W - Weight loss with inhibitor

W_0 - Weight loss without inhibitor

Surface coverage θ was calculated by using this formula

3.5.4 FREE ENERGY OF ADSORPTION (G)

G = Frumkins slope x 2.303 x R

R - 1.987 calories.

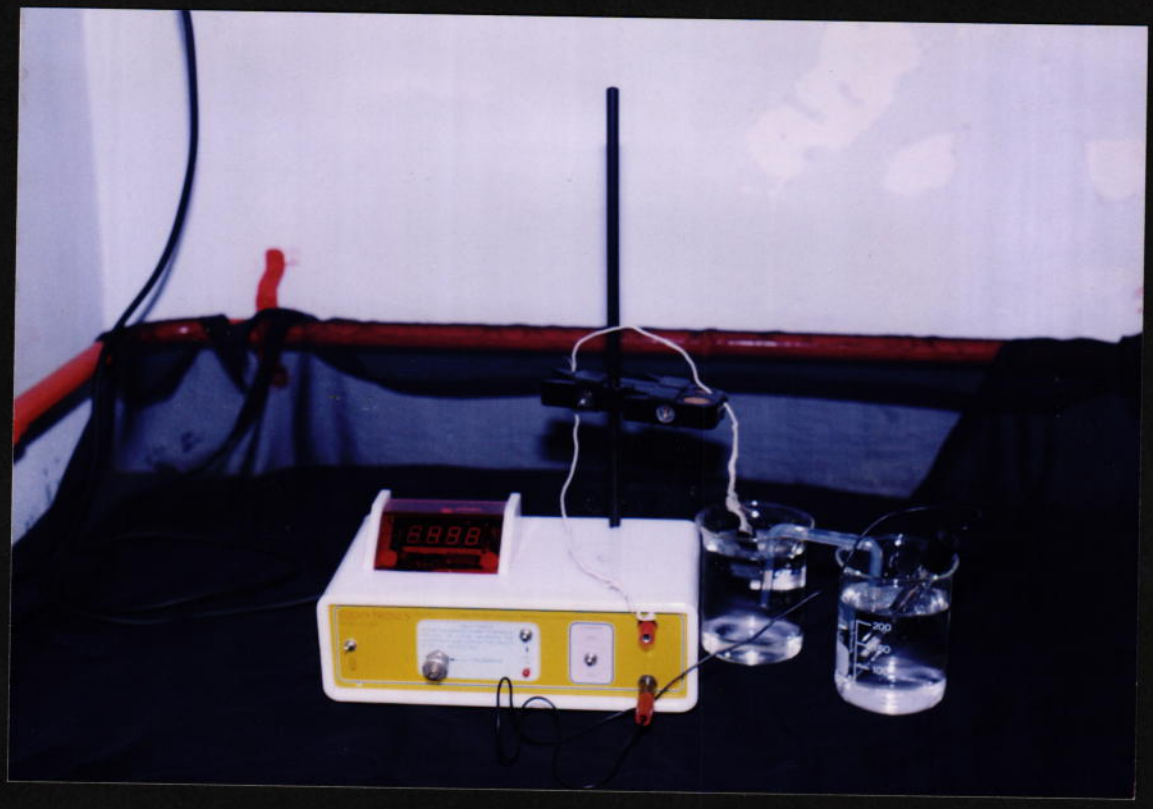
3.6 OPEN CIRCUIT POTENTIAL

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

250 ml of the same media is used as in weight loss method. The aluminium sheets were 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 and open circuit potential.

PLATE - II

OPEN CIRCUIT POTENTIAL



Chapter - IV

Results and Discussion

RESULTS AND DISCUSSIONS

4.1 CORROSION BEHAVIOUR OF ALUMINIUM IN VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACID:

The aluminium alloy was found to be more corroded in 1.5 M hydrochloric acid. The extent of corrosion is such that the alloy has even dissolved fully in the acid during fourth hour of immersion as noted during the experimental work. The alloy is less corrosive in 0.5 M hydrochloric acid. (Table - II)

TABLE - II

VARIATION OF CORROSION RATE OF ALUMINIUM - 1100 IN HYDROCHLORIC ACID

S.NO	Concs. (M)	CORROSION RATE (mpy)			
		1hr	2hrs	3hrs	Average corrosion rate
1	0.5	18.92	14.19	12.62	15.48
2	0.75	223.66	18.92	14.19	18.92
3	1.0	33.13	21.28	17.35	23.92
4	1.25	37.86	26.03	22.08	28.56
5	1.5	37.86	26.03	25.24	29.71

The studies shows that as concentration of the acid increases, the corrosion rate increases. (Fig. 1). But it was observed that the corrosion rate decreases with time for all the concentrations of the acid. (Fig. 2). The same results were obtained by R.S Dubey (1996) during his work on corrosion of aluminium in orthophosphoric acid.

The aluminium sheet was kept under open circuit condition in 0.5M; 0.75 M; 1.0 M 1.25M and 1.5 M concentrations and OCP values were recorded as function of time. The results were plotted in the Fig 3.

It has been observed that the open circuit potential initially shifts in the positive direction and thereafter it remains constant for a long time. (Table II). This behaviour may be explained on the basis of the formation of thin oxide film on aluminium surface. The initial shift of OCP in the positive direction shows that the corrosion of aluminium alloys is under anodic control in hydrochloric acid.

It is clear from the OCP values, that the steady state corrosion potentials increases with acid concentration (Table-III). The same behaviour was experienced by Dubey (1996).

The corrosion rate was found to increase with increase of acid concentration and decrease with time. The corrosion potential shifts to anodic direction. These two observations shows the increased polarisation at the cathode.

TABLE III

OPEN CIRCUIT POTENTIAL VALUES WITH TIME FOR VARIOUS CONCENTRATIONS OF HYDROCHLORIC ACIDS

S.No.	Time (Minutes)	E_{corr} (mv)				
		0.5	0.75	1.0	1.25	1.5
1	5	-742	-776	-825	-1042	-1090
2	10	-758	-789	-830	-1052	-1096
3	15	-766	-791	-820	-1046	-1090
4	20	-770	-785	-815	-1037	-1089
5	25	-772	-782	-810	-1035	-1088
6	30	-772	-782	-810	-1035	-1088

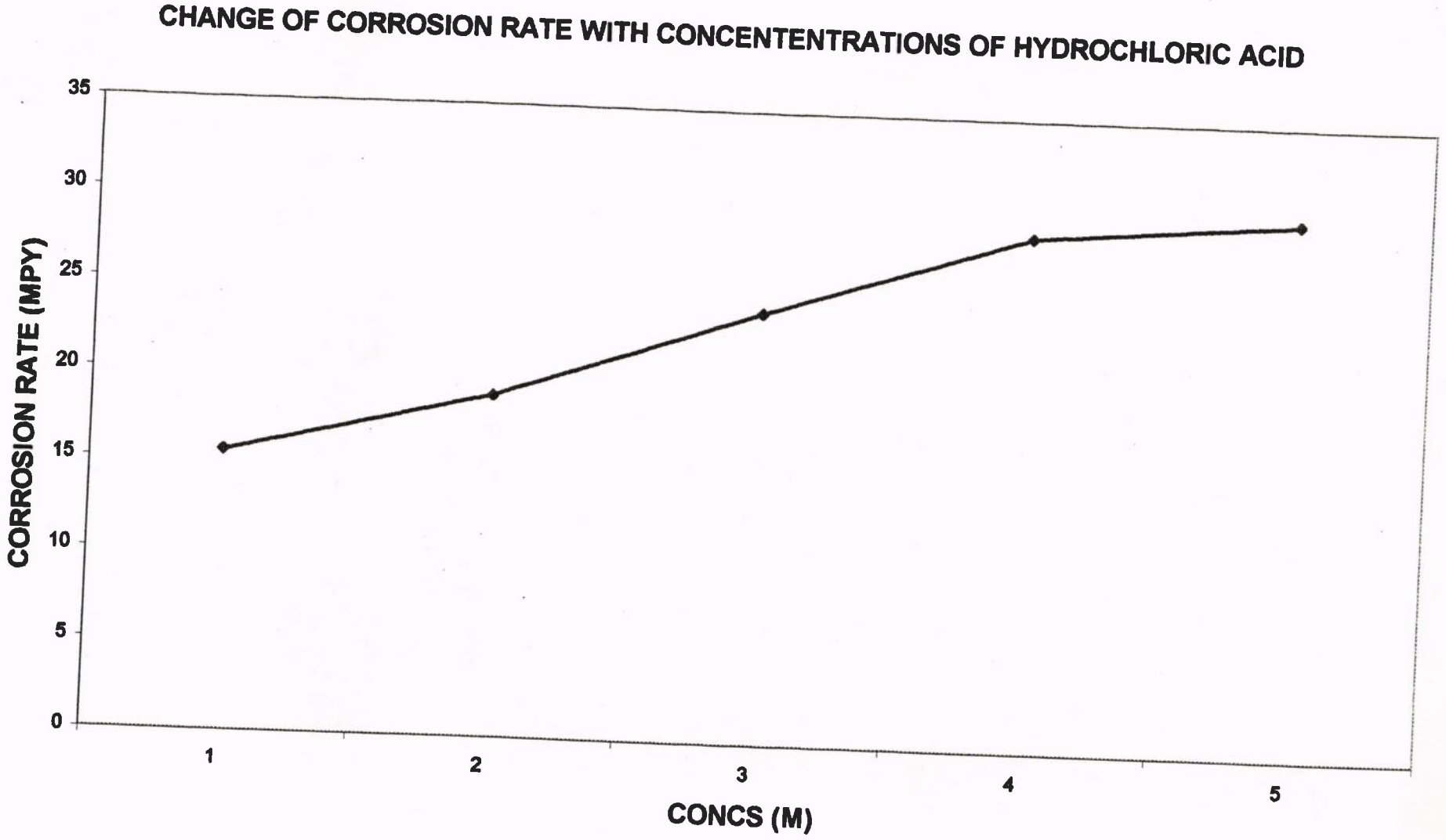

CHANGE OF CORROSION RATE WITH CONCENTENTRATIONS OF HYDROCHLORIC ACID
CORROSION RATE (MPY)
35
30
25
20
15
10
5
0
1
2
3
4
5
CONCS (M)

FIGURE - 1

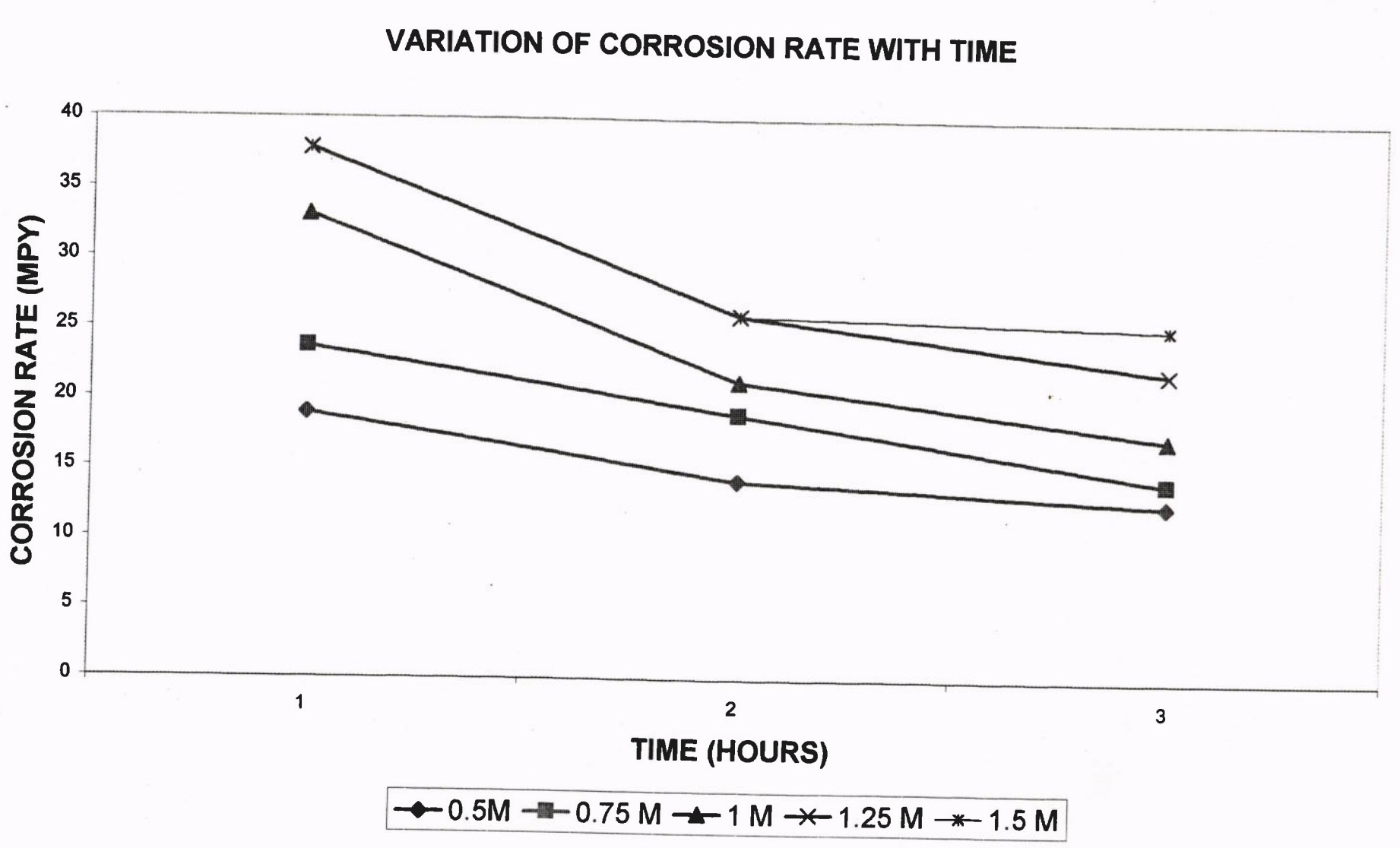

VARIATION OF CORROSION RATE WITH TIME
CORROSION RATE (MPY)
40
35
30
25
20
15
10
5
0
1
2
3
TIME (HOURS)
0.5M
0.75 M
1 M
1.25 M
1.5 M

FIGURE - 2

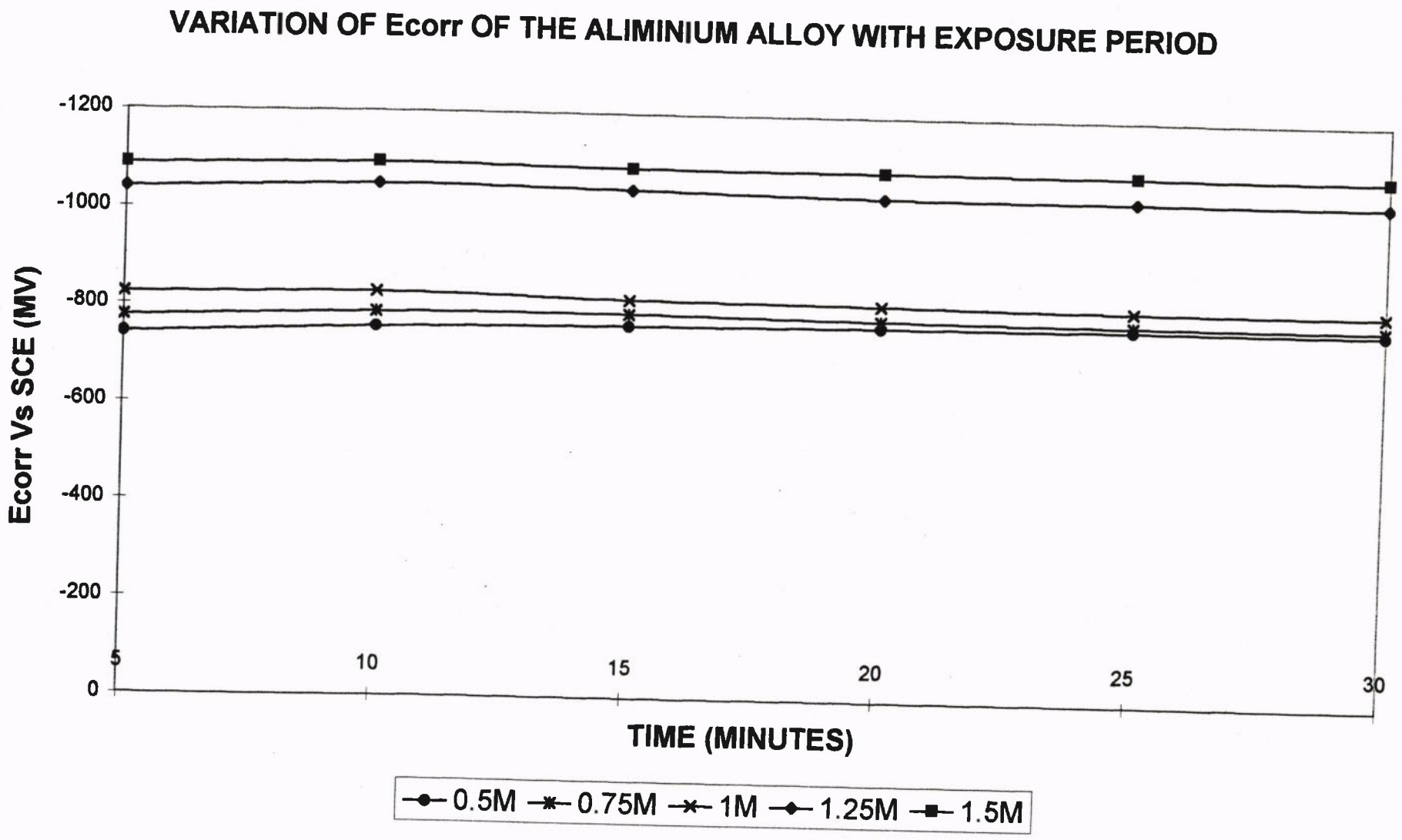

VARIATION OF Ecorr OF THE ALIMINIUM ALLOY WITH EXPOSURE PERIOD
-1200
-1000
-800
-600
-400
-200
0
Ecorr Vs SCE (MV)
5
10
15
20
25
30
TIME (MINUTES)
0.5M
0.75M
1M
1.25M
1.5M

FIGURE - 3

4.2 EFFECT OF OCTADECYLAMINE ON THE CORROSION RATE OF ALUMINIUM-1100 IN 1.5 M HYDROCHLORIC ACID

In the case of octadecylamine the corrosion rate was found to be minimum at 10^{-5} M and 5 x 10^{-5} M concentrations of the inhibitor. (Table IV). The other concentrations show more corrosion rate. The maximum was observed in 5 x 10^{-8} and 10^{-8} concentrations. Therefore the corrosion rate increases with decrease in concentration of the inhibitor. The corrosion rate was found to be almost a constant with time with the inhibitor of concentrations $5x10^{-5}$M, 10^{-5}M; $5x10^{-6}$M; 10^{-6}M and $5x10^{-7}$M. In the case of solutions with 5 x 10^{-7} and 10^{-8} the corrosion rate increases with time. It was found to be maximum at the fourth hour of 10^{-8} concentration.(Fig. 4 and Fig. 5).

The corrosion rate was decreased by the presence of octadecylamine inhibitor and it varies with the concentrations of inhibitor. Subramanyam and Mayanna (1984) noted the sane result.

The above results were supported by the inhibitor efficiency calculation. The inhibitor efficiency was found to be 88.8 for inhibitor with concentration 10^{-5} M. The value was 33.3 for 5 x 10^{-8} M concentrations. (Table-V). The inhibitor efficiency was proved to be constant with time for the concentrations 5 x 10^{-5}M; 10^{-5}M; 5 x 10^{-6}M; 10^{-6}M; and 5 x 10^{-8}M. The inhibitor efficiency was found to be maximum

in the concentration 10^{-8} during the fourth hour (Fig. 6). The values of inhibition efficiency were low and increase with increase in concentration of inhibitor. The same were observed by Ramakrishnan and Subramanyan(1976).

The calculation of surface coverage θ gave additional support for the above experimental fact. Maximum area of the sample was covered by the inhibitor of concentrations 10^{-5} and 5×10^{-5}M. As seen above, except 5×10^{-8}M and 10^{-8}M concentrations of the inhibitor the other concentrations of the inhibitor exhibited a constant coverage area. In the above two concentrations the inhibitor showed a minimum surface coverage. (Table-VI). The surface covered by the oxide film found to decrease with time in all the concentrations of the inhibitors except $5x10^{-5}$M; 10^{-5}M; $5x10^{-6}$M; 10^{-6}M concentrations. In these concentrations the surface coverage stood almost the same.

The region of constancy observed could be due to complete coverage of surface by the inhibitor. Hesham Mansour (1988) recorded the same results during the corrosion of aluminium in orthophosphoricacid.

The OCP measurements shows a constant steady state potential after the first 20 minutes. The value was found to increase as dilution increases (Fig. 7 and table VII). An increase in cathodic surface will shift the

potential in the more noble direction. Thus the pronounced shift of potential in the negative direction, indicative of cathodic polarisation with the steady state potential shifting in the positive direction on the addition of inhibitors. This was found to be in agreement with the results obtained by Desai, Thakkar, Chhaya and Gandhi (1976)

TABLE IV

EFFECT OF CONCENTRATION AND TIME ON CORROSION RATE OF ALUMINIUM – 11100 IN 1.5 M HYDROCHLORIC ACID WITH OCTADECYLAMINE INHIBITOR

S.NO	Concs (M)	CORROSION RATE (MPY)				
		1 hour	2 hours	3 hours	4 hours	Average corrosion rate (mpy)
1	$5x10^{-5}$	18.92	18.94	17.35	15.38	13.1
2	$1 x 10^{-5}$	9.46	23.66	9.468	10.64	13.31
3	$5 x 10^{-6}$	23.66	23.66	22.08	20.11	14.41
4	$1 x 10^{-6}$	23.66	23.66	23.66	23.66	23.66
5	$5 x 10^{-7}$	28.39	33.14	25.24	23.66	21.39
6	$1 x 10^{-7}$	18.92	16.56	20.51	28.06	21.19
7	$5 x 10^{-8}$	33.13	85.18	33.13	33.13	22.47
8	$1 x 10^{-8}$	23.66	26.03	29.97	41.41	20.50

TABLE – V

DEPENDENCE OF PERCENTAGE INHIBITORS EFFICIENCY ON CONCENTRATIONS OF OCTADECYLAMINE IN 1.5M HYDROCHLORIC ACID

S.NO	CONCS (M)	PERCENTAGE INHIBITOR EFFICIENCY				
		1 hour	2 hours	3 hours	4 hours	Average efficiency
1	$5x10^{-5}$	66.60	65.20	66.66	69.05	66.9
2	$1 x 10^{-5}$	88.80	88.80	88.80	83.93	80.2
3	$5 x 10^{-6}$	58.30	56.52	57.57	59.52	54.7
4	$1 x 10^{-6}$	58.33	72.22	72.22	64.29	66.8
5	$5 x 10^{-7}$	50	52.17	51.52	52.38	51.5
6	$1 x 10^{-7}$	56.60	80.50	75.93	58.93	70.5
7	$5 x 10^{-8}$	41.6	39.13	36.36	33.3	37.6
8	$1 x 10^{-8}$	58.3	69.4	64.8	37.5	57.5

TABLE VI

SURFACE COVERAGE θ OF ALUMINUM – 1100 IN THE PRESENCE OF OCTADECYLAMINE INHIBITORS

S.NO	CONCS (M)	SURFACE COVERAGE θ				
		1 hour	2 hours	3 hours	4 hours	Average θ
1	5×10^{-5}	0.6666	0.6522	0.6666	0.6905	0.6690
2	1×10^{-5}	0.8333	0.8888	0.8888	0.8393	0.8626
3	5×10^{-6}	0.5833	0.5652	0.5757	0.5952	0.5799
4	1×10^{-6}	0.5833	0.7222	0.7222	0.6428	0.6676
5	5×10^{-7}	0.5000	0.5217	0.5152	0.5238	0.5152
6	1×10^{-7}	0.6666	0.8055	0.7593	0.5893	0.7052
7	5×10^{-8}	0.4166	0.3913	0.3636	0.3333	0.3762
8	1×10^{-8}	0.5833	0.6944	0.6481	0.3750	0.5752

TABLE VII

$E_{Corr.}$ VALUES OF ALUMINIUM – 1100 IN 1.5M HYDROCHLORIC ACID WITH OCTADECYLAMINE

		E pot Vs SCE (mv)								
S.No	TIME (MINUTES)	BLANK	5×10^{-5}	1×10^{-5}	5×10^{-6}	1×10^{-6}	5×10^{-7}	1×10^{-7}	5×10^{-8}	1×10^{-8}
1	5	-1097	-1103	-1102	-1109	-1100	-1099	-1106	-1100	-1110
2	10	-1094	-1100	-1108	-1106	-1107	-1103	-1103	-1105	-1107
3	15	-1090	-1098	-1100	-1103	-1103	-1101	-1101	-1102	-1105
4	20	-1089	-1096	-1097	-1099	-1100	-1099	-1100	-1099	-1101
5	25	-1086	-1094	-1094	-1096	-1097	-1077	-1098	-1098	-1099
6	30	-1086	-1094	-1094	-1096	-1097	-1077	-1098	-1098	-1099

CORROSION BEHAVIOUR OF ALIMINUM 11OO IN HYDROCHOLORIC ACID AND OCTADECYLAMINE WITH TIME

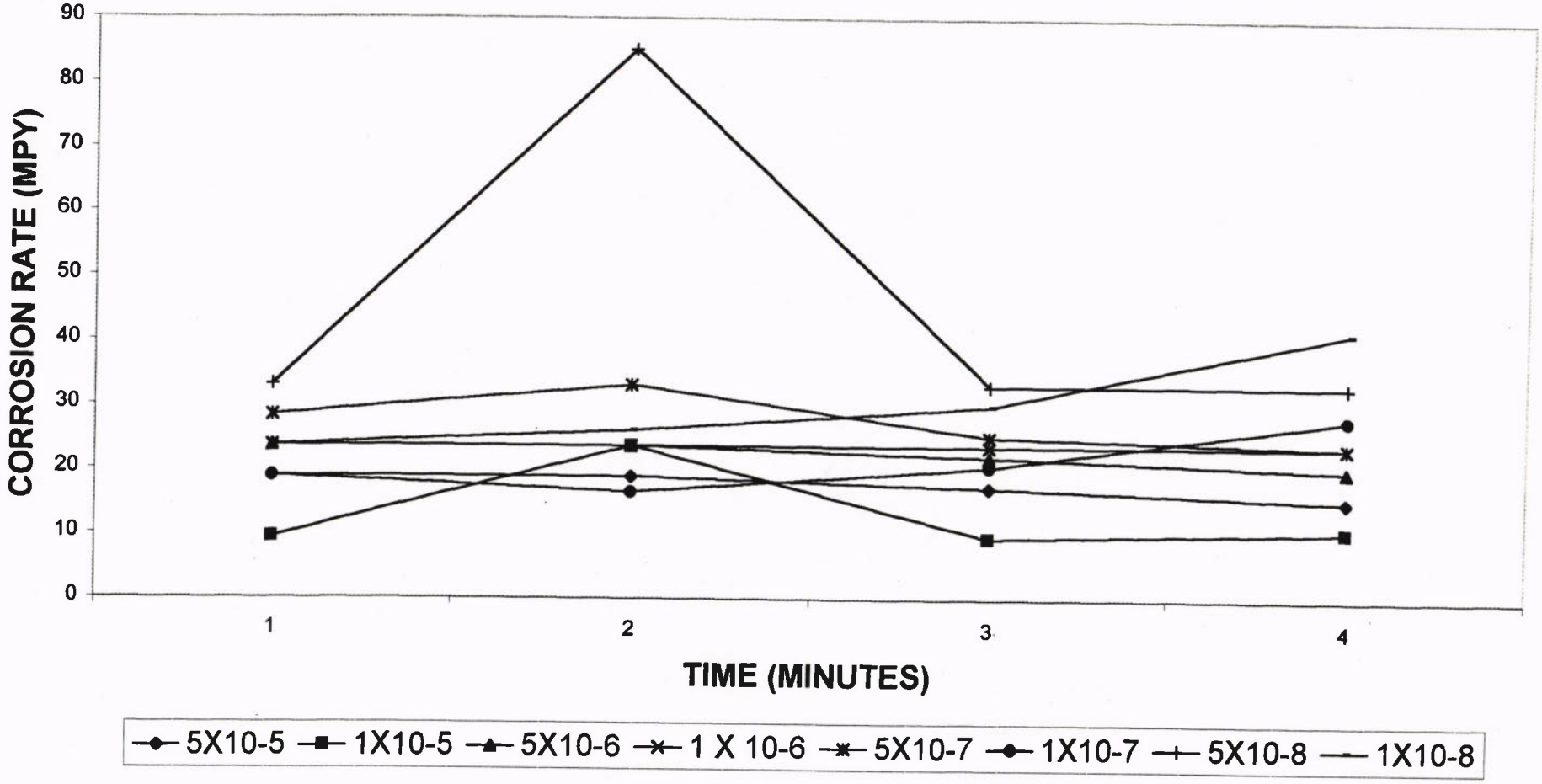


FIGURE - 4

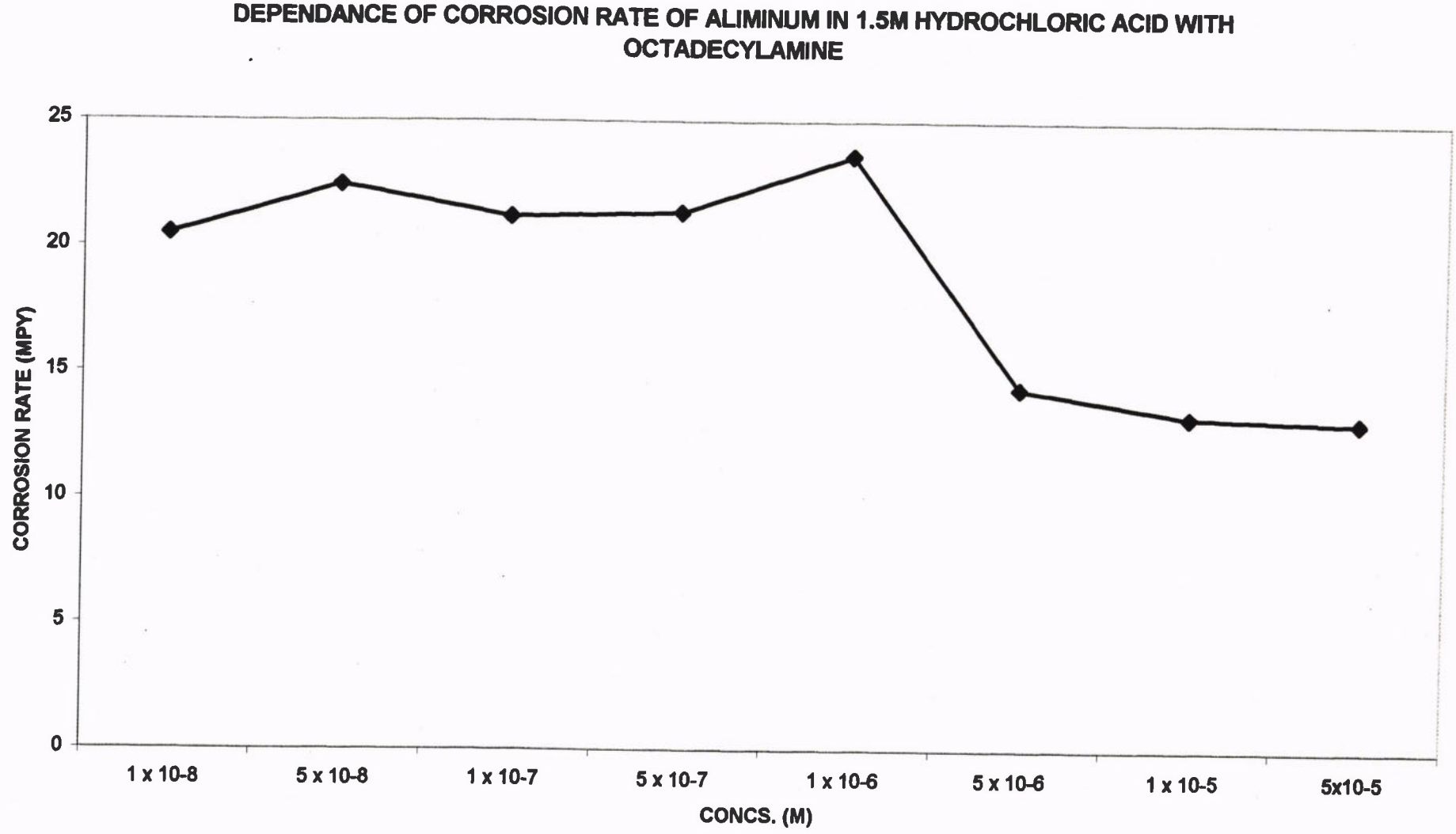

DEPENDANCE OF CORROSION RATE OF ALIMINUM IN 1.5M HYDROCHLORIC ACID WITH OCTADECYLAMINE
CORROSION RATE (MPY)
25
20
15
10
5
0
1 x 10-8
5 x 10-8
1 x 10-7
5 x 10-7
1 x 10-6
5 x 10-6
1 x 10-5
5x10-5
CONCS. (M)

FIGURE - 5

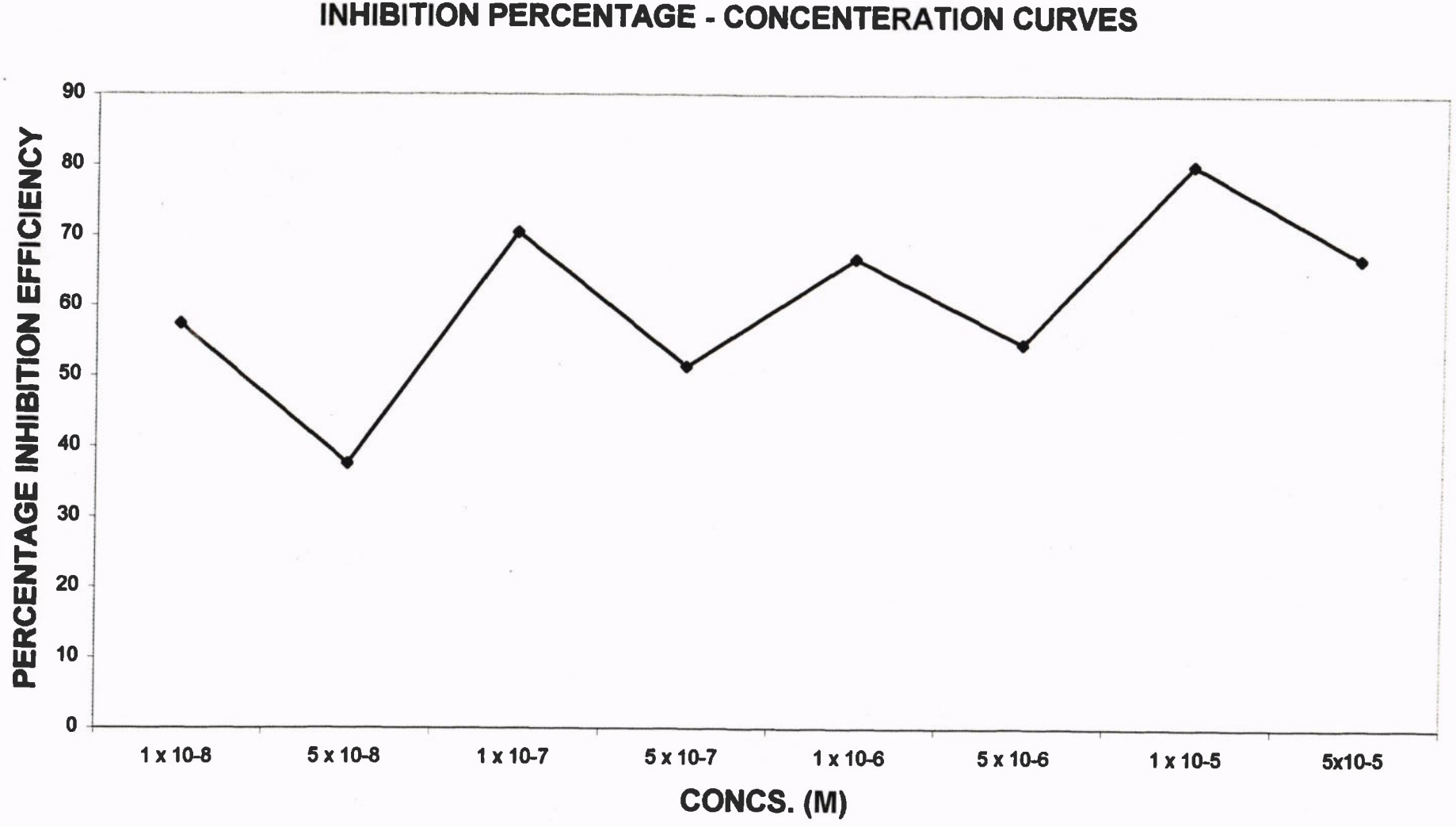

INHIBITION PERCENTAGE - CONCENTERATION CURVES
PERCENTAGE INHIBITION EFFICIENCY
90
80
70
60
50
40
30
20
10
0
1 x 10-8
5 x 10-8
1 x 10-7
5 x 10-7
1 x 10-6
5 x 10-6
1 x 10-5
5x10-5
CONCS. (M)

FIGURE - 6

VARIATION Ecorr OF ALUMINUM - 1100 IN HYDROCHOLORIC ACID AND OCTADECYLAMINE WITH EXPOSURE OF TIME

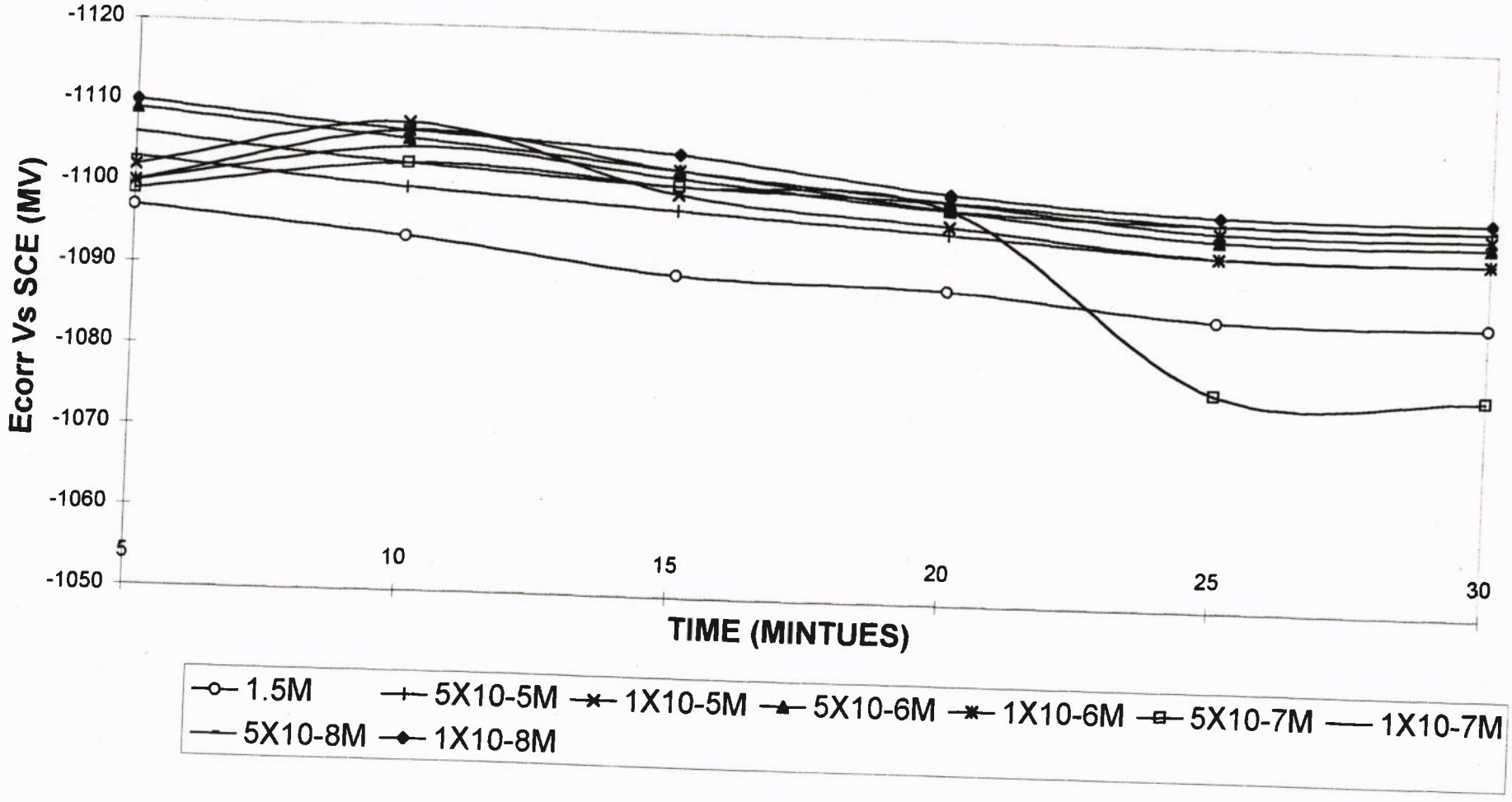


FIGURE - 7

4.3 INHIBITIVE ACTION OF HEXADECYLAMINE ON THE CORROSION RATE OF ALUMINIUM – 1100 IN 1.5M HYDROCHLORIC ACID

The aliphatic hexadecylamine proved to be a better inhibitor for the acid of aluminium. Among the various concentrations of the inhibitor used, 10^{-5} M and 5 x 10^{-5}M concentrations have shown maximum inhibition. In these concentrations, the corrosion rate was minimum. Maximum corrosion rate was seen in concentrations 10^{-8} M, 5 x $^{10-8}$ M, 10^{-7} M; 5 x 10^{-7}M. From these data, it can be concluded that the corrosion rate decreases with increase of concentrations of the inhibitors. (Table VIII).

TABLE – VIII

EFFECT OF CONCENTRATIONS AND TIME ON CORROSION RATE OF ALUMINUM – 1100 IN 1.5M HYDROCHLORIC ACID WITH HEXADECYLAMINE

S.NO	CONCS (M)	CORROSION RATE (mpy)				
		1 hour	2 hours	3 hours	4 hours	Average corrosion rate.
1	5×10^{-5}	14.19	16.56	11.04	10.65	13.11
2	1×10^{-5}	9.46	11.82	12.61	14.19	12.02
3	5×10^{-6}	14.19	14.19	14.19	15.38	14.49
4	1×10^{-6}	14.19	14.19	14.19	15.38	14.49
5	5×10^{-7}	23.66	21.28	20.51	20.11	21.39
6	1×10^{-7}	18.93	21.28	22.08	22.48	21.19
7	5×10^{-8}	18.92	23.66	23.66	23.66	22.47
8	1×10^{-8}	18.92	18.92	20.51	23.66	20.50

Hence the effectiveness of the inhibitors increases with increasing concentration and the extent of corrosion decreases with increase in the concentration of inhibitor. The decrease in corrosion rate may be attributed to physical and chemical adsorption. The similar results have been reported by Talati and Pandya; Hesham Mansour (1986).

TABLE IX

DEPENDENCE OF PERCENTAGE INHIBITIVE EFFICIENCY ON THE CONCENTRATIONS OF HEXADECYLAMINE IN 1.5M HYDROCHLORIC ACID

S.NO	CONCS (M)	PERCENTAGE OF INHIBITOR EFFICIENCY				
		1 hour	2 hours	3 hours	4 hours	Average inhibitor efficiency
1	5×10^{-5}	50	64.28	61.1	70	61.3
2	1×10^{-5}	83.3	78.26	75.75	71.43	77.2
3	5×10^{-6}	50	57.14	50	56.6	53.4
4	1×10^{-6}	75	73.91	72.72	69.05	72.7
5	5×10^{-7}	16.6	35.71	27.7	43.3	30.8
6	1×10^{-7}	66.67	60.86	57.58	54.76	61.2
7	5×10^{-8}	33.3	28.57	16.6	33.3	27.9
8	1×10^{-8}	66.67	65.22	60.61	52.38	61.2

83.3% inhibitor efficiency was shown by the inhibitor of concentration 10^{-5} M and 70% inhibitive efficiency was shown by 5×10^{-5} concentrations of the inhibitor. Minimum inhibitor efficiency was exhibited by the diluted hexadecylamine solution. (Table IX and Fig. 8).

The inhibition efficiency was found to decrease with decreasing concentrations of the inhibitors. The inhibition mechanism may be due to

film formation / complex formation / due to adsorption. This fact has been supported by Lakhan Jha and Gurmeet Singh (1990).

The above results were substantiated by the surface coverage calculation. The specimen was maximum covered by 10^{-5}M and $5x10^{-5}$M inhibitor concentrations. In all the concentrations, the surface coverage decreases with time. The maximum coverage was noted in the first hour of study. (Table X)

TABLE X

SURFACE COVERAGE θ OF ALUMINIUM – 1100 IN THE PRESENCE OF HEXADECYLAMINE

S.NO	CONCS (M)	SURFACE COVERAGE θ				
		1 hour	2 hours	3 hours	4 hours	Average θ
1	5×10^{-5}	0.5000	0.6429	0.6111	0.7000	0.6135
2	$1x10^{-5}$	0.8333	0.7826	0.7576	0.7143	0.7719
3	5×10^{-6}	0.5000	0.5743	0.5000	0.5666	0.5352
4	1×10^{-6}	0.7500	0.7391	0.7273	0.6905	0.7267
5	5×10^{-7}	0.1666	0.3571	0.2778	0.4333	0.3087
6	1×10^{-7}	0.6666	0.6522	0.6060	0.5238	0.5937
7	5×10^{-8}	0.3333	0.2857	0.1667	0.3330	0.2797
8	1×10^{-8}	0.6666	0.6522	0.6061	0.5238	0.6121

According to Lakhan Jha and Gurmeet Singh (1990), at higher concentrations of the inhibitor, there is maximum surface coverage and a better inhibiting effect results due to the formation of insoluble complex which blocks the most active sites of metal surface and at lower concentration metal inhibitor forms soluble complex which subsequently accelerates the corrosion rate. This was found to be true in the above case.

The OCP measurements shows a constant steady state potential after first 20 minutes. The value was found to increase as dilution increases. (Table – XI). The shift of potential in the negative direction is a direct consequent of the adsorption of inhibitor molecules on the metal surface. This data was found to be in agreement with Hesham Mansour (1988).

TABLE XI

OCP VALUES OF ALUMINIUM – 1100 IN 1.5M HYDROCHLORIC ACID WITH HEXADECYLAMINE

		E pot Vs SCE (mv)							
S.No	TIME (MINUTES)	5×10^{-5}	1×10^{-5}	5×10^{-6}	1×10^{-6}	5×10^{-7}	1×10^{-7}	5×10^{-8}	1×10^{-8}
1	5	-1107	-1109	-1105	-1100	-1097	-1098	-1108	-1099
2	10	-1101	-1103	-1103	-1102	-1103	-1102	-1110	-1104
3	15	-1096	-1094	-1097	-1099	-1101	-1100	-1107	-1102
4	20	-1093	-1090	-1095	-1097	-1100	-1098	-1102	-1100
5	25	-1089	-1092	-1094	-1095	-1098	-1097	-1098	-1099
6	30	-1089	-1092	-1094	-1095	-1098	-1097	-1098	-1099

THE EFFECT OF HEXADECYLAMINE ON THE CORROSSION RATE OF ALUMINIUM IN 1.5M HYDROCHLORIC ACID WITH TIME

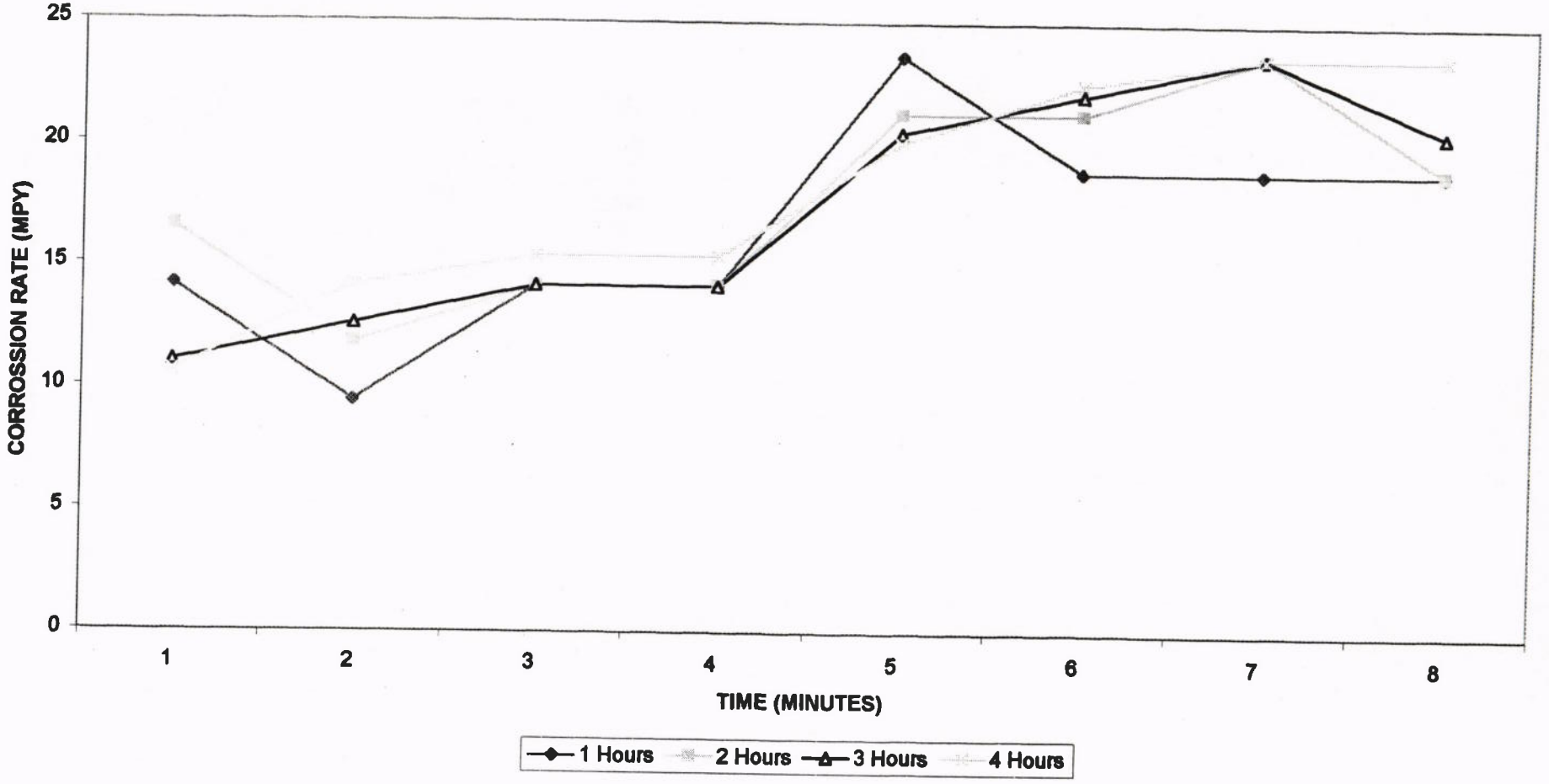


FIGURE - 8

INFLUENCE OF HEXADECYLAMINE ON THE CORROSION RATE OF ALIMINIUM IN 1.5M HYDROCHLORIC ACID

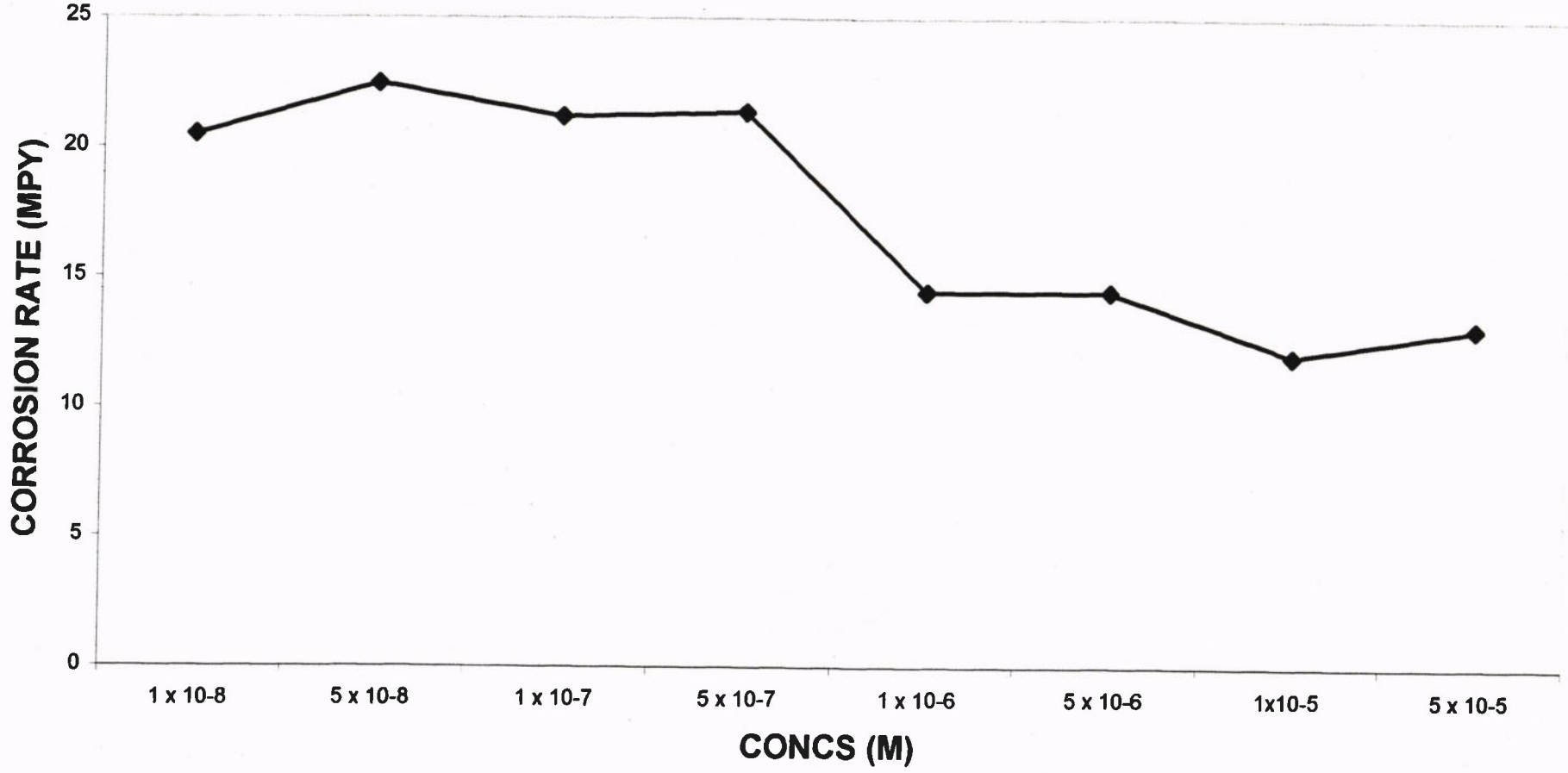


FIGURE - 9

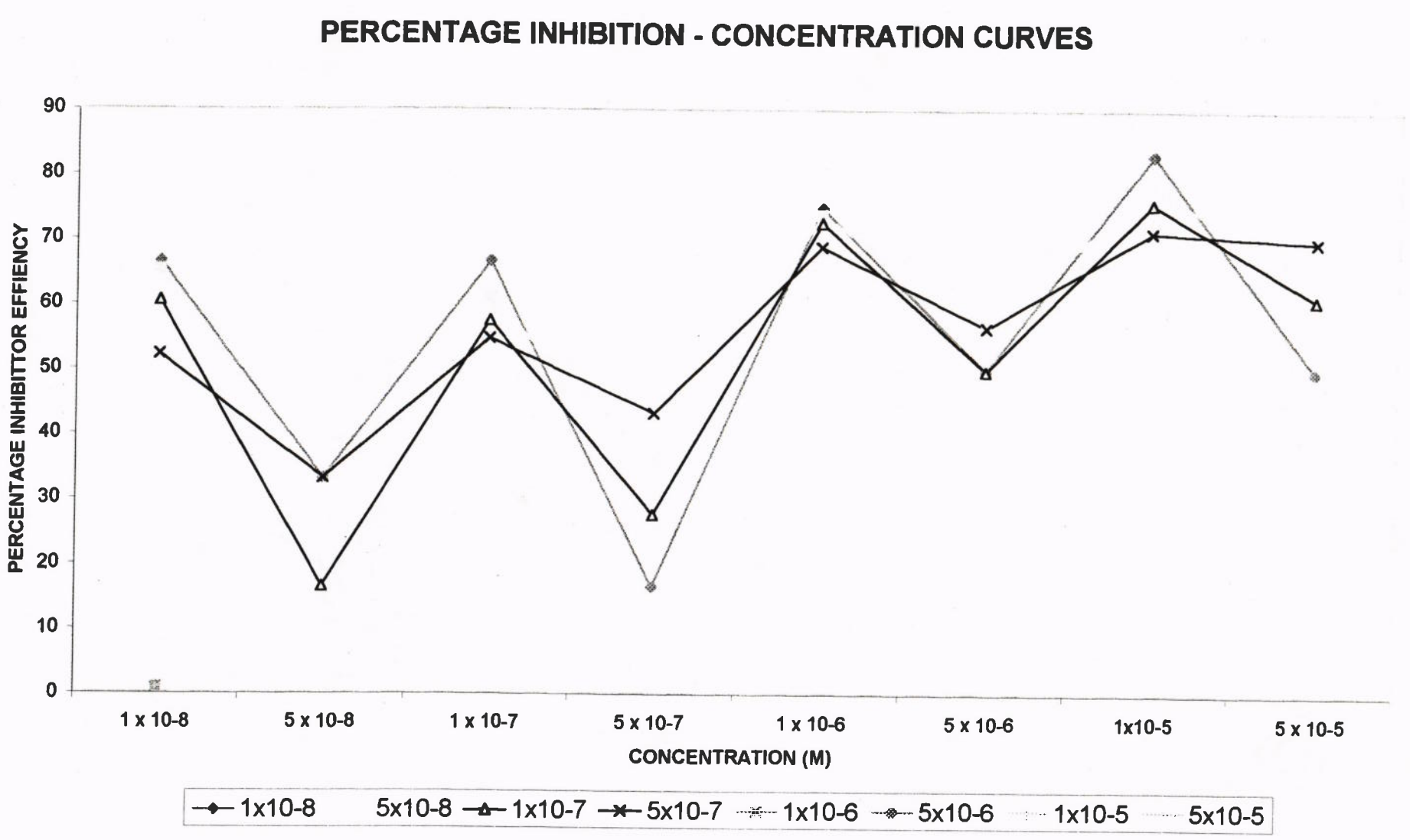

PERCENTAGE INHIBITION - CONCENTRATION CURVES
PERCENTAGE INHIBITTOR EFFIENCY
90
80
70
60
50
40
30
20
10
0
1 x 10-8
5 x 10-8
1 x 10-7
5 x 10-7
1 x 10-6
5 x 10-6
1x10-5
5 x 10-5
CONCENTRATION (M)
1x10-8
5x10-8
1x10-7
5x10-7
1x10-6
5x10-6
1x10-5
5x10-5

FIGURE - 10

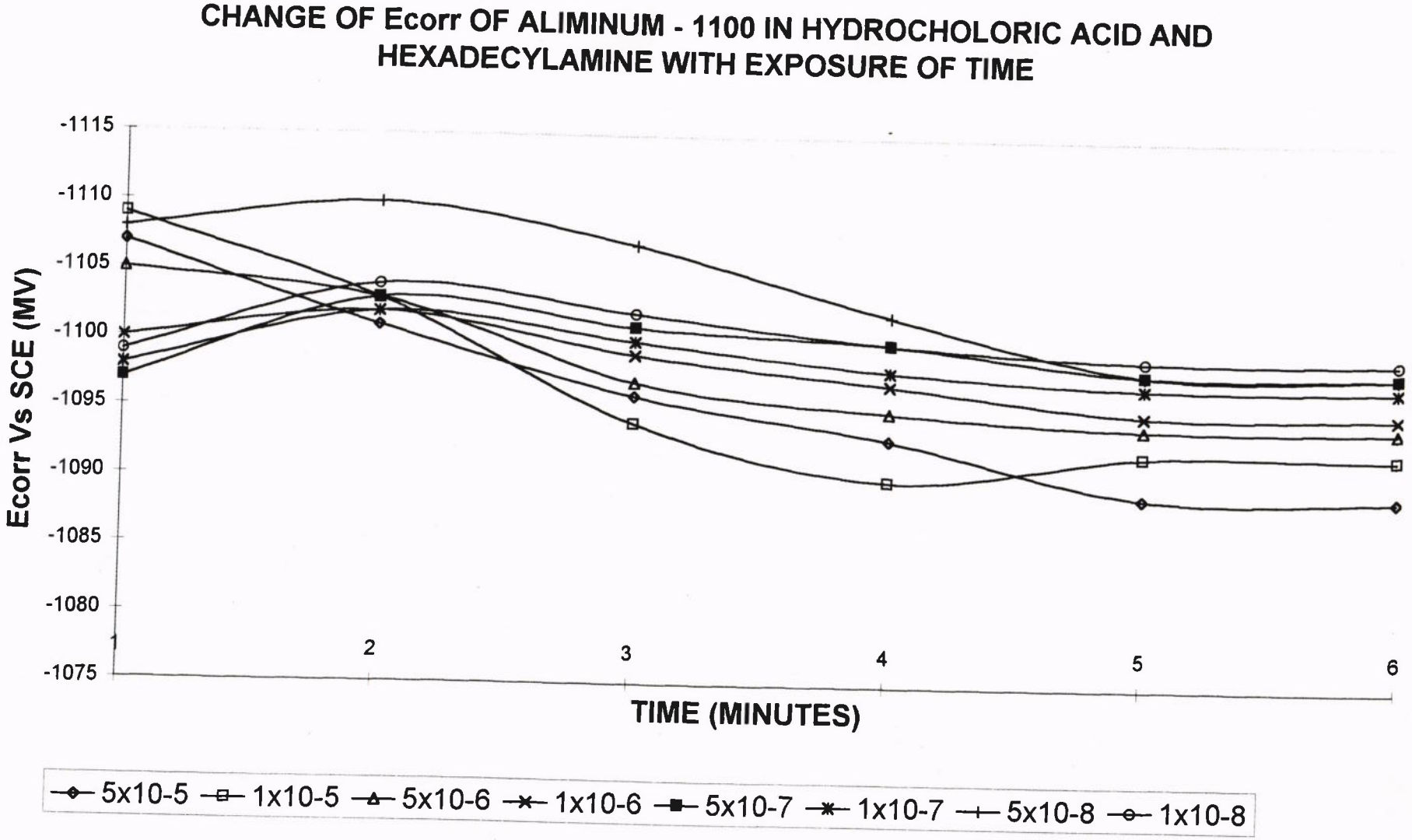

CHANGE OF Ecorr OF ALIMINUM - 1100 IN HYDROCHOLORIC ACID AND HEXADECYLAMINE WITH EXPOSURE OF TIME
Ecorr Vs SCE (MV)
-1115
-1110
-1105
-1100
-1095
-1090
-1085
-1080
-1075
1
2
3
4
5
6
TIME (MINUTES)
5x10-5
1x10-5
5x10-6
1x10-6
5x10-7
1x10-7
5x10-8
1x10-8

FIGURE - 11

4.4 COMPARISON OF INHIBITIVE ACTION OF OCTADECYLAMINE AND HEXADECYLAMINE

Octadecylamine and hexadecylamine proved to have inhibitive action on the acid corrosion of aluminium. Hexadecylamine comparatively showed greater inhibitive action than octadecylamine. This has been proved by the measurement of corrosion rate, inhibitor efficiency, surface coverage and free energy calculations. (Table – XII).

TABLE - XII

CORROSION PARAMETERS OF ALUMINIUM IN INHIBITED (OCTADECYLAMINE AND HEXADECYLAMINE) IN 1.5M HYDROCHLORIC ACID

S.No.	Inhibitors	Concs (M)	Corrosion rate (mpy)	% of inhibitive efficiency	Surface coverage θ	$E_{corr.}$ (mv)	Free energy of adsorption
1	Octadecylamine	10^{-5}	23.66	66.9	0.6137	-1094	-1.9310
		$5x10^{-5}$	18.94	80.2	0.7719	-1094	
2.	Hexadecylamine	10^{-5}	14.19	61.3	0.6690	-1089	-2.2791
		$5x10^{-5}$	10.65	77.2	0.8626	-1092	

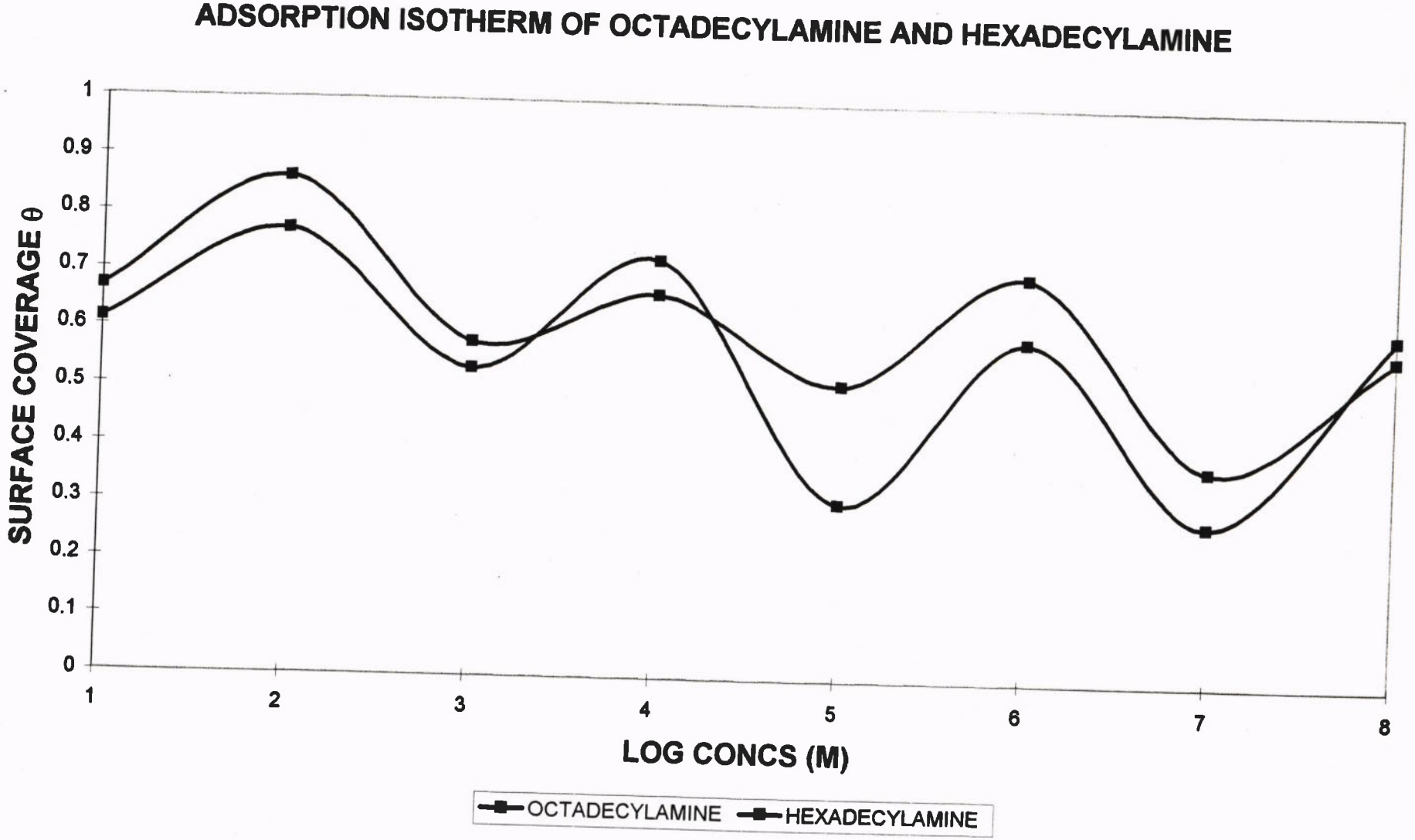

ADSORPTION ISOTHERM OF OCTADECYLAMINE AND HEXADECYLAMINE
SURFACE COVERAGE θ
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
8
LOG CONCS (M)
OCTADECYLAMINE
HEXADECYLAMINE

FIGURE - 12

4.5 EFFECT ON NEUTRALISING ACTION OF AMINES

Amines are weak bases. Hence their inhibitive action may be partly due to the neutralisation of acid. These inhibitors function mainly by adsorption and their neutralising effect has a secondary role in inhibition. (Desai, Thakkar, Chhaya and Gandhi, 1976).

A plot of log C Vs θ was found to be S-shape curve for both the amines. This indicates, they follow Frumkins adsorption isotherm. From the slope of these lines, the free energy of adsorption was calculated. The negative value of free energy proved the phenomenon of adsorption during inhibition. (Fig. 12).

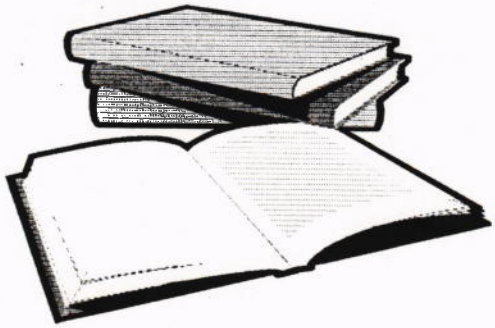
Chapter - V

Summary and Conclusion

SUMMARY AND CONCLUSIONS

The outcome of this study is summarised as follows.

1. The corrosion of aluminium – 1100 increases with increases of acid concentration
2. Octadecylamine and Hexadecylamine were proved to have inhibitive action towards the acid corrosion of aluminium.
3. The corrosion of aluminium under the experimental condition is due to cathodic polarisation.
4. The corrosive action of these two amines is through adsorption mechanism obeying Frumkins adsorption isotherm.
5. Both the amines exhibit maximum inhibitive action at higher concentrations. (5×10^{-5} M and 10^{-5} M)
6. The inhibitive action is maximum during the second hour of corrosion for both the amines.
7. Hexadecylamine amine is found to be better inhibitor than octadecylamine.



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