# EFFECTS OF INHIBITORS ON CORROSION OF LOW CARBON STEEL IN HYDROCHLORIC ACID PICKLING SOLUTION

BY

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## CERTIFICATION

This project report/thesis/dissertation entitled Effects of Inhibitors on corrosion of Low Carbon Steel in Hydrochloric Acid Pickling Solution by Njoku Romanus Egwuonwu meets the regulations governing the award of the degree of Master of Science in Metallurgical Engineering of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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# DEDICATION

To the loving memory of my beloved Emmanuel Nduka Njoku.

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***I LOVE YOU ALL.***

# ABSTRACT

The effects of inhibitors on corrosion of low carbon steel in hydrochloric acid pickling solution was investigated by weight loss and hydrogen evolution measurements using a beaker-funnel-burette arrangement.

Corrosion and hydrogen evolution rates were computed for steel samples immersed in hydrochloric acid pickling solutions with the addition of varying concentrations of organic (formaldehyde, acetaldehyde. and benzaldehyde) and inorganic (sodium dichromate and sodium nitrite) inhibitors.

The organic compounds inhibit both the corrosion and hydrogen evolution rates while the inorganic salts stimulate the corrosion but inhibit hydrogen evolution rate.

Acetaldehyde showed the highest inhibition efficiency. Inhibition by the organic compounds could be attributed to adsorption phenomena while corrosion stimulation by the inorganic salts was due to their inability to form stable passivating film on the steel surface.

## TABLE OF CONTENTS


Title Page . . . . . i

Declaration . . . . . ii

Certification . . . . . iii

Dedication . . . . . iv

Acknowledgements . . . . . iv

Abstract . . . . . v

*Table of Contents* . . . . . vi

List of Tables . . . . . vii

List of Figures . . . . . viii

Notations . . . . . ix

**CHAPTER ONE**

*INTRODUCTION* . . . . . 1

1.0 General Introduction . . . . . 1

**CHAPTER TWO**

LITERATURE REVIEW . . . . . 4

2.1 General Principles of Corrosion Inhibitors . . . . . 10

2.2 Classification of Corrosion Inhibitors . . . . . 12

2.3 Factors affecting Corrosion Inhibition of Plain Carbon Steels in Acid Solutions . . . . . 14

2.4 Corrosion of Steel in Acid Pickling Solutions . . . . . 16

**CHAPTER THREE**

EXPERIMENTAL PROCEDURE . . . . . 18

3.1 Apparatus . . . . . 18

3.2 Materials . . . . . 18

3.2.1 Steel Sample . . . . . 18

3.2.2 Inhibitors . . . . . 20

3.2.3 Acid Solution . . . . . 20

3.3 Sample Preparation . . . . . 21

3.4 Experimental Procedure . . . . . 21

**CHAPTER FOUR**

RESULTS AND DISCUSSION . . . . . 22

4.1 Calculation of Corrosion Parameters . . . . . 29

4.2 Discussion of Experimental Results . . . . . 43

4.2.1 Choice of Experimental Means . . . . . 43

4.2.2 Effects of Aldehydes on the Corrosion of Low Carbon Steels in HCl Solution . . . . . 43

4.2.3 Effects of Sodium Dichromate and Sodium Nitrite on the Corrosion of Low Carbon Steels in HCl Solution . . . . . 46

4.2.4 Effect of Sodium Dichromate Sodium Nitrite on the rate of Hydrogen Evolution of Low Carbon Steels in HCl Solution . . . . . 48

4.2.5 Effect of time on the volume of Hydrogen evolved by Low Carbon Steels in HCl Solution . . . . . 48

4.2.6 Effects of time on Corrosion of Low Carbon Steels in inhibited HCl Pickling Solution . . . . . 49

5.1 **CHAPTER FIVE**

CONCLUSIONS AND RECOMMENDATIONS . . . . . 51

5.2 Conclusions . . . . . 51

Recommendations . . . . . 52

References . . . . . 54

*Appendix* . . . . . 59

# LIST OF TABLES


| TABLE | TITLE | PAGE |
|---|---|---|
| 3.1 | Chemical composition of steel samples | 20 |
| 4.1 | Corrosion behaviour of low carbon steel samples in HCl Pickling solution with the addition of formaldehyde | 23 |
| 4.2 | Hydrogen evolution characteristics of low carbon steel samples in HCl Pickling Solution with the addition of formaldehyde | 23 |
| 4.3 | Corrosion behaviour of low carbon steel samples in HCl Pickling Solution with the addition of acetaldehyde | 24 |
| 4.4 | Hydrogen evolution characteristics of low carbon steel samples in HCl Pickling Solution with the addition of acetaldehyde | 24 |
| 4.5 | Corrosion behaviour of low carbon steel samples in HCl Pickling Solution with the addition of benzaldehyde | 25 |
| 4.6 | Hydrogen evolution characteristics of low carbon steel samples in HCl Pickling Solution with the addition of benzaldehyde | 25 |
| 4.7 | Corrosion behaviour of low carbon steel samples in HCl Pickling Solution with the addition of sodium dichromate | 26 |
| 4.8 | Hydrogen evolution characteristics of low carbon steel samples in HCl Pickling Solution with the addition of sodium dichromate | 26 |
| 4.9 | The Corrosion behaviour of low carbon steel samples in HCl Pickling Solution with the addition of sodium nitrite | 27 |
| 4.10 | Hydrogen evolution characteristics of low carbon steel samples in HCl Pickling Solution with the addition of sodium nitrite | 27 |
| 4.11 | Comparison of the degree of inhibition exhibited by the aldehydes as a function of inhibitor concentration | 28 |
| 4.12 | Comparison of the extent of hydrogen evolution retardation exhibited by the aldehydes as a function of inhibitor concentration | 28 |

## LIST OF FIGURES


2.1 Anodic and Cathodic Current-Potential relationships in a corroding system . . . . 13

2.2 Illustration of inhibition phenomenon:
(top) Cathodic inhibition; (bottom) anodic inhibition . . . . . 13

2.3 Illustration of both Anodic and Cathodic inhibition . . . . . 13

3.1 Experimental set-up . . . . . 19

4.1 Effect of aldehydes concentration on the corrosion rate of low carbon steel samples in HCl Pickling Solution . . . . . 31

4.2 Effect of aldehydes concentration on the hydrogen evolution rate of steel samples in HCl Pickling Solution . . . . . 32

4.3 Effect of sodium dichromate and sodium nitrite on the corrosion rate of steel sample in HCl Pickling Solution . . . . . 33

4.4 Effect of sodium dichromate and sodium nitrite on the hydrogen evolution rates of steel samples in HCl Pickling Solution . . . . . 34

4.5 Comparison of corrosion inhibition efficiency of the aldehydes as a function for inhibitor concentration . . . . . 35

4.6 Comparison of the efficiency of hydrogen evolution retardation exhibited by the aldehydes as a function of inhibitor concentration . . . . . 36

4.7 Plots of volume of hydrogen evolved by low carbon steel samples in HCl Pickling Solution with varying concentrations of formaldehyde . . . . . 37

4.8 Plots of volume of hydrogen evolved by low carbon steel samples in HCl Pickling Solution with varying concentrations of acetaldehyde . . . . . 38

4.9 Plots of volume of hydrogen evolved by low carbon steel samples in HCl Pickling Solution with varying concentrations of benzaldehyde . . . . . 39

4.10 Plots of volume of hydrogen evolved by low carbon steel samples in HCl Pickling Solution with varying concentrations of sodium dichromate . . . . . 40

4.11 Plots of volume of hydrogen evolved by steel samples in HCl Pickling Solution with varying concentrations of sodium nitrite . . . . . 41

# NOTATIONS

| | | |
|---|---|---|
| C | = | Concentration of inhibitor |
| $\theta$ | = | Degree of metal coverage |
| K | = | Equilibrium constant for the adsorption reaction |
| F | = | Parameter connected with the variation of adsorption energy with coverage. |
| $\Delta G^{o}(org)$ | = | Standard free energy of adsorption of organic compound from the solution |
| $\Delta G^{o}_{(W)}$ | = | Standard free energy of water adsorption from the solution. |
| $P^{o}_{(W)}$ | = | Vapour pressure of water at temperature T. |
| P(org) | = | Vapour pressure of pure organic compound at temperature T. |
| $C_s$ | = | Saturation concentration of organic compound. |
| n | = | Number of water molecules. |
| z | = | Number of electrons transferred in the electrochemical reaction. |
| R | = | Universal gas constant. |
| T | = | Absolute temperature ($^{o}$K) |
| t | = | Temperature in ($^{o}$C). |

# CHAPTER ONE

## 1.0 INTRODUCTION:

Metals exhibit a natural tendency of spontaneously reacting with their environments (Corrosion) and this produces a destructive effect on their mechanical and physical properties. Corrosion of metals contributes to economic losses, impairs the safety of operating equipment and invariably depletes our metal reserves - the natural supply of which is limited.

As a result of the problems arising from corrosion, several methods of corrosion control and prevention have been deviced. These include: use of protective coatings, selection of materials, proper design, alloying, cathodic protection and the use of inhibitors. The choice and application of any of the methods are based on their efficiency, economic considerations and the nature of the corrosive environment.

Corrosion inhibitors are most effectively utilized in mitigating corrosion of metals in closed cooling systems (motor vehicle radiator), and in corrosion protection of machines, apparatus and other articles in air medium during transportation and storage. Corrosion inhibitors are also extensively used in petroleum, petrochemical, agro-chemical and chemical processing plants for protecting metal components - operating under corrosive environments.

Inhibitors are also appreciably used during pickling (chemical removal of surface oxides from metal by immersion in an acid solution, Taylor. L, 1964) operations. Steel structures undergoing pickling in acid solutions are spontaneously attacked and rendered



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highly susceptible to hydrogen embrittlement and blistering (Moore, 1981). This results in irreparable loss of the base metal and deterioration of the properties of the steel material. Inhibitors are, therefore, added to acid pickling baths to overcome these shortcomings of chemically removing scales from steel surfaces in bare acid solutions. Moreover, the most recent development in pickling techniques - ultrasonic pickling does not eliminate the use of inhibitors but rather proffers solutions to the problems of environmental pollution and improvement of pickling yield (Goode et al, 1996).

In this work, the corrosion inhibition of low carbon steels in hydrochloric acid pickling solution was investigated using some organic (formaldehyde, acetaldehyde and benzaldehyde) belonging to the aldehydes homologous series and inorganic (sodium dichromat and sodium nitrite) inhibitors. The aldehydes were chosen due to the fact that there has been little or no research work on the aldehydes series even though they are less expensive than the amines, alcohols and thioureas and compare favourably with them as inhibitors. Also the inorganic inhibitors (sodium dichromate and sodium nitrite) were chosen for the purposes of comparison and verification of existing results.

The choice of low carbon steels was due to their unique qualities which include: excellent formability, comparative cheapness and availability. These properties make low carbon steels to be widely used in many engineering applications and their subjection to acidic environments is also a common feature during processing and in some areas of application. Thus it has become imperative to investigate the corrosion behaviour of low carbon steels in acid solution as well as their response to inhibition in such media.

The choice of hydrochloric acid was not unconnected with its predominant use in chemical treatment of steels like pickling and etching. Moreover, hydrochloric acid

specifically offers the following advantages over others in pickling operations: uniform light-grey surface is consistently produced on carbon steels hence uniform and adherent electroplated coatings are subsequently formed; cost of heating the pickling bath is less and rinsing of pickled steel materials is easy due to high solubility of chlorides in water (Taylor Lyman, 1964).

During the experiment, both weight loss and volume of hydrogen evolved by low carbon steel samples were simultaneously measured from an experimental set-up which consisted of a beaker-funnel-burette arrangement. Corrosion and hydrogen evolution rates were respectively computed from these measurements. The results obtained showed that up to 87% corrosion inhibition was possible with the aldehydes and that acetaldehyde produced the highest inhibition efficiency. Also, from the analysis of the experimental results, an optimum inhibitor concentration of 0.20% and pickling time of 30 minutes were recommended.

# CHAPTER TWO

## 2.0 LITERATURE REVIEW:

The use of inhibitors in pickling operations is as old as the art of pickling itself. Originally, animal wastes and flour materials derived from grains were used (Taylor.L, 1964). This was followed by the use of petroleum bye-products and later, by the use of synthetic organic materials. Recently, synergistic combinations of two or more inhibiting substances have been proprietarily formulated to improve inhibitors performances (Burger and Chestnut, 1992).

Edward *et al* (1959) investigated the effects of acetylenic inhibitors in acid pickling solutions and noted that in addition to inhibiting corrosion, the inhibitors were also found to prevent hydrogen embrittlement of steel during pickling.

Cavallaro, Felloni and Trabanelli (1960) studying the corrosion of steel in hydrochloric acid with various thioureas as inhibitors, attributed inhibition to an increase in hydrogen overvoltage. They concluded that the main effect of inhibitors in the corrosion of the samples was on the cathodic reaction, although, an influence on anodic reaction could not be excluded.

Ross and Jones (1962) using radioactive technique to study the effect of thiourea upon action of sulphuric acid on mild steel, reported that inhibition was achieved by adsorption of thiourea over the metal surfaces at all concentrations. They further stated that the adsorption was more on the anodic than cathodic sites.

Hoar and Khera (1960) discussing corrosion of steel in 5% Sulphuric acid, considered inhibition by formaldehyde, pyridine and various amines as mainly anodic.

Liliana and Alberto (1967) investigated Hoar and Khera's work but differed in observations. They observed that the corrosion potential in the presence of formaldehyde becomes more negative and as the concentration of formaldehyde is increased, a low anodic inhibition and an increase in the cathodic inhibition occurs.

Selim *et al* (1977) studied the corrosion kinetics of mild steel in the presence of cyanoguanidine formaldehyde resins and discovered that the presence of the resins decreased both the rate of hydrogen evolution and corrosion rate to the same degree. The activation energy of hydrogen evolution and of the overall corrosion reaction were found to be equal and characteristic of diffusion controlled processes. They suggested that cyanoguanidine formaldehyde resins act as cathodic inhibitors of the acid corrosion of mild steel.

For organic compounds which have inhibitive properties, it is widely believed that their adsorption onto the metal substrate is an initial step to the inhibition process (Szkarska *et al*, 1971 and Selim *et al*, 1977).

Issa *et al* (1973) studying the effect of some carbonyl compounds on the corrosion of aluminium in hydrochloric acid solution, concluded that absorption of carbonyl compounds on the aluminium metal surface takes place through the C=O group and that it depends on their charge density. They concluded that, the adsorption of these compounds occurred in two stages yielding a monolayer of adsorbate on the metal surface, followed by the formation of a second layer on the primary adsorbed monolayer.

Meakins (1963) pointed out that, for simple n-alkyl amines, the inhibition increases with the chain-length up to five carbon atoms, above which solubility in aqueous liquid becomes too low to produce inhibition directly; however, inhibitors with longer chains can be applied by immersion in benzene solution before addition to acid.

Szkarska *et al* (1971) investigated the adsorption isotherm on mild steel in sulphuric acid solutions for primary aliphatic amines, alcohols and acids containing 6 to 12 carbon atoms and observed that these compounds were adsorbed on the steel surface according to the Frumklin's adsorption isotherm:

$$\frac{\theta}{1-\theta} \exp(f\theta) = KC \qquad (2.1)$$

where K is equilibrium constant of the adsorption reaction and f is a parameter connected with the variation of absorption with coverage.

The degree of coverage of the steel surface by the adsorbed molecules was found to be influenced by the following factors:

(i) Solubility of the given compound,

(ii) Presence of functional groups, and

(iii) Interaction between adsorbed molecules.

They further reported that, within a given homologous series, the contribution of the functional group to adsorption decreases with length of chain of aliphatic compounds, and conversely, the contribution of the interaction between adsorbed molecules increases with their length.

According to Bockris and Swinkels (1964), for an organic compound to be adsorbed on the metal surface from an aqueous solution, each organic molecule has to displace n molecules of water. They derived an equation for the standard free energy of the

thermodynamic cycle for adsorption and desorption of water and organic compounds as follows:

$$\Delta G_a = \Delta G_v(org) - n\Delta G^o_{(w)} - RT \ln \frac{P(org)}{P_w^n} + RT \ln \frac{C_s}{55.5} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

where n is the number of water molecules. The first two terms depend on the interaction energy of the organic compound and water with the metal surface; the third and fourth terms characterize the properties of the substance under consideration.

Todd and Butze (1964) discussing the mechanism of corrosion inhibition of steel by acetylenic alcohols in acid solutions, disclosed that adsorbates of acetylenic alcohols on steel surfaces successively undergo two stages of reactions: reduction and dehydration in the acid solutions. The reduction of these compounds produces a "diene" which are ineffective corrosion inhibitors by comparison to the acetylenic compounds. However, subsequent formation of a hydrocarbon to produce a hydrophobic surface contributes to the effectiveness of these compounds as corrosion inhibitors. They concluded that the effectiveness of these compounds as corrosion inhibitors depends on the chemical and physical properties of the reaction products as well as their rate of formation.

Antropov (1967) in a research work based on the correlation between kinetics of corrosion and mechanism of inhibition by organic compounds emphasized that adsorption is an inevitable part of the process of inhibition. He stated that the inhibition efficiency of a chemically stable surface-active compound is related primarily on its ability to adsorb on the metal-solution interface and that for a given solution, the absorbability of an inhibitor depends firstly on the charge of the metal under the specific corrosion condition. Consequently, cationic inhibitors will readily adsorb on corroding metal surfaces which have negative charges but not on surfaces with positive charges. He

concluded that any deviation from the simple dependence of inhibition on absorbability of inhibitors on metal surface indicates that in addition to adsorption, some other process(es) such as reduction, protonation and polymerization are occurring at the metal-solution interface and the ultimate inhibitor efficiency depends on the properties of the products of these secondary processes.

Gouda *et al* (1972) studied the role of anions in the corrosion and corrosion inhibition of zinc in aqueous solutions and made a distinction between corrosive and inhibitive anions. They observed that $SO_4^{2-}$, $Cl^-$, $I^-$, $ClO_4^-$ and $NO_3^-$ stimulated the corrosion of zink in aqueous solutions and the extent of corrosion stimulation increases with salt concentration while $NO_2^-$, $CrO^{2-}_4$, $H_2PO^-_4$ and $H_2PO^{2-}_4$ acted bifunctionally, promoting corrosion at high dilutions and stifling it at higher concentrations. They classified $Cl^-$, $Br^-$ $I^-$, $ClO^-_3$ and $NO^-_3$ as corrosive anions and $NO^-_2$, $CrO^{2-}_4$,$H_2PO^-_4$ and $H_2PO^{2-}_4$ as inhibitive anions.

Kruger (1963) investigating the inhibitive properties of sodium nitrite, adopted an ellipsometric technique. He exposed an iron to a sodium nitrite solution and observed the alteration of a certain optical property. He concluded that a solid film is formed by the nitrite.

Okamoto (1956) after studying the inhibitive mechanism by chromates, indicated that inhibition by chromates is attributed to a solid film rather than adsorption.
Mclareen *et al* (1951) researching on a radiotracer study of the passivation of zinc in chromate solution noted that chromates act as corrosion inhibitors for metals in aqueous solutions. In discussing their results, they stated that chromate ions have pronounced

surface-active properties and believed that this propensity is responsible for their inhibiting capability, the subsequent formation of oxide layer being merely incidental.

Rosenfeld (1981) presented a theoretical discussion and the use of quantum chemistry calculations, x-ray photoelectron spectroscopy, radioactive tracer and chemical polarization as a tool for studying inhibition mechanism by $CrO_4^{2-}$ and $NO_3^-$. He showed that protection is largely dependent on the adsorption displacement of activators (of corrosion) from the surface by the passivating ions and lesser on the oxidizing power of the anion. He concluded that inhibitor mechanism irrespective of the amount adsorbed by the surface, consists in changing the electrophysical properties of surface atoms by the donor-acceptor inhibitor/metal reaction, rather than in screening the metal surface from the corrosive environment.

Burger and Chestnut (1992) in their research work on screening corrosion inhibitors used in acids for downhole scale removal concluded that the effectiveness of acid corrosion inhibitors is a function of acid type and metallurgy of the metal and that low alloy steels are easier to protect than higher alloys. The inhibitors were proprietary mixtures of heterocyclic quaternary amine salts plus alcohols while the acid was composed of a blend of hydrochloric and hydrofluoric acids.

In summary, adsorption has been identified as a fundamental phenomenon in the inhibition mechanism of metals in aqueous solutions by organic compounds which have inhibitive properties but whether it occurs spontaneously on the entire metal surface or at specific sites is discordant. However, little research work has so far been carried out on the corrosion inhibitive properties of the aldehydes homologous series and Chromates and nitrites have been shown to have excellent inhibition efficiencies in neutral solutions, thus their effectiveness in acid pickling solution was investigated.

This research effort attempts to specifically study the corrosion inhibition propensities of the aldehydes, chromate and nitrite in acid pickling operation with the view of making invaluable inputs to the field of corrosion and corrosion inhibition of metals.

## 2.1 General Principle of Corrosion Inhibition

Marcel Pourbaix (1973), defined a corrosion inhibitor as a substance which when added in small quantities to a corroding medium brings about an appreciable reduction in its corrosive action.

Corrosion inhibition is generally described as the interference of a substance foreign to a medium with the corrosion reaction or reactions, and it is visualized that such interference takes place through the following processes (Hausler, 1979 and Cohen, 1979):

(i) Adsorption of the inhibitor on the metal surface,

(ii) Poisoning of metal surface for hydrogen evolution and/or oxygen reduction.

(iii) Increasing electronic resistance, and

(iv) Interfering with the anodic dissolution process by assisting in the formation and preservation of oxide film.

The oxidative conversion of a metal to its metal ion in aqueous solutions is electrochemical in nature. This implies the existence of simultaneous anodic and cathodic currents of equal magnitude across the interface of the metal. The verification of the electrochemical nature of the corrosion process leads to the realization of four distinct and separate basic processes involved in corrosion. These are:

(i) The anodic or oxidation process,

(ii) The cathodic or reduction process,

(iii) The electronic charge transfer process in both directions across the interface,

(iv) The ionic charge transfer process which is required to maintain charge neutrality on the electrolyte side due to the formation of ionic charges in the anodic process and the disappearance of ionic charge in the cathodic process.

One of these four processes is usually the slowest and hence the rate determining for the overall process. Corrosion inhibition takes advantage of the complexity of these reactions by attempting to interfere with any of them individually or collectively. According to Hausler (1979), while it is generally known that corrosion inhibitors may affect the anodic or the cathodic reaction, it is less well known that inhibitive action may affect either the electrolytic or the electronic conduction process.

The partial reactions of the corrosion process are represented as follows:

$M = M^{z+} + ze$.....2.3 (anodic or oxidation reaction)

$M^{z+} + ze = M$.....2.4 (cathodic or reduction reaction)

These partial reactions proceed with equal reaction rates when the metal is freely corroding. The behaviour of each of the partial reactions is shown in figure 2.1 (Potential vs log Current Density Curves). The point of intersection of the two curves defines the potential at which the anodic and cathodic reaction rates are equal.

Inhibitors generally cause a shift of the point of intersection of the anodic and cathodic polarization curves to the left, thereby, causing a reduction in the overall rate of corrosion. Inhibitors do not affect both the anodic and cathodic reactions to the same degree. Cathodic reaction rate may be reduced while the anodic reaction rate remains the same or vice versa. Cathodic inhibition results in a shift of corrosion potential in the anodic or negative direction while anodic inhibition results in a potential shift in the cathodic or more positive direction with a corresponding reduction in the overall corrosion rate (figures 2.2) Ec and Ea are the equilibrium electrode potentials for the

cathodic and anodic reactions respectively. Some systems exhibit a combination of anodic and cathodic inhibition in varying degrees. Consequently, if both anodic and cathodic reaction rates are reduced to the same extent as shown in figure 2.3, no shift in the corrosion potential is observed and the inhibitive effect is the largest possible.

## 2.2. Classification of Corrosion Inhibitors

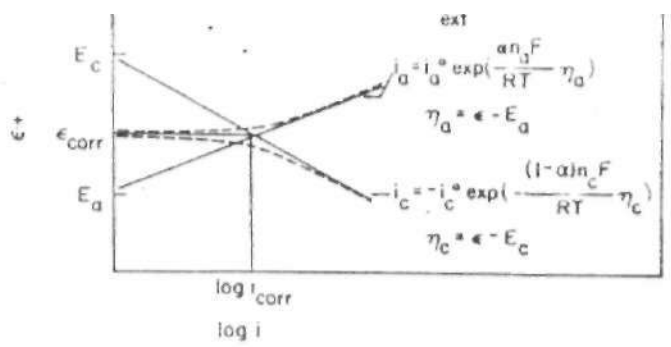
Several substances which have been observed to have corrosion inhibitive properties have often been classified in various ways.

Evans (1960), Brockris and Drazk (1972) simply classified corrosion inhibitors into two: Anodic and Cathodic Inhibitors depending on whether their action cause a decrease of the anodic reaction (oxidation-generally termed the corrosion reaction) or of the cathodic reaction (reduction-hydrogen evolution or oxygen reduction reaction).

A more complex classification was advanced by Fisher (1971) based on the specific mechanism by which they achieve inhibition: Interface-Inhibition and Electrolyte-layer- and Electrolyte-layer-inhibition. According to him, interface inhibition results from substances which are adsorbed at the metal surface and decrease the rates of physical, chemical or electrochemical processes in the corrosion mechanism while electrolyte-layer-inhibition arises if an inhibitor interferes with processes which are not on the metal surface but in its vicinity such as the electrolyte layer closest to the metal surface.

Antropov (1972) and Uhlig (1963) classified corrosion inhibitors as liquid-and vapour-phase (Volatile), depending on their states of use. According to Antropov, the inhibitors most often used for neutral solutions are inorganic compounds of the anionic type and that corrosion inhibitors for acid solutions are almost exclusively organic substances in the form of amino, imino, carboxyl, carbonyl and thio groups.

Pourbaix (1973), West (1980), and Fontana (1987), identified the following general classification of inhibitors: adsorption-type, oxidizers, hydrogen evolution poison and scavengers.




$$i_{ext} = \Sigma i_a, i_c$$

$$i_{ext} = i_{corr}\left[\exp(\frac{\alpha n_a F}{RT}\eta_{corr}) - \exp(\frac{-(1-\alpha)n_c F}{RT}\eta_{corr})\right]$$

*Figure 2-1 Anodic and cathodic current–potential relationships in a corroding system*

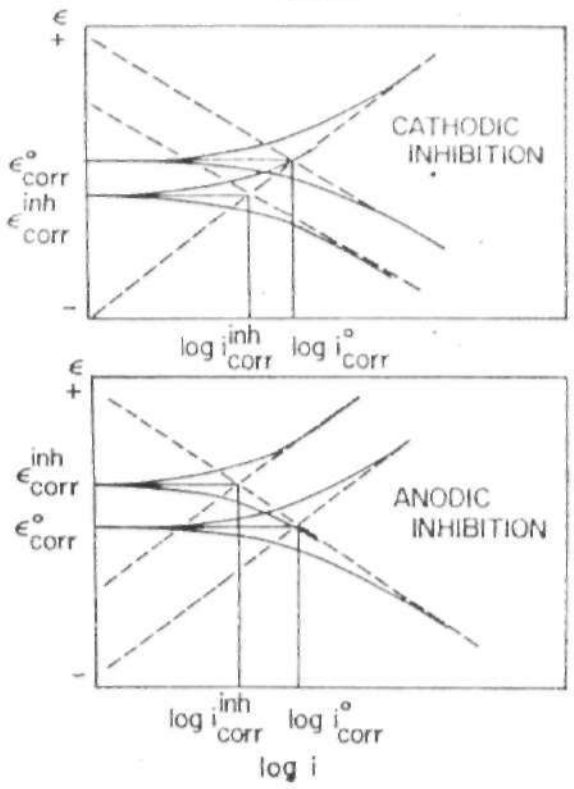



*Figure 2-2 Inhibition: (top) cathodic inhibition; (bottom) anodic inhibition*

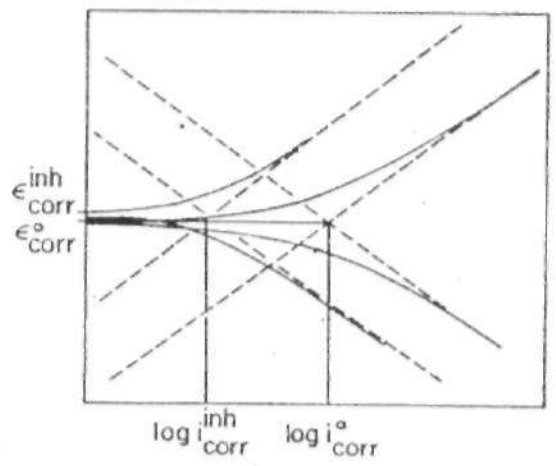



*Figure 2-3 Inhibition, both anodic and cathodic*

## 2.3. Factors Affecting Corrosion Inhibition of Low Carbon Steels in Acid Solutions

### 2.3.1. Composition of Steel

Abdul and Sanad (1972) investigated the Corrosion and corrosion inhibition of carbon steel and cast iron in acid solutions and reported that inhibitor efficiency increases as the carbon content of steel was increased. They observed that the inhibitor (quinoline ethiodide) efficiency was highest at carbon content $\geq 0.97\%$. Discussing the observed phenomenon, they suggested that the attachment of the discharged inhibitor molecule on ferrite or pearlite phase was less tenacious than on a separate phase of cementite or graphite.

### 2.3.2. Concentration and Inhibitor Type

Vosta and Eliasek (1971) in their study of corrosion inhibition from aspect of quantum chemistry, noted that the physio-chemical properties of corrosion inhibitors such as molecular weight, basicity, solubility, electron density, dipole moment, electronic structure, ion size and charge play important roles in the determination and selection of inhibitors. Discussing their results, they stated that inhibitor efficiency depends mostly upon the energy of highest occupied molecular orbital (HOMO); $K_1$, which is a theoretical analogue to the ionization potential of the substance, and the energy of the lowest free molecular orbital (LFMO); K(-1), which illustrates the electron affinity of the molecule. They showed that inhibition efficiency increases with the energy of HOMO orbital and that inhibitor molecules act as electron donors when blocking corrosion reactions. This view of corrosion inhibitors acting as electron donors was upheld by Desai *et al* (1971), and Issa *et al* (1973).

Ammar and Riad (1969), and Gouda *et al* (1972), showed that oxidizers play a bifunctional role in the corrosion of metals in aqueous solutions - intensifying the attack on metals at very low concentrations and inducing passivation at higher ones.

Maitra and Barua (1974), Sampat and Vora (1974) and Talati and Modi (1979) reported that at constant acid concentration, inhibition efficiency (of organic inhibitors) increases with increased concentration of inhibitor but reaches a maximum at a certain inhibitor concentration beyond which it remains practically constant.

### 2.3.3. Concentration and Type of Acid

Gouda, Khedr and Shams (1967) arranged some inorganic acids according to increasing order of aggressiveness: $HClO_4 < H_2SO_4 < HCl < HNO_3$. Gouda and Shatter (1970), and Selim and Ateya (1977), reported that percentage inhibition and degree of coverage were found to be higher in HCl than $H_2SO_4$ for comparable inhibitor concentration. This was attributed to the adsorption of chloride ions on the metal surface, thus forming oriented dipoles which enhance the adsorption of inhibitors.

Talati and Pandya (1976) showed that at constant inhibitor concentration, its efficiency decreases with increase in acid concentration.

### 2.3.4. Temperature

The effect of temperature on the corrosion of metal in pure HCl solution and for solution containing $Cr_2O_7^{2-}$ was studied by Ammar and Riad (1969). They observed that the corrosion rate of the metal increases with temperature both in the presence and absence of the dichromate. The results followed a linear relationship:

$$P = a + bt\ (^{o}C) \quad \text{.....(2.5)}$$

where P is the corrosion rate of metal, a and b are constants which depends on the concentrations of acid and dichromate and t is temperature. For a wider range of temperature, corrosion rate increases with temperature in a non-linear pattern as was suggested by Radovici (1965):

$$\log P = a' + b' t\ (^{\circ}C) \quad \ldots\ldots(2.6).$$

However, for organic compounds which show inhibitive properties, the effect of temperature varies according to inhibitors. Hoar and Holliday (1953) noticed that while some organic compounds are better inhibitors at elevated temperatures presumably due to increase in adsorption at higher temperatures, others are more efficient at room temperature.

### 2.3.5. Interaction Between Inhibitor and Metal in Acid Solution

Several organic compounds that show inhibitive properties undergo one or a combination of these processes at the metal-solution interface: hydrogenation or reduction, protonation and polymerization (Antropov, 1967). The overall inhibition efficiency of these compounds depends on the electro-physical properties of the products of these reactions and the rate at which they are formed (Todd and Butze, 1964).

## 2.4. Corrosion of Steel in Acid Solutions

Metals undergoing acid pickling operations are irreparably lost due to the aggressive and corrosive actions of the solution on the base metal. Uhlig (1963) reported that the corrosion rate of steel at 20°C in uninhibited 2.ON HCl is 240 mdd. HCl is one of the most active acids and reacts with many metals to form chlorides which are soluble except for the chlorides of silver, mercury, copper and lead. According to Larrabee and Mathay (1960), acid solutions are mildly - to - strongly corrosive to ferrous metals because:

(i) The high hydrogen - ion - concentration of acid solutions promote hydrogen evolution.

(ii) The invisible oxide layer normally present on iron is rapidly destroyed by acids.

The corrosion of iron in pickling solution occurs by an electrochemical process in which the overall reaction may be divided into two partial and separate electrode reactions:

(i) The anodic or oxidation reaction:

$$Fe = Fe^{2+} + 2e \text{ and}$$

(ii) The cathodic or reduction reactions;

$$2H^{+} + 2e = H_2$$

Certain metallic phases are more favourably oriented for the occurrence of either of these reactions. Azim and Anad (1972) and Staicopolus (1963) reported that the discharge of hydrogen ions ($H^{+}$) takes place more readily on cementite than on ferrite phases because cementite enhances corrosion by acting as cathodic sites.

During the corrosion of iron in acid solutions, iron dissolution reaction proceeds to the right with the discharge of two electrons (iron corrodes) correspondingly, the hydrogen evolution reaction proceeds to the left with the acceptance of the electrons. The corrosion rate for iron in acid solution is defined (in the absence of external currents) by the condition that the total oxidation current ($Fe = Fe^{2+} + 2e$) and the total reduction current ($2H^{+} = H_2 + 2e$) are equal and corresponds to the overall reaction.

$$Fe + 2H = Fe^{2+} + H_2.$$

The electrode potential corresponding to this condition of zero net current is called the corrosion potential.

# CHAPTER THREE

## 3.0. EXPERIMENTAL PROCEDURE

### 3.1 Apparatus

The experimental apparatus consist of beaker, containing the pickling solution and into which, the steel samples were immersed, a funnel which forms an enclosure over the samples and channels the evolved hydrogen bubbles unto the burette. The burette protects the corroding steel samples from atmospheric interferences and volume of hydrogen evolved are noted from its calibrations, and a retort stand for firmly holding the burette in upright position.

Other ancillary equipment include an analytical mass balance for weight measurements, a grinding desk for preliminary preparation of the samples and a desiccator for protecting the prepared samples from interacting with the environment prior to analysis. The experimental set-up is shown in figure 3.1

### 3.2. Materials

#### 3.2.1. Steel Sample

For the purpose of this investigation, as-received steel rod rolled at Ajaokuta Steel Company of composition shown in Table 3.1 was used.

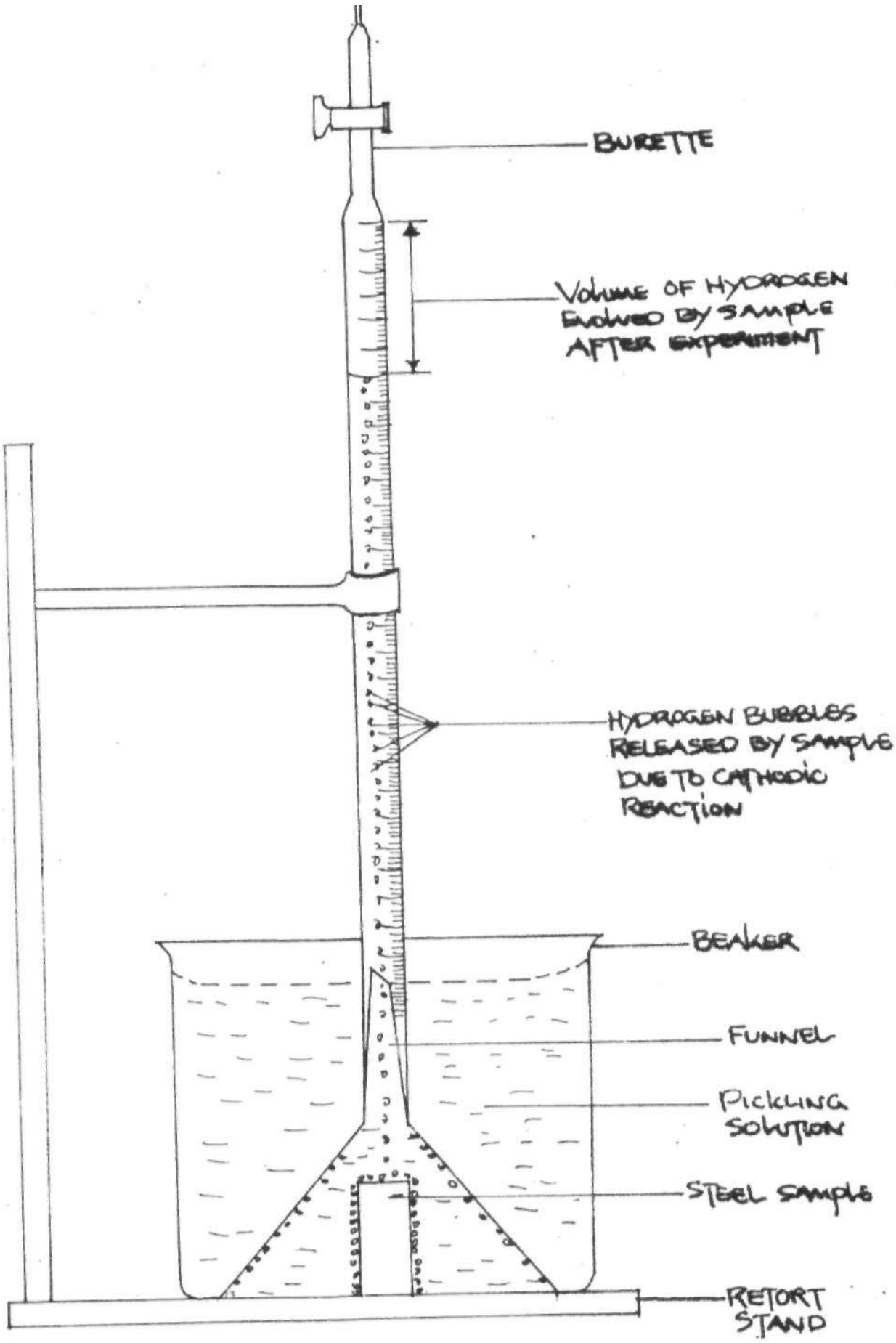



FIGURE 3.1: EXPERIMENTAL SET-UP.

Table 3.1 CHEMICAL COMPOSITION OF THE STEEL SAMPLE USED IN THE CORROSION TEST

| ELEMENT | C | Si | Mn | P | S |
|---|---|---|---|---|---|
| % COMPOSITION | 0.19 | 0.35 | 0.70 | 0.03 | 0.04 |

### 3.2.2 Inhibitors

The inhibitors used include three organic compounds belonging to the aldehydes homologous series (Uhlig, 1963 and Antropov, 1972).

1. Formaldehyde (HCHO) $H-\overset{H}{C}=O$

2. Acetaldehyde ($CH_3CHO$) $CH_3-\overset{H}{C}=O$

3. Benzaldehyde ($C_6H_5CHO$) $-\overset{H}{C}=O$

and two inorganic compounds:

4. Sodium dichromate ($Na_2Cr_2O_7$)

5. Sodium nitrite ($NaNO_2$)

### 3.2.3 Acid Solution

The acid solution was composed of 20% HCl, varying concentrations of the inhibitors - (0.05 to 0.5%) for the aldehydes, 0.05 to 2.0% of 0.80M solution for the sodium nitrite and sodium dichromate and the balance was distilled water. 20% HCl was used because the tests were carried out at room temperature, and because of the small surface areas of the test coupons, the amount of reacted materials was very little and accurate measurements of weight losses and volume of hydrogen evolved were difficult at lower concentrations. However, 20% HCl concentration still falls within the range of normal acid concentrations for pickling operations.

## 3.3 SAMPLE PREPARATION

The steel sample was in the form of rod. It was cut into specimen sizes of (Ø11.0 x 19.0mm $\pm$ 1.0mm) and abraded in sequence on silicon carbide paper of the following grit size: 240, 320, 400 and 600. The specimens were washed with running water and dried with a clean cotton towel. They were then degreased by immersion in benzene bath, dried, weighed on an analytical balance and stored in a desiccator.

## 3.4 Experimental Procedure

A pickling solution was prepared by diluting concentrated HCl with distilled water to 20% concentration (by volume) in a beaker and 400cm$^3$ acid solution was used. An initially weighed sample was immersed in the solution together with a funnel to form an enclosure over the specimen. A burette lubricated with petroleum jelly was pushed over the funnel and firmly held in an upright position by means of a retort stand. Consequently, the solution was sucked up to the 50cm$^3$ mark on the burette (50cm$^3$ was used as a datum mark for all the experiments) and the burette was locked to prevent the interference of the atmospheric pressure on volume of hydrogen evolved as indicated on the burette. The experiment was run for 5 hours to allow a measurable amount of the specimens to react in the HCl pickling solution. Finally, the volume of hydrogen evolved was recorded and the steel sample removed from the solution, washed with water, dried and re-weighed.

The experiment was repeated with the addition of formaldehyde, acetaldehyde, benzaldehyde, sodium dichromate and sodium nitrite in concentrations ranging from 0.05 to 0.5% (by volume of acid solution) and 0.05 to 2.0% for the aldehydes and inorganic compounds respectively.

Finally the experiment was conducted by varying the concentration of acetaldehyde from 0.05 to 0.5% and for each of the concentrations, the experiment was run for 30 minutes, 1 hour, 2 hours, 3 hours, 4 hours and 5 hours. In all cases the tests were duplicated to ensure the consistency of the data.

# CHAPTER FOUR

## 4.0 RESULTS AND DISCUSSION

### 4.1. Results

In this chapter, the experimental results of weight loss and hydrogen evolution measurements are presented in tabular form. Moreover, the effects of the inhibitors on the corrosion and hydrogen evolution rates of the low carbon steel samples in hydrochloric acid solution are shown graphically. Also, curves of inhibition efficiency versus inhibitor concentration are presented.

Thus, tables 4.1 to 4.10 present in an alternating system the corrosion behaviour and hydrogen evolution characteristics of the low carbon steel coupons immersed in HCl solution with the addition of some corrosion inhibitors, while in tables 4.11 and 4.12, the efficiencies of the aldehydes in stifling the anodic and cathodic reactions are presented.

TABLE 4.1: Corrosion Behaviour of Low Carbon Steel Samples in HCl Pickling Solution with the addition of Varying Concentrations of Formaldehyde

| S/N. | SAMPLE SIZE (mm) | SAMPLE SURFACE AREA X $10^{-4}$ ($m^2$) | INHIBITOR CONC. (%) | INITIAL WEIGHT (g) | FINAL WEIGHT (g) | WEIGHT LOSS (g) | WEIGHT LOSS/UNIT AREA ($g/m^2$) | CORROSION RATE ($g/m^2$/min) |
|---|---|---|---|---|---|---|---|---|
| 1. | Ø11.7 x 19.6 | 9.35 | - | 16.2685 | 16.2410 | 0.0275 | 29.4118 | 0.0980 |
| 2. | Ø11.6 x 19.7 | 9.22 | 0.05 | 16.0582 | 16.0417 | 0.0165 | 17.8959 | 0.0680 |
| 3. | Ø11.6 x 19.4 | 9.18 | 0.10 | 15.8565 | 15.8485 | 0.0090 | 9.8039 | 0.0327 |
| 4. | Ø11.7 x 19.4 | 9.28 | 0.15 | 16.2043 | 16.1968 | 0.0075 | 8.0819 | 0.0269 |
| 5. | Ø11.6 x 19.7 | 9.29 | 0.20 | 16.2185 | 16.2120 | 0.0065 | 6.9968 | 0.0233 |
| 6. | Ø11.6 x 19.2 | 9.11 | 0.25 | 15.7820 | 15.7760 | 0.0060 | 6.5862 | 0.0220 |
| 7. | Ø11.7 x 19.4 | 9.28 | 0.30 | 16.2040 | 16.1987 | 0.0053 | 5.7112 | 0.0190 |
| 8. | Ø11.8 x 19.2 | 9.30 | 0.40 | 16.2375 | 16.2330 | 0.0045 | 4.8387 | 0.0161 |
| 9. | Ø11.6 x 19.2 | 9.11 | 0.50 | 15.7460 | 15.7420 | 0.0040 | 4.3908 | 0.0146 |

TABLE 4.2: Hydrogen Evolution Characteristics of Low Carbon Steel Samples in HCl Solution with the Addition of Varying Concentrations of Formaldehyde

| S/N | $V_{60}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | $V_{120}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | $V_{180}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | $V_{240}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | $V_{300}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | RATE OF $H_2$ EVOLUTION ($cm^3$/min) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | 1.60 | 1711.23 | 3.80 | 4064.17 | 6.10 | 6524.06 | 8.80 | 9411.76 | 1.20 | 12834.23 | 42.78 |
| 2. | 1.20 | 1301.52 | 2.40 | 2603.04 | 3.60 | 3904.56 | 4.90 | 5314.53 | 6.40 | 6941.43 | 23.14 |
| 3. | 0.60 | 653.59 | 1.30 | 1416.12 | 1.80 | 1960.78 | 2.50 | 2723.31 | 3.20 | 3485.84 | 11.62 |
| 4. | 0.50 | 538.79 | 0.00 | 1077.59 | 1.40 | 1400.86 | 1.60 | 1724.14 | 1.90 | 2047.41 | 6.82 |
| 5. | 0.30 | 322.93 | 0.70 | 753.50 | 1.00 | 1076.43 | 1.30 | 1399.35 | 1.60 | 1722.28 | 5.74 |
| 6. | 0.30 | 329.31 | 0.70 | 768.39 | 0.90 | 987.93 | 1.20 | 1317.23 | 1.50 | 1646.54 | 5.49 |
| 7. | 0.30 | 323.28 | 0.60 | 646.55 | 0.80 | 862.07 | 1.00 | 1077.59 | 1.20 | 1400.86 | 4.67 |
| 8. | 0.20 | 215.05 | 0.40 | 430.11 | 0.60 | 645.16 | 0.80 | 860.22 | 1.00 | 1075.23 | 3.58 |
| 9. | 0.20 | 219.54 | 0.40 | 439.08 | 0.60 | 658.62 | 0.80 | 878.16 | 0.90 | 987.93 | 3.29 |

TABLE 4.3: Corrosion Behaviour of Low Carbon Steel Samples in HCl Solution with the Addition of Varying Concentrations of Acetaldehyde

| S/N | SAMPLE SIZE (mm) | SAMPLE SURFACE AREA X $10^{-4}$ ($m^2$) | INHIBITOR CONC. % | INITIAL WEIGHT (g) | FINAL WEIGHT (g) | WEIGHT LOSS (g) | WEIGHT LOSS/UNIT AREA ($g/m^2$) | CORROSION RATE $g/m^2/min$ |
|---|---|---|---|---|---|---|---|---|
| 10. | Ø11.6 x 19.8 | 9.33 | 0.05 | 16.2515 | 16.2415 | 0.0100 | 10.7181 | 0.0340 |
| 11. | Ø11.7 x 19.6 | 9.34 | 0.10 | 16.3012 | 16.2932 | 0.0080 | 8.5653 | 0.0286 |
| 12. | Ø11.5 x 19.6 | 9.16 | 0.15 | 16.0400 | 16.0328 | 0.0072 | 7.8603 | 0.0262 |
| 13. | Ø11.6 x 19.5 | 9.22 | 0.20 | 16.0581 | 16.0521 | 0.0060 | 6.5076 | 0.0217 |
| 14. | Ø11.6 x 19.7 | 9.29 | 0.25 | 16.2182 | 16.2125 | 0.0057 | 6.1356 | 0.0205 |
| 15. | Ø11.7 x 19.5 | 9.32 | 0.30 | 16.2490 | 16.2437 | 0.0053 | 5.6867 | 0.0190 |
| 16. | Ø11.5 x 20.1 | 9.34 | 0.40 | 16.2525 | 16.2485 | 0.0040 | 4.2827 | 0.0143 |
| 17. | Ø11.6 x 20.2 | 9.48 | 0.50 | 16.6910 | 16.6875 | 0.0035 | 3.6920 | 0.0123 |

TABLE 4.4: Hydrogen Evolution Characteristics of Low Carbon Steel Samples in HCl Pickling Solution with the Addition of Varying concentrations of Acetaldehyde

| S/N. | $V_{60}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | $V_{120}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | $V_{180}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | $V_{240}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | $V_{300}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | RATE OF $H_2$ EVOLUTION ($cm^3/min$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10. | 0.70 | 750.27 | 1.40 | 1500.54 | 2.10 | 2250.80 | 2.70 | 2893.89 | 3.10 | 3322.62 | 11.08 |
| 11. | 0.60 | 642.40 | 1.00 | 1070.66 | 1.30 | 1391.86 | 1.70 | 1820.13 | 2.10 | 2248.39 | 7.49 |
| 12. | 0.50 | 545.85 | 1.00 | 1091.70 | 1.20 | 1310.04 | 1.50 | 1637.55 | 1.90 | 2074.24 | 6.91 |
| 13. | 0.40 | 433.84 | 0.60 | 650.76 | 1.00 | 1084.60 | 1.30 | 1409.98 | 1.60 | 1735.36 | 5.78 |
| 14. | 0.30 | 322.93 | 0.60 | 645.86 | 1.00 | 1076.43 | 1.30 | 1399.35 | 1.50 | 1614.64 | 5.38 |
| 15. | 0.30 | 321.89 | 0.50 | 536.48 | 0.80 | 858.36 | 1.10 | 1180.26 | 1.20 | 1287.55 | 4.29 |
| 16. | 0.20 | 214.13 | 0.30 | 321.20 | 0.50 | 535.33 | 0.70 | 749.46 | 0.90 | 963.60 | 3.21 |
| 17. | 0.20 | 210.97 | 0.30 | 316.46 | 0.50 | 527.43 | 0.70 | 738.40 | 0.90 | 949.40 | 3.16 |

TABLE 4.5: Corrosion Behaviour of Low Carbon Steel Samples in HCl Solution with the Addition of Varying Concentrations of Benzaldehyde

| S/N. | SAMPLE SIZE (mm) | SAMPLE SURFACE AREA X $10^{-4}$ ($m^2$) | INHIBITOR CONC. % | INITIAL WEIGHT (g) | FINAL WEIGHT (g) | WEIGHT LOSS (g) | WEIGHT LOSS/UNIT AREA ($g/m^2$) | CORROSION RATE $g/m^2/min$ |
|---|---|---|---|---|---|---|---|---|
| 18. | Ø11.5 x 19.7 | 9.19 | 0.05 | 16.0486 | 16.0326 | 0.0160 | 17.4102 | 0.0580 |
| 19. | Ø11.6 x 19.5 | 9.22 | 0.10 | 16.0580 | 16.0470 | 0.0110 | 11.9306 | 0.0398 |
| 20. | Ø11.5 x 19.6 | 9.16 | 0.15 | 16.0800 | 16.0700 | 0.0100 | 10.9170 | 0.0360 |
| 21. | Ø11.6 x 19.7 | 9.22 | 0.20 | 16.2092 | 16.2002 | 0.0090 | 9.6878 | 0.0323 |
| 22. | Ø11.5 x 20.0 | 9.30 | 0.25 | 16.2374 | 16.2284 | 0.0090 | 9.6774 | 0.0322 |
| 23. | Ø11.7 x 19.7 | 9.39 | 0.30 | 16.3098 | 16.3014 | 0.0084 | 8.9457 | 0.0298 |
| 24. | Ø11.6 x 19.8 | 9.33 | 0.40 | 16.2515 | 16.2440 | 0.0075 | 8.0386 | 0.0268 |
| 25. | Ø11.7 x 20.1 | 9.54 | 0.50 | 16.7788 | 16.7718 | 0.0070 | 7.3375 | 0.0245 |

TABLE 4.6: Hydrogen Evolution Characteristics of Low Carbon Steel Samples in HCl Solution with the Addition of Varying Concentrations of Benzaldehyde

| S/N. | $V_{60}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | $V_{120}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | $V_{180}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | $V_{240}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | $V_{300}$ ($cm^3$) | $H_2Vol/m^2$ ($cm^3$) | RATE OF $H_2$ EVOLUTION ($cm^3$/min) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18. | 1.00 | 1088.14 | 1.80 | 1958.65 | 2.80 | 3046.79 | 3.70 | 4026.12 | 4.90 | 5331.88 | 17.77 |
| 19. | 0.80 | 867.68 | 1.70 | 1843.82 | 2.60 | 2819.96 | 3.50 | 3904.56 | 4.70 | 5097.61 | 16.99 |
| 20. | 0.70 | 764.19 | 1.40 | 1528.38 | 2.00 | 2183.41 | 2.90 | 3165.94 | 3.70 | 4039.30 | 13.46 |
| 21. | 0.60 | 645.85 | 1.20 | 1291.71 | 1.80 | 1937.57 | 2.40 | 2583.42 | 3.20 | 3444.56 | 11.48 |
| 22. | 0.50 | 537.63 | 1.00 | 1075.27 | 1.70 | 1827.96 | 2.30 | 2473.12 | 3.00 | 3225.81 | 10.75 |
| 23. | 0.40 | 425.99 | 1.00 | 1064.96 | 1.60 | 1703.94 | 2.20 | 2342.92 | 2.90 | 3088.39 | 10.29 |
| 24. | 0.40 | 428.72 | 0.80 | 857.45 | 1.30 | 1393.35 | 1.70 | 1822.08 | 2.10 | 2250.80 | 7.50 |
| 25. | 0.30 | 314.47 | 0.70 | 733.75 | 1.10 | 1153.04 | 1.60 | 1677.15 | 2.00 | 2096.44 | 6.99 |

TABLE 4.7: Corrosion Behaviour of Low Carbon Steel Samples in HCl Solution with the Addition of Varying Concentration of Sodium Dichromate

| S/N. | SAMPLE SIZE (mm) | SAMPLE SURFACE AREA X $10^{-4}$ ($m^2$) | INHIBITOR CONC. (%) | INITIAL WEIGHT (g) | FINAL WEIGHT (g) | WEIGHT LOSS (g) | WEIGHT LOSS/UNIT AREA ($g/m^2$) | CORROSION RATE ($g/m^2$/min) |
|---|---|---|---|---|---|---|---|---|
| 26. | Ø11.1 x 19.4 | 8.70 | 0.05 | 15.2059 | 15.1669 | 0.039 | 44.7126 | 0.1490 |
| 27. | Ø11.1 x 19.2 | 8.63 | 0.20 | 15.0080 | 14.9630 | 0.045 | 52.1437 | 0.1738 |
| 28. | Ø11.0 x 19.2 | 8.54 | 0.40 | 14.9145 | 14.8635 | 0.0510 | 59.7190 | 0.1991 |
| 29. | Ø11.0 x 19.5 | 8.64 | 0.60 | 15.0170 | 14.9570 | 0.0600 | 69.4444 | 0.2315 |
| 30. | Ø11.0 x 19.8 | 8.74 | 0.80 | 15.3087 | 15.2387 | 0.0700 | 80.0915 | 0.2670 |
| 31. | Ø11.3 x 20.0 | 9.11 | 1.00 | 16.1492 | 16.0692 | 0.0800 | 87.8156 | 0.2927 |
| 32. | Ø11.1 x 19.6 | 8.77 | 1.20 | 15.3173 | 15.2293 | 0.0800 | 100.3421 | 0.3345 |
| 33. | Ø11.2 x 20.1 | 9.04 | 1.40 | 15.8858 | 15.7818 | 0.1040 | 115.0443 | 0.3835 |
| 34. | Ø11.3 x 19.4 | 8.89 | 1.80 | 15.1201 | 15.0051 | 0.1150 | 129.3588 | 0.4312 |
| 35. | Ø11.2 x 19.6 | 8.87 | 2.00 | 15.2473 | 15.1203 | 0.1270 | 143.1773 | 0.4773 |

TABLE 4.8: Hydrogen Evolution Characteristics of Low Carbon Steel Samples in HCl Solution with the Addition of Varying Concentrations of Sodium Dichromate.

| S/N. | $V_{60}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | $V_{120}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | $V_{180}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | $V_{240}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | $V_{300}$ ($cm^3$) | $H_2$Vol/$m^2$ ($cm^3$) | RATE OF $H_2$ EVOLUTION ($cm^3$/min) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 26. | 2.20 | 2585.19 | 5.00 | 5875.44 | 8.30 | 9753.23 | 12.00 | 14101.06 | 16.10 | 18918.92 | 63.06 |
| 27. | 2.50 | 2744.24 | 5.40 | 5927.55 | 8.80 | 9659.71 | 12.50 | 13721.19 | 16.60 | 18221.73 | 60.74 |
| 28. | 2.40 | 2810.30 | 5.30 | 6206.09 | 8.20 | 9601.87 | 11.10 | 12997.66 | 14.80 | 17330.21 | 57.76 |
| 29. | 2.20 | 2546.30 | 4.40 | 5092.59 | 6.80 | 7870.37 | 10.00 | 11574.07 | 13.60 | 15740.74 | 52.47 |
| 30. | 2.40 | 2572.35 | 4.80 | 5144.69 | 7.20 | 7717.04 | 10.60 | 11361.20 | 14.10 | 15112.54 | 50.38 |
| 31. | 2.40 | 2634.47 | 4.70 | 5159.17 | 7.20 | 7903.40 | 10.50 | 11525.80 | 14.00 | 15367.73 | 51.23 |
| 32. | 2.40 | 2736.60 | 4.60 | 5245.15 | 7.00 | 7981.76 | 10.00 | 11402.51 | 13.60 | 15507.41 | 51.69 |
| 33. | 2.40 | 2654.87 | 4.90 | 5420.35 | 7.30 | 8075.22 | 10.80 | 11946.90 | 14.20 | 15707.97 | 52.36 |
| 34. | 2.40 | 2699.66 | 4.80 | 5399.33 | 7.30 | 8211.47 | 10.70 | 12036.00 | 14.10 | 15860.52 | 52.87 |
| 35. | 2.50 | 2818.49 | 4.80 | 5411.50 | 7.50 | 8455.47 | 10.80 | 12175.87 | 14.40 | 16234.50 | 54.12 |

TABLE 4.9: Corrosion Behaviour of Low Carbon Steel Samples in HCl Solution with the Addition of Varying Concentrations of Sodium Nitrite

| S/N. | SAMPLE SIZE (MM) | SAMPLE SURFACE AREA X $10^{-4}$ ($M^2$) | INHIBITOR CONC. (%) | INITIAL WEIGHT (g) | FINAL WEIGHT (g) | WEIGHT LOSS (g) | WEIGHT LOSS/UNIT AREA ($g/m^2$) | CORROSION RATE ($g/m^2$/min) |
|---|---|---|---|---|---|---|---|---|
| 36. | Ø11.6 x 19.8 | 9.33 | 0.05 | 16.2512 | 16.2012 | 0.0500 | 53.5906 | 0.1786 |
| 37. | Ø11.5 x 19.6 | 9.16 | 0.20 | 16.0800 | 16.0290 | 0.0510 | 55.6769 | 0.1856 |
| 38. | Ø11.6 x 19.8 | 9.33 | 0.40 | 16.2515 | 16.1915 | 0.0600 | 64.3087 | 0.2144 |
| 39. | Ø11.6 x 19.7 | 9.29 | 0.60 | 16.2185 | 16.1485 | 0.0700 | 75.3498 | 0.2512 |
| 40. | Ø11.7 x 19.5 | 9.32 | 0.80 | 16.2502 | 16.1722 | 0.0780 | 83.6910 | 0.2790 |
| 41. | Ø11.6 x 19.7 | 9.29 | 1.00 | 16.2092 | 16.1172 | 0.0820 | 88.2667 | 0.2942 |
| 42. | Ø11.5 x 20.0 | 9.30 | 1.20 | 16.2374 | 16.1444 | 0.0930 | 100.0000 | 0.3333 |
| 43. | Ø11.6 x 19.7 | 9.29 | 1.40 | 16.2184 | 16.1144 | 0.1040 | 111.9483 | 0.3732 |
| 44. | Ø11.6 x 19.8 | 9.33 | 1.80 | 16.2515 | 16.1355 | 0.1160 | 124.3301 | 0.4144 |
| 45. | Ø11.7 x 20.1 | 9.54 | 2.00 | 16.7788 | 16.6508 | 0.1280 | 134.1719 | 0.4472 |

TABLE 4.10: Hydrogen Evolution Characteristics of Low Carbon Steel Samples in HCl Solution with the Addition of Varying Concentrations of Sodium Nitrite

| S/N. | $V_{60}$ | $H_2Vol/m^2$ ($cm^3$) | $V_{120}$ | $H_2Vol/m^2$ ($cm^3$) | $V_{180}$ | $H_2Vol/m^2$ ($cm^3$) | $V_{240}$ | $H_2Vol/m^2$ ($cm^3$) | $V_{300}$ | $H_2Vol/m^2$ ($cm^3$) | RATE OF $H_2$ EVOLUTION ($cm^3$/min) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 36. | 3.40 | 3644.16 | 6.90 | 7395.50 | 11.00 | 11789.93 | 15.40 | 16505.90 | 20.20 | 21650.59 | 72.17 |
| 37. | 3.50 | 3820.96 | 7.00 | 7641.92 | 10.80 | 11790.39 | 15.00 | 16375.55 | 19.20 | 20960.70 | 69.87 |
| 38. | 3.10 | 3322.62 | 6.50 | 6966.77 | 10.10 | 10825.30 | 14.20 | 15219.72 | 18.70 | 20042.87 | 66.81 |
| 39. | 2.90 | 3121.64 | 6.20 | 6673.84 | 9.40 | 10118.41 | 13.80 | 14854.68 | 18.40 | 19806.24 | 66.02 |
| 40. | 2.70 | 2896.99 | 5.70 | 6115.88 | 9.20 | 9871.24 | 12.70 | 13626.61 | 16.90 | 18133.05 | 60.44 |
| 41. | 2.40 | 2583.42 | 5.00 | 5382.13 | 7.50 | 8073.20 | 10.90 | 11733.05 | 14.40 | 15500.54 | 51.67 |
| 42. | 2.40 | 2580.65 | 5.20 | 5591.40 | 8.30 | 8924.73 | 11.20 | 12043.01 | 14.80 | 15913.98 | 53.05 |
| 43. | 2.50 | 2691.07 | 5.30 | 5705.06 | 7.60 | 8180.84 | 11.30 | 12163.62 | 15.00 | 16146.39 | 53.82 |
| 44. | 2.50 | 2679.53 | 5.30 | 5680.60 | 8.40 | 9003.22 | 11.60 | 12433.01 | 15.20 | 16291.53 | 54.31 |
| 45. | 2.60 | 2725.37 | 5.40 | 5660.38 | 8.60 | 9014.68 | 11.90 | 12473.80 | 15.80 | 16561.85 | 55.21 |

TABLE 4.11: Comparison of the Efficiency of Corrosion Inhibition Exhibited by the Aldehydes as a Function of Inhibitor Concentration

| INHIBITOR CONC. (%) | EFFICIENCY OF INHIBITION $\eta_a = \frac{P_o - P_{inh}}{P_o} \times 100\%$ | | |
|---|---|---|---|
| | FORMALDEHYDE | ACETALDEHYDE | BENZALDEHYDE |
| 0.05 | 38.78 | 65.31 | 40.82 |
| 0.10 | 66.63 | 70.82 | 59.39 |
| 0.15 | 72.55 | 73.26 | 62.86 |
| 0.20 | 76.22 | 77.86 | 67.04 |
| 0.25 | 77.55 | 79.08 | 67.04 |
| 0.30 | 80.61 | 80.61 | 69.59 |
| 0.40 | 83.57 | 85.41 | 72.65 |
| 0.50 | 85.10 | 87.49 | 75.00 |

TABLE 4.12: Comparison of the Efficiency of Hydrogen Evolution Retardation Exhibited by the Aldehyde as a Function of Inhibitor Concentration

| INHIBITOR CONC. (%) | EFFICIENCY OF $H_2$ EVOLUTION RETARDATION $\eta_c = \frac{V_o - V_{inh}}{V_o} \times 100\%$ | | |
|---|---|---|---|
| | FORMALDEHYDE | ACETALDEHYDE | BENZALDEHYDE |
| 0.05 | 45.91 | 74.10 | 58.46 |
| 0.10 | 72.83 | 82.49 | 60.29 |
| 0.15 | 84.06 | 84.34 | 68.54 |
| 0.20 | 86.58 | 86.49 | 73.17 |
| 0.25 | 87.17 | 87.42 | 74.87 |
| 0.30 | 89.08 | 89.97 | 75.95 |
| 0.40 | 91.63 | 92.50 | 82.47 |
| 0.50 | 92.31 | 92.61 | 83.66 |

## 4.1 CALCULATION OF CORROSION PARAMETERS

The following sequences were adopted in the computation of corrosion and hydrogen evolution rates of the steel samples as well as inhibition efficiency of the aldehydes as shown in tables 4.1 to 4.12.

$$\text{Corrosion rate} = \frac{\text{weight loss}}{\text{surface area x time}} \quad (g/m^2/min)$$

Example: Experiment 1

Diameter of sample = Ø11.7mm

Length of sample = 19.6mm

Surface area of sample = $2\pi r\,(L + r) \equiv \pi d(L + {}^{d}/_{2})$

$= {}^{22}/_{7} \times 11.7\,(19.6 + 5.85)$

$= {}^{22}/_{7} \times 11.7 \times 25.45$

$= 935.456mm^2$

$= 9.35 \times 10^{-4}m^2$

Initial weight of sample (Wo) = 16.2685g

Final weight of sample (Wi) = 16.2410g

Weight loss (Wo - Wi) = 0.0275g

Exposure time = 5 hours = 300 minutes

$$\therefore \text{Corrosion rate} = \frac{0.0275}{9.35 \times 10^{-4} \times 300}$$

$= 0.0980g/m^2/min$

$$\text{Hydrogen evolution rate} = \frac{V_{300}}{\text{surface area x time}} \quad (cm^3/min)$$

Where $V_{300}$ = Volume of hydrogen evolved after 300 minutes.

$V_{300} = 12cm^3$ for experiment 1

$\therefore$ Hydrogen evolution rate = $\frac{12.0}{9.35 \times 10^{-4} \times 300}$

= 42.78cm$^3$/min

Inhibition efficiency ($\eta_g$) = $\frac{P_o - P_{inh}}{P_o} \times 100\%$

Where $P_o$ = Corrosion rate of steel sample without inhibitor.

$P_{inh}$ = Corrosion rate of steel sample with inhibitor.

Example: Experiment 2:

$P_o$ = 0.0980 g/m$^2$/min

$P_{inh}$ = 0.0618 g/m$^2$/min

$\eta_g = \frac{0.0980 - 0.0618}{0.0980} \times 100\%$

= 38.78%

Inhibition efficiency ($\eta_e$) = $\frac{V_o - V_{inh}}{V_o} \times 100\%$

Where $V_o$ and $V_{inh}$ are volume of hydrogen evolved by the steel samples with and without inhibitors in the HCl Solution.

Example: $V_o$ and $V_{inh}$ are respectively equal to 42.78 and 23.22 cm$^3$/min from experiments 1 and 2.

Hence $\eta_e = \frac{42.78 - 23.14}{42.78} \times 100$

= 45.91%

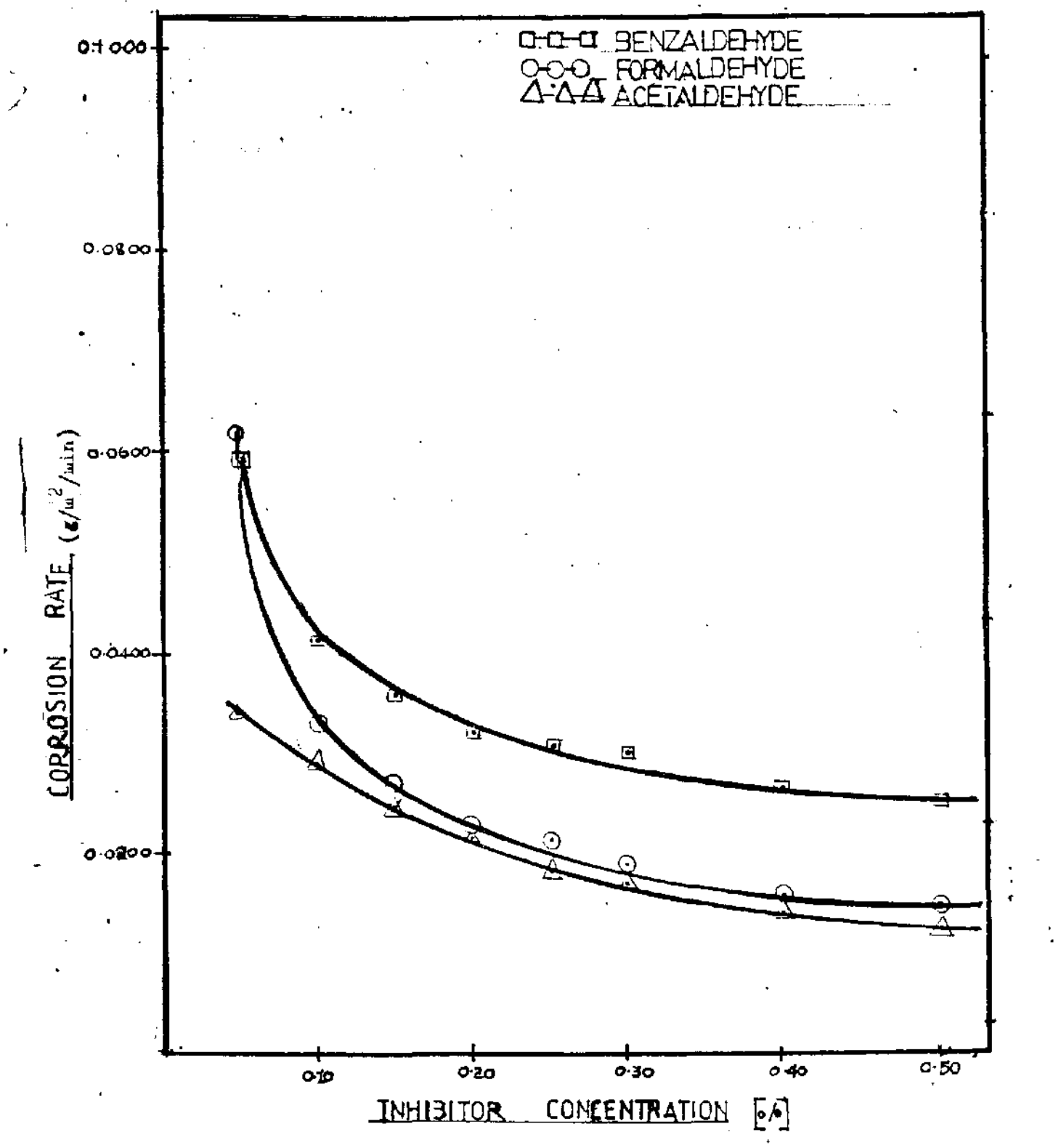



FIGURE 4.1: EFFECT OF ALDEHYDES CONCENTRATION ON CORROSION RATE OF LOW CARBON STEEL SAMPLES IN HCl PICKLING SOLUTION



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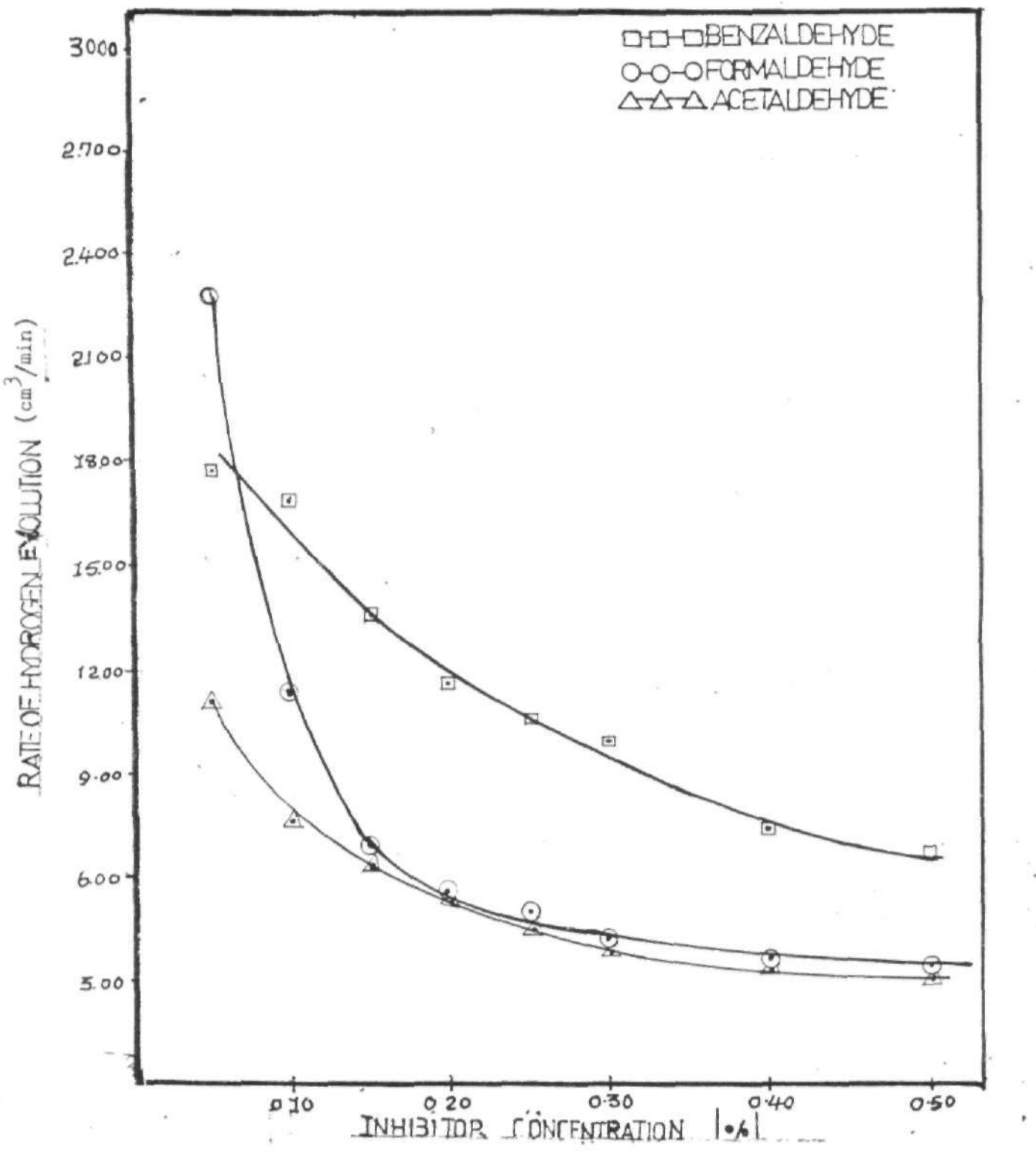



FIGURE 4.2: EFFECT OF ALDEHYDES CONCENTRATION ON THE RATE OF HYDROGEN EVOLUTION OF LOW CARBON STEEL SAMPLES IN HCl PICKLING SOLUTION

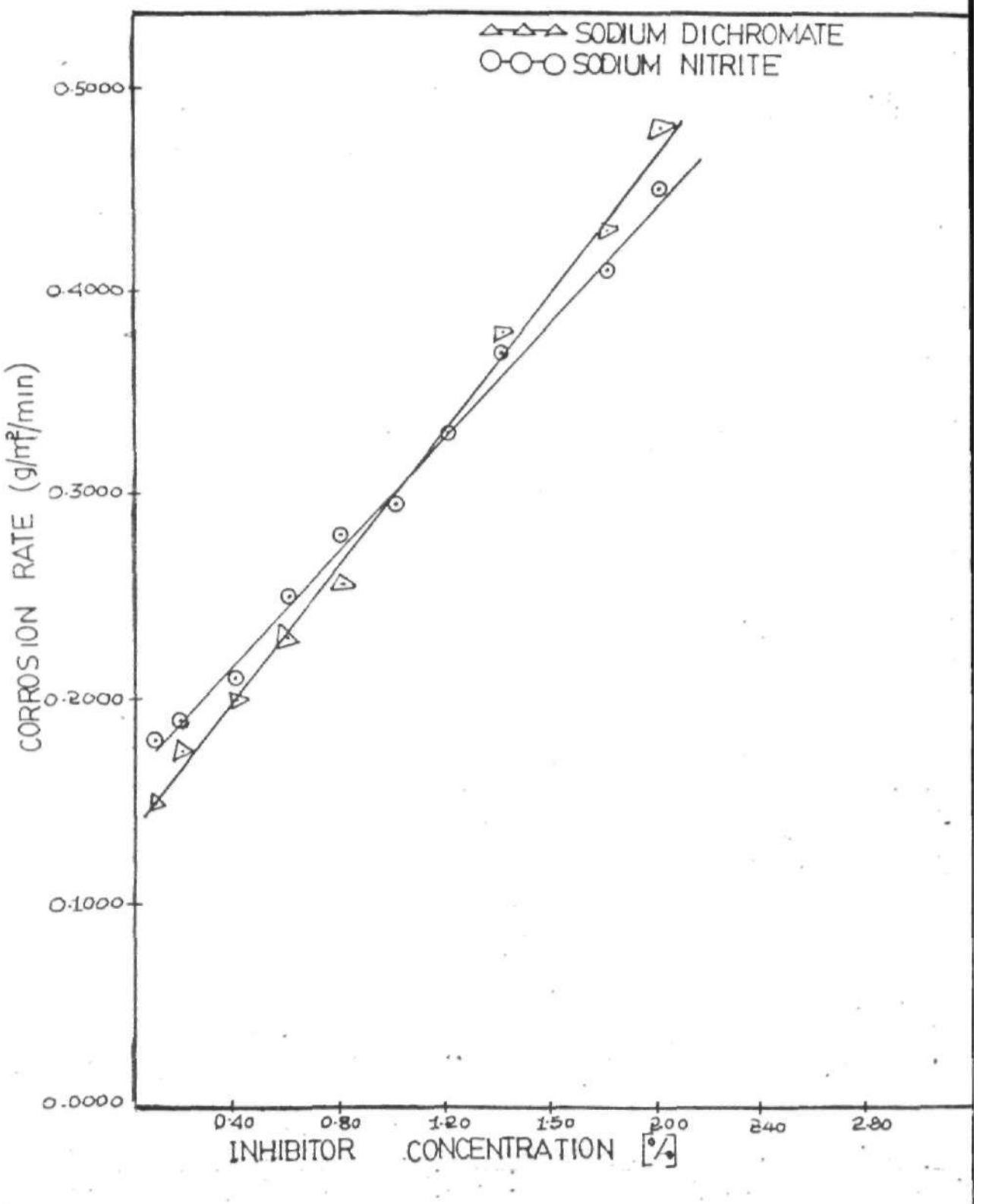



FIGURE 4.3: EFFECT OF SODIUM DIGHROMATE AND SODIUM NITRITE ON THE CORROSION RATE OF LOW CARBON STEEL SAMPLES IN HCl PICKLING SOLUTION

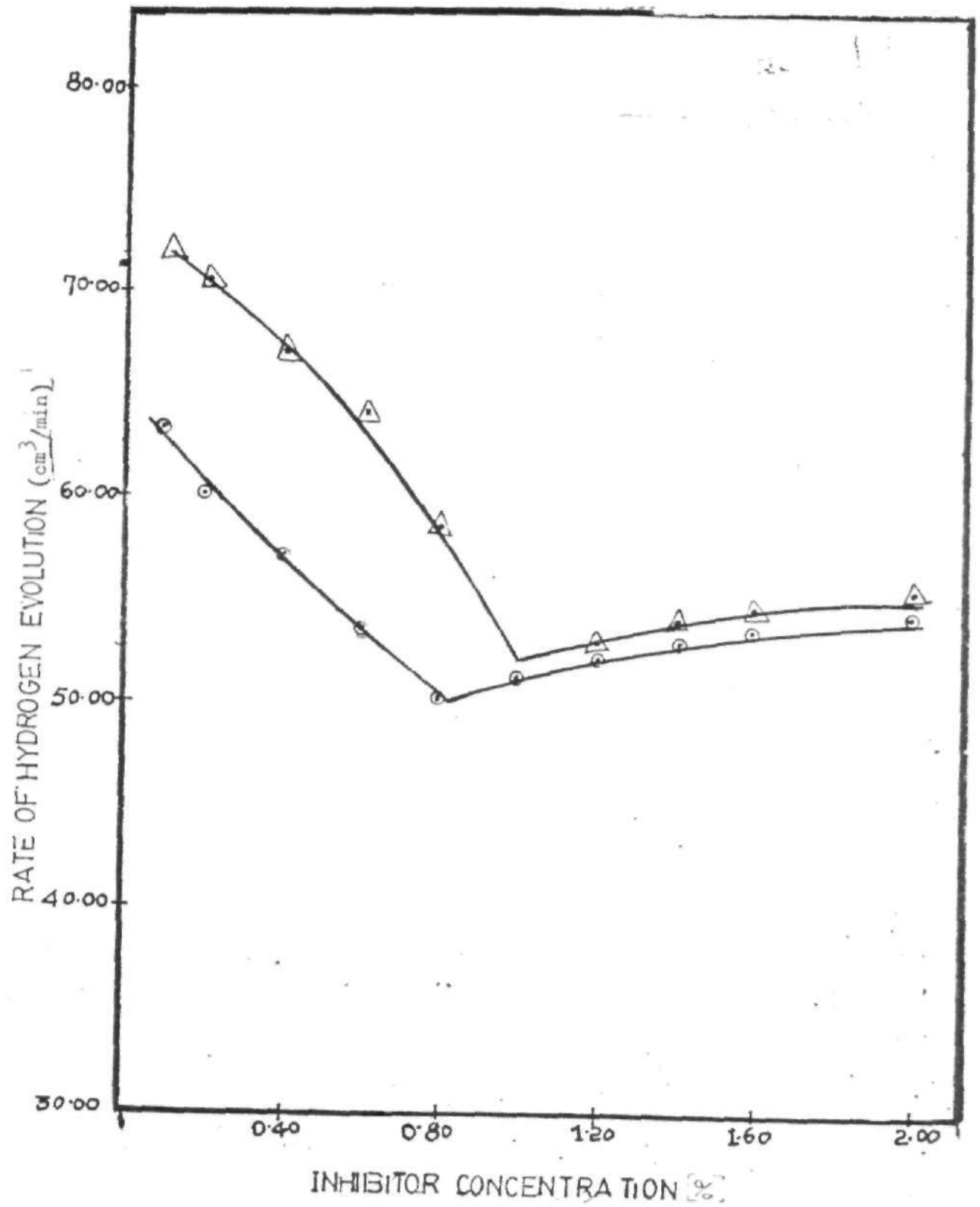



FIGURE 4.4: THE EFFECT OF $Na_2Cr_2O_7$ AND $NaNO_2$ ON THE RATE OF TYDROGEN EVOLUTION OF LOW CARBON STEEL SAMPLES IN HCl PICKLING SOLUTION

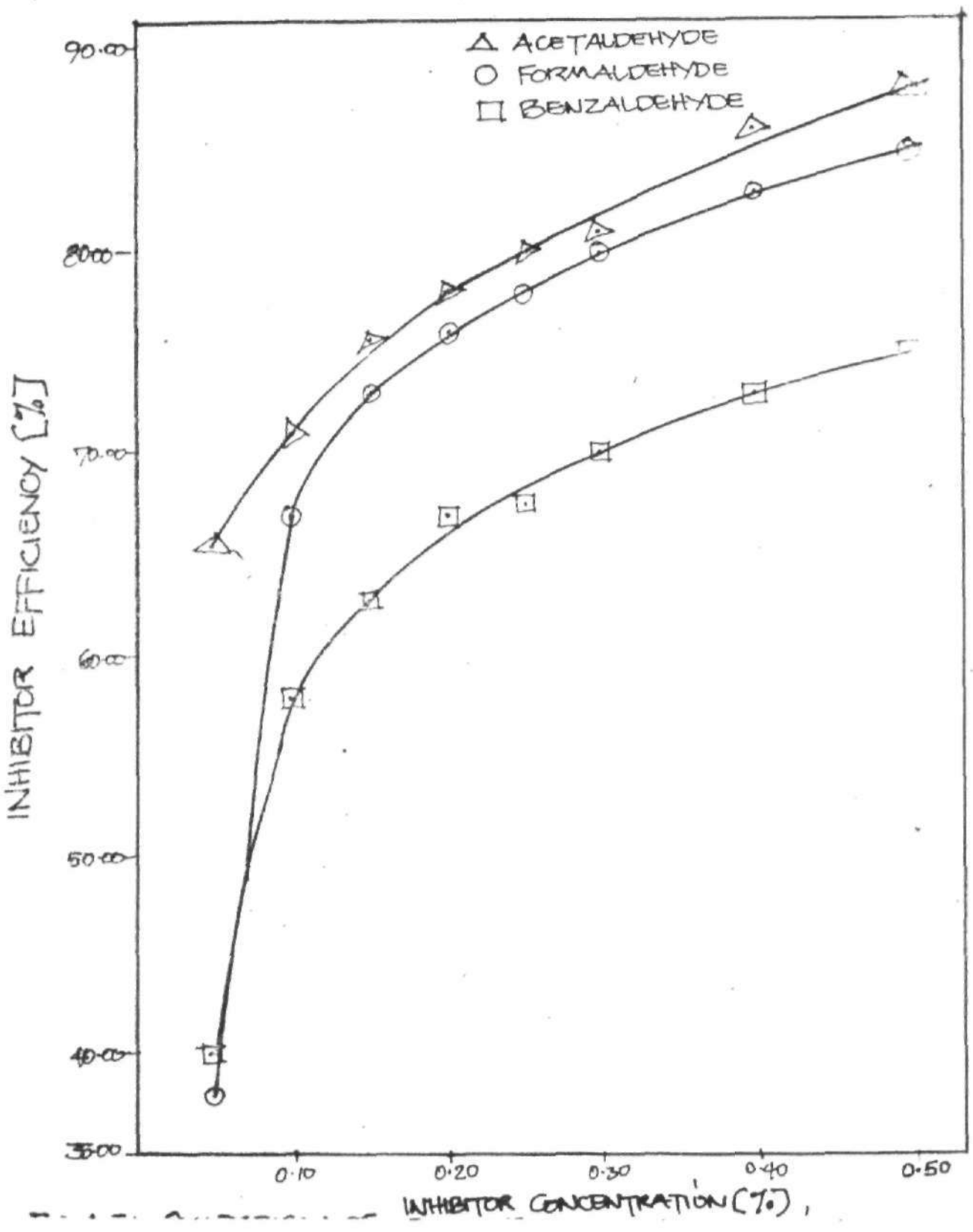



FIGURE 4.5: COMPARISON OF EFFICIENCY OF CORROSION INHIBITION EXHIBITED BY THE ALDEHYDES AS A FUNCTION OF INHIBITOR CONCENTRATION

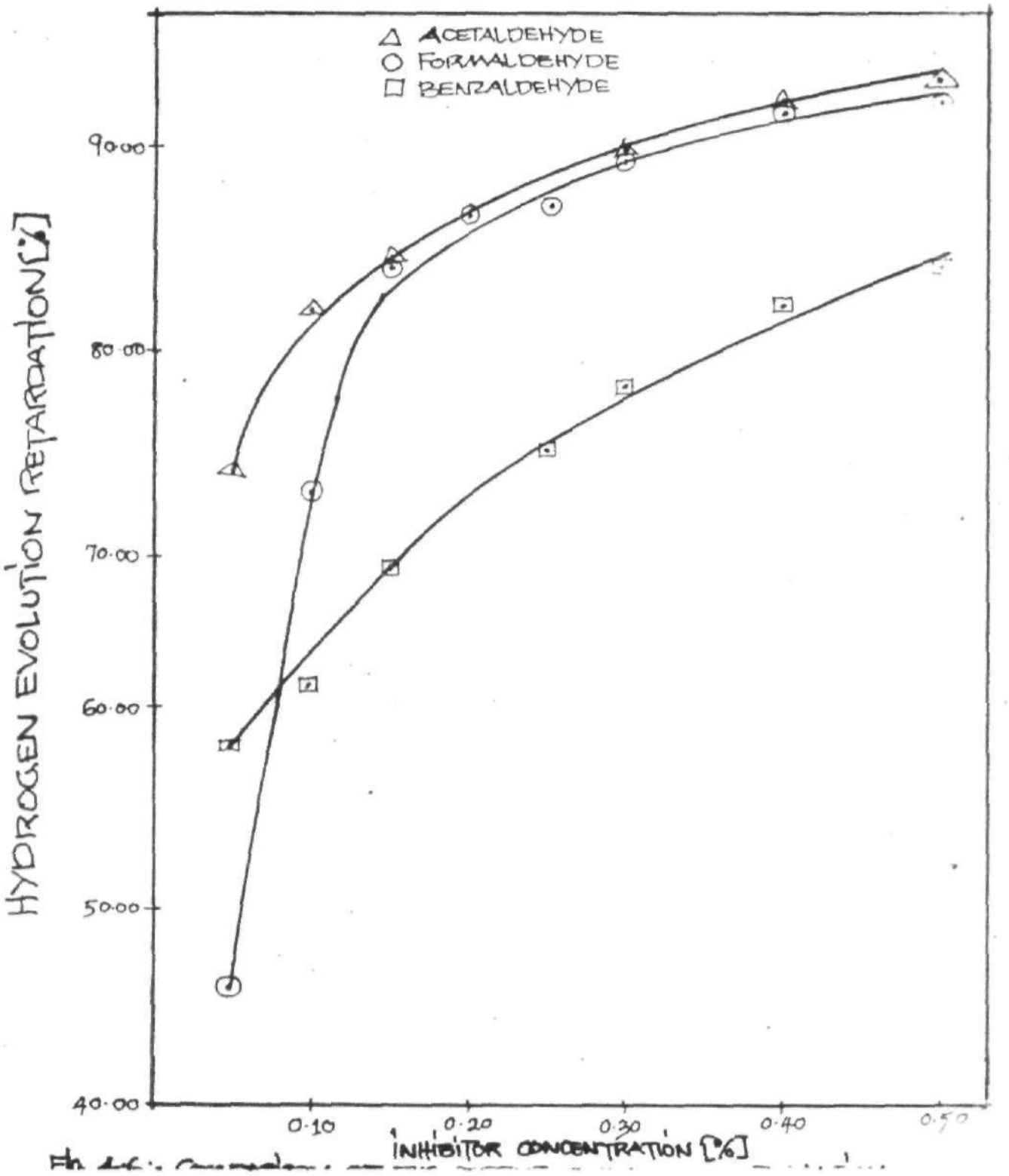



FIGURE 4.6: COMPARISON OF THE EXTENT OF HYDROGEN EVOLUTION RETARDATION EXHIBITED BY THE ALDEHYDES AS A FUNCTION OF INHIBITOR CONCENTRATION

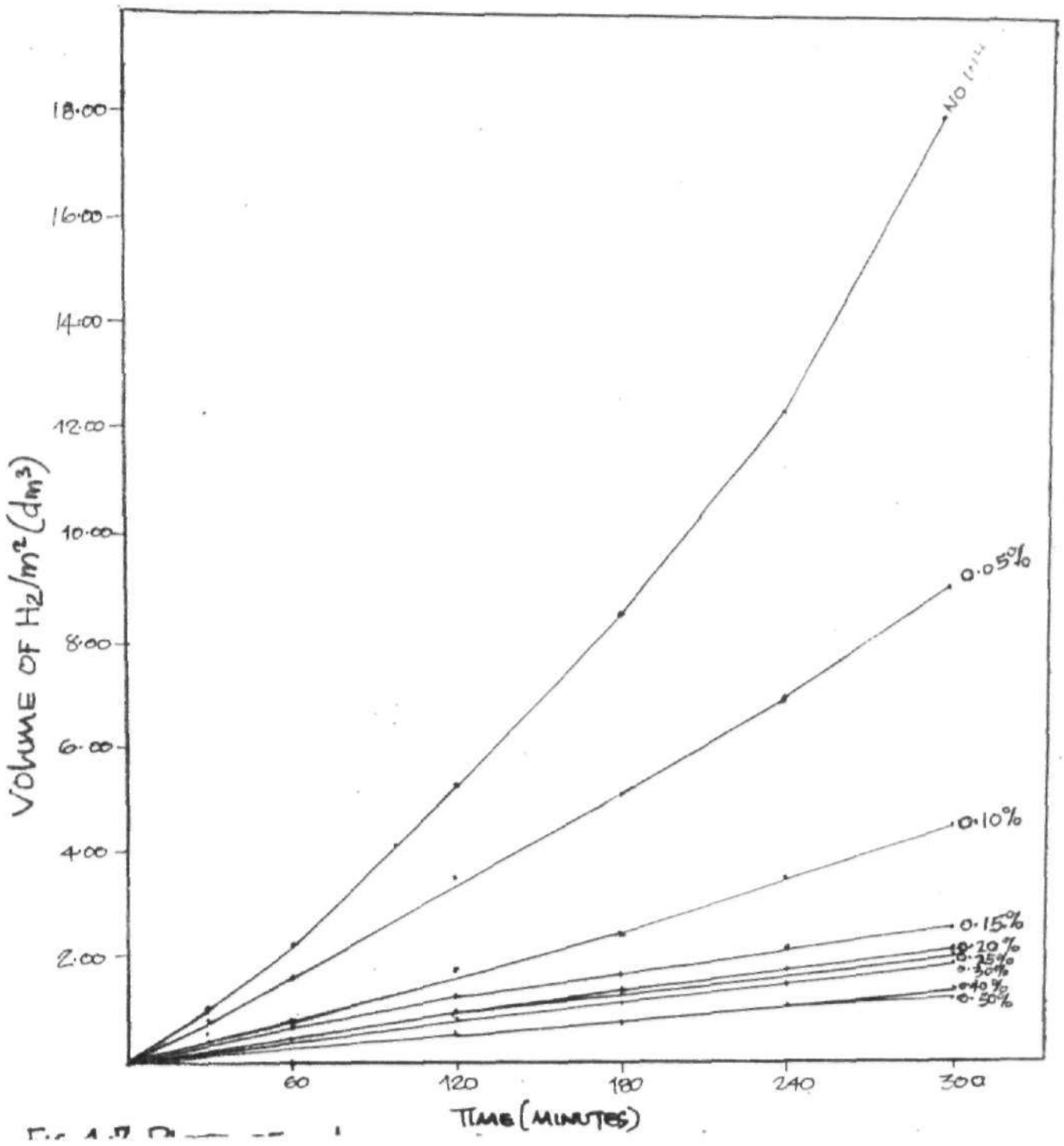



FIGURE 4.7: PLOT OF VOLUME OF HYDROGEN EVOLVED BY LOW CARBON STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION WITH VARYING CONCENTRATIONS OF FORMALDEHYDE VS TIME

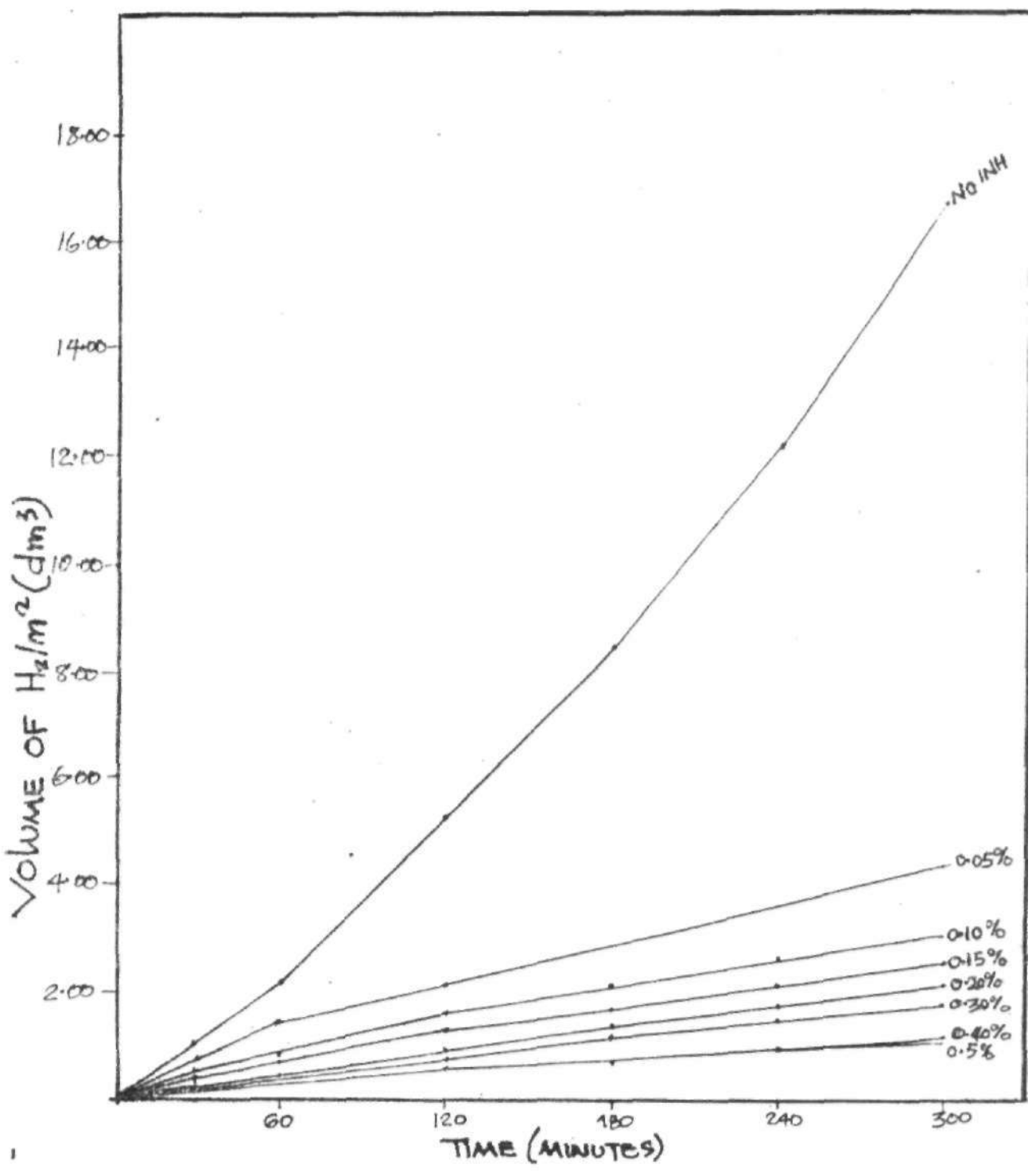



FIGURE 4.8: PLOT OF VOLUME OF HYDROGEN EVOLVED BY LOW CARBON STEEL IMMERSED IN HCl PICKLING SOLUTION AS A FUNCTION OF TIME, WITH VARYING CONCENTRATIONS OF ACETALDEHYDE.

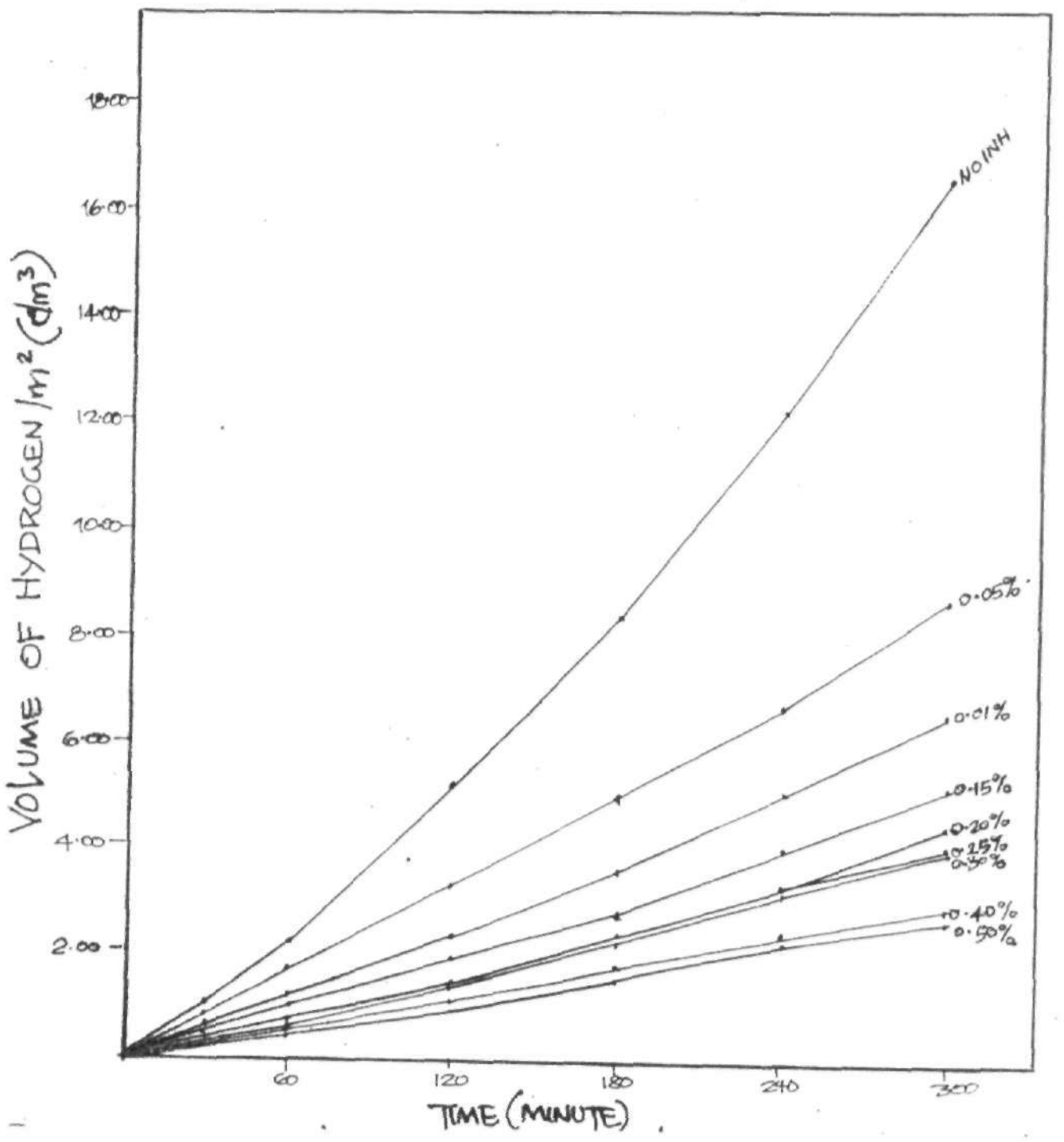



FIGURE 4.9: PLOT OF VOLUME OF HYDROGEN EVOLVED BY LOW CARBON STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTIONS WITH VARYING CONCENTRATIONS OF BENZALDEHYDE V.S TIME

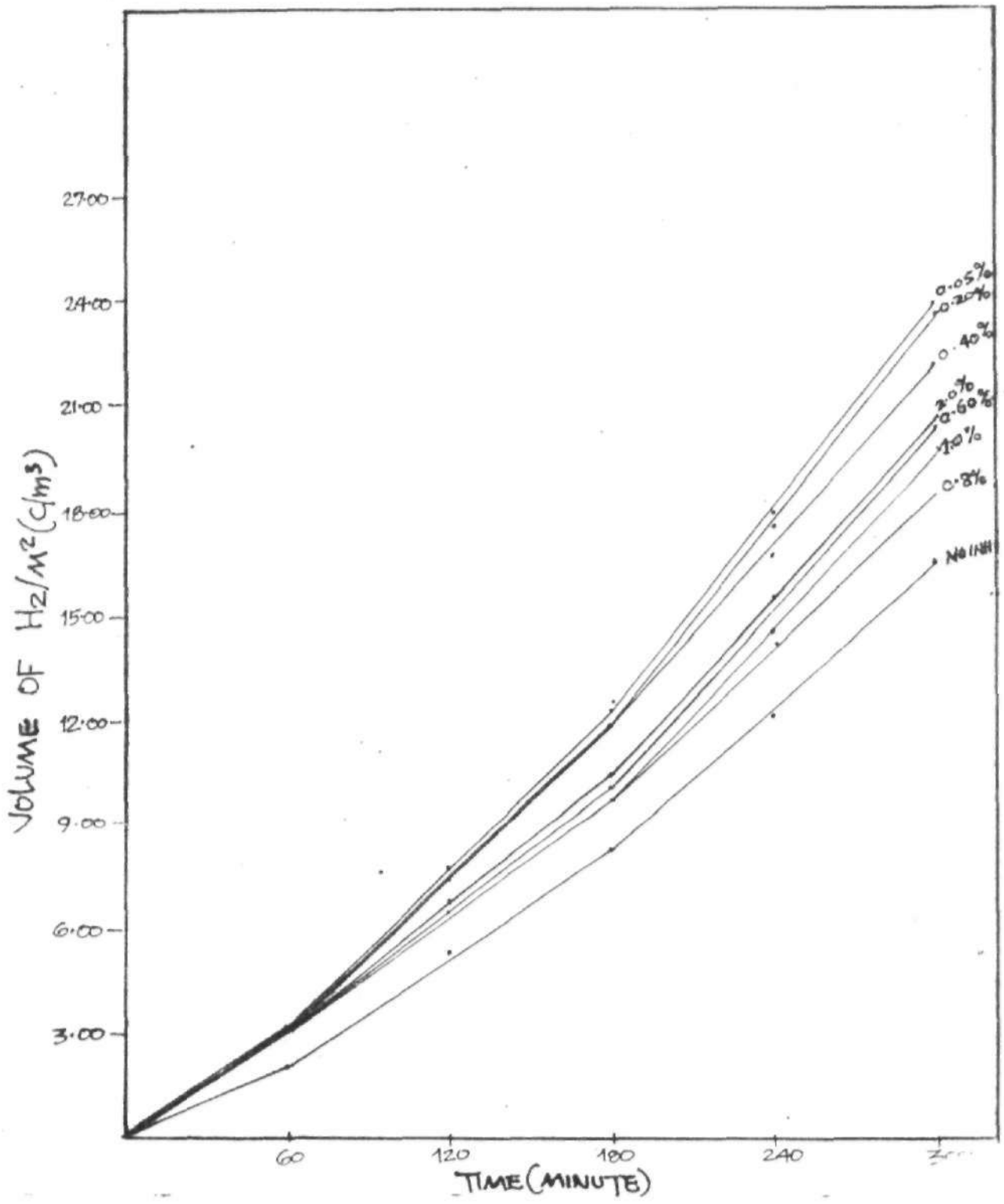



FIGURE 4.10 PLOT OF VOLUME HYDROGEN EVOLVED BY LOW CARBON STEEL SAMPLES IN HCl PICKLING SOLUTION WITH VARYING CONCENTRATION OF SODIUM DICHROMATE VS TIME

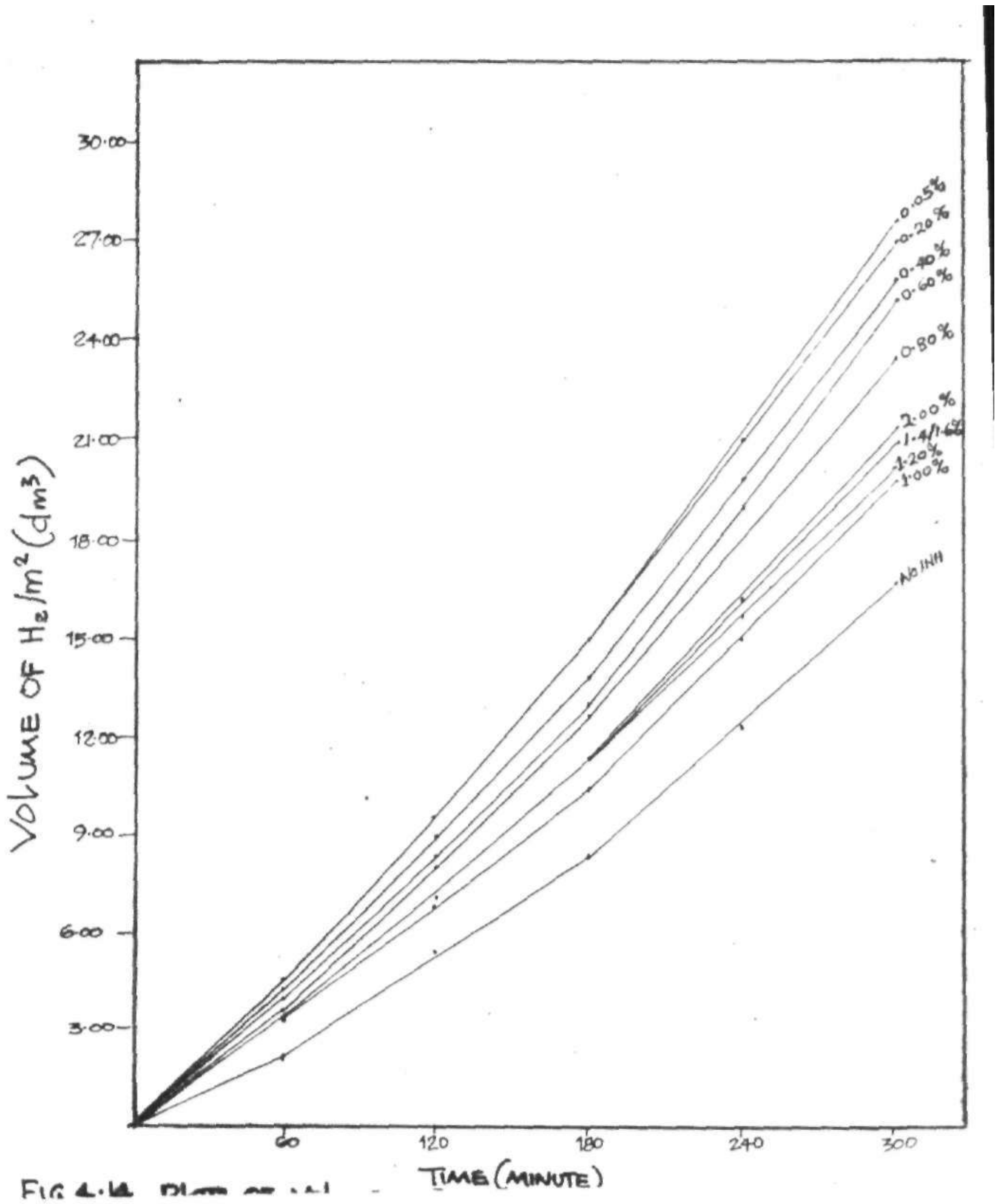



FIGURE 4.11: PLOT OF VOLUME OF HYDROGEN EVOLVED BY LOW CARBON STEEL SAMPLE IMMERSED IN HCl PICKLING SOLUTION WITH VARYING CONCENTRATION OF SODIUM NITRITE VS TIME

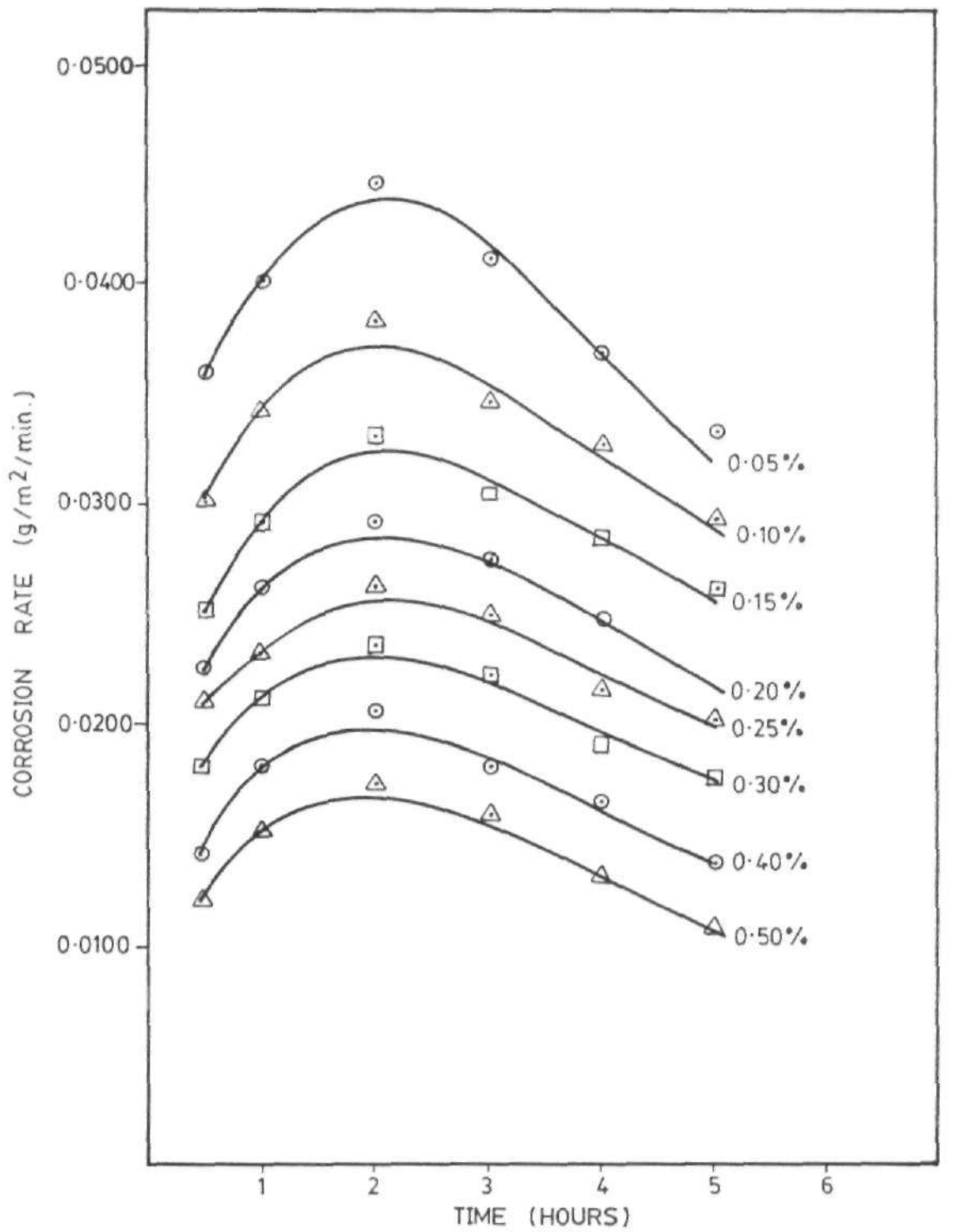



FIGURE 4.12: EFFECT OF TIME OF IMMERSION ON THE CORROSION RATE OF LOW CARBON STEEL SAMPLES IN HCl PICKLING SOLUTION INHIBITED WITH ACETALDEHYDE

## 4.2 DISCUSSION OF RESULTS

### 4.2.1 Choice of Experimental Means

From mixed potential theory, corrosion of iron in aqueous solutions is accomplished by two partial reactions:

$$Fe = Fe^{2+} + 2e \text{ (Anodic Reaction)} \quad (5.1)$$

and $$2H^{+} + 2e = H_2 \text{ (Cathodic Reaction)} \quad (5.2)$$

given, $$Fe + 2H = Fe^{2+} + H_2 \text{ (Net Reaction)} \quad (5.3)$$

The experimental means is capable of simultaneously measuring the extent of both the anodic and cathodic reaction. The degree of anodic reaction is determined from weight loss measurements while the cathodic, from the volume of hydrogen evolved as shown in (Figure 3.1). It suffices to mention that inhibitors do not affect anodic and cathodic reactions to the same degree (Hausler, 1979). A knowledge of the rate of anodic and cathodic reactions is thus necessary for clearer understanding of inhibitive effect of the inhibitors on each of the partial reactions.

The accuracy of the results of the experiment is based on the following assumptions:

(i) The effects of atmospheric pressure on the volume of hydrogen evolved as indicated on the burette is neglected and,

(ii) Other possible instrumental (alignment) and human (misreading and inconsistent acid solution) errors are ignored.

### 4.2.2. Effects of Aldehydes on the Corrosion of Low Carbon Steels in HCl Solution

It is evident from tables 4.1 to 4.6 and figures 4.1 and 4.2 that the aldehydes considerably and progressively reduce the corrosion and hydrogen evolution rates of the steel samples as the concentration of aldehyde is increased. It is also evident that the

efficiency of the aldehydes (tables 4.11 to 4.12 and figures 4.5 to 4.6) in decreasing the rate of hydrogen evolution is higher than in reducing the corrosion rate, thus suggesting that the inhibitors (aldehydes) produce a kind of mixed inhibition in which cathodic inhibition is more predominant than the anodic. This is in agreement with the investigation carried out by Felloni and Cozzi (1967).

Inhibition mechanism of the steel samples in the acid solution by the aldehydes could be attributed to the adsorption of their molecules on the corroding metal surfaces, thus screening them from the actions of the aggressive ions in the solution (Meakins, 1963, Antropov, 1967 and Issa *et al*, 1973).

As suggested by Donnelly and Hamburg (1974), the adsorption of an inhibitor on the metallic surface induces a partial negative charge at the point of attraction.

At first the forces may be weak and electrostatic in nature but these develop into stronger forces at the chemisorption stage with the residual negative charge on the iron atom at the centre of attraction becoming larger. In the critical range of inhibitor concentration, the adsorption of the inhibitor is substantial and rapid and the total adsorbed compound consists of easily desorbed molecules (physical adsorption) and comparatively strongly adsorbed molecules (chemisorption). According to electroneutrality principle, the tendency for the atom in the metal to be as near as possible to oxidation state-zero will be disturbed as soon as adsorption occurs (Pauling, 1948). Moreover, adsorption in another related mechanism prevents the diffusion of the reacting species to the reaction interface.

Regressional analysis of the experimental data using the least square method have shown that the corrosion rate P, of the steel samples in 20% HCl Solution is inversely

proportional to the concentration C, of the aldehydes according to the equation:

$$P = KC^{-n} \text{----------} (5.4)$$

where K is the specific reaction rate and depends on acid concentration, inhibitor type, composition and surface properties of the corroding metal, and n is a kinetic parameter which expresses the change of corrosion rate with inhibitor concentration. The parameters K and n have been derived for the aldehydes investigated and the equation may be written as follows for each of them:

$$P = 0.00964\ C^{-0.5965} \quad \text{(Formaldehyde)} \quad (5.5)$$

$$P = 0.0102\ C^{-0.4325} \quad \text{(Acetaldehyde)} \quad (5.6)$$

and $$P = 0.01901\ C^{-0.3596} \quad \text{(Benzaldehyde)} \quad (5.7)$$

The aldehydes progressively reduce both corrosion and hydrogen evolution rates up to the concentration of 0.2%, beyond which further increase does not produce any appreciable effect. This is attributable to the fact that every inhibitor has a limit to which it can exert influence on the corrosion of metals and this is dependent on its physio-chemical and electrophysical properties (Vosta and Eliasek, 1971), as well as the properties of its reaction products (Antropov, 1967).

Examination of figures 4.5 and 4.6 reveals that the efficiencies of corrosion inhibition and hydrogen evolution retardation increase with inhibitor concentration, and in the following order: Benzaldehyde < Formaldehyde < Acetaldehyde. Acetaldehyde showed the highest inhibition efficiency in comparison with the other aldehydes because of its complete solubility in the pickling solution and moderate chain length which are more favourable conditions for adsorption phenomenon. The inhibition efficiency of formaldehyde is slightly lower than that of acetaldehyde. Its relatively high inhibition

is probably due to its complets solubility in the pickling medium and the fact that in aqueous solutions, formaldehyde is present as a hydrate while higher aldehydes are much less hydrated. The type of bond in adsorption is thus different (Putilova, *et al*, 1960). Benzaldehyde produced the least inhibition despite its longest chain length and this could be attributed to its poor solubility in the pickling solution and the rapid volatilization of reaction products (Duwell, *et al*, 1964).

Separate curves of the effects of inhibitor concentration on corrosion and hydrogen evolution rates are shown in figures 4.13 to 4.15 and figures 4.18 tp 4.20 respectively (Appendix).

### 4.2.3 Effect of $Na_2Cr_2O_7$ and $NaNO_2$ on the Corrosion of the Steels in HCl Solution

The addition of sodium dichromate and sodium nitrite to the acid solution tremendously stimulates the attack on the steel samples and also produces a fluctuating effect on the rate of hydrogen evolution.

The effect of $Na_2Cr_2O_7$ on the corrosion rate of the steel samples is shown in figure 4.3 and table 4.7 while its effect on the rate of hydrogen evolution is represented in figure 4.4 and table 4.8. It could be deduced that corrosion is stimulated and the corrosion rate of the samples increases monotonously with $Na_2Cr_2O_7$ concentration. An empirical equation expressing corrosion rate P, of the samples and concentration C, of the inorganic compounds of the anionic type was derived from a regressional analysis of the experimental data to be:

$$P = K + nC \text{----------} (5.8)$$

where K is specific rate constant and n is kinetic parameter expressing the change in corrosion rate with concentration. The parameters K and n have been evaluated for the dichromate and nitrite. For the dichromate,

$$P = 0.1300 + 0.1694\ C \text{----------} (5.9)$$

The rate of hydrogen evolution is highest at the salt concentration of 0.05%, reduces gradually until 0.8% (by volume) of $Na_2Cr_2O_7$ and starts increasing again when the dichromate concentration was increased. The rate of hydrogen evolution at 0.8% concentration is however, higher than its rate in the bare acid solution.

The nitrite produces a similar effect to the corrosion and hydrogen evolution rates of the steel samples as shown in figures 4.3 and 4.4 respectively. The corrosion rate of the steel samples P, has been found to vary linearly with $NaNO_2$ concentration C, according to the equation:

$$P = 0.1600 + 0.1417\ C \text{----------(5.10).}$$

The rate of hydrogen evolution followed a similar pattern as that of the dichromate and was least at the concentration of 1.00%.

The observed phenomenon of lack of corrosion inhibition of the steel samples by these inorganic compounds could be explained on the basis that it is highly improbable that $Na_2Cr_2O_7$ and $NaNO_2$ (which are anionic compounds) can appreciably adsorb on the corroding metal surface since the active ions ($No^-_2$ and $Cr_2O^{2-}_7$) have negative charges and iron equally has a negative potential on the Ø - Potential scale (Antropov, 1967). However, the most probable mechanism through which $Na_2Cr_2O_7$ and $NaNO_2$ can achieve inhibition in aqueous solution is through the formation of a passivating oxide film but since the acid pickling solution contains highly mobile ions, this film re-dissolves as soon as it is formed (Mclareen, Green and Kingsbury, 1961). Hence, corrosion is stimulated by these compounds and the extent of stimulation increases with salt concentration. These salts have been found to facilitate the cathodic reaction (Gouda *et al*, 1972).

This also gives credence to Uhlig's (1963), postulation that nitrites and chromates are inhibitors in solutions whose pH's are above 6.0 and that in more acid environments, they decompose and tend to induce pitting at concentrations near their critical concentrations for inhibition in presence of $Cl^-$ or $SO_4^{2-}$.

Separate curves of the effects of sodium dichromate and sodium nitrite on the corrosion and hydrogen evolution rates are shown in figures 4.16 to 4.17 and 4.21 to 4.22 respectively (Appendix).

### 4.2.4. Effect of $Na_2Cr_2O_7$ and $NaNO_2$ on the Rate of Hydrogen Evolution of the Steels in HCl Solution

The addition of $Na_2Cr_2O_7$ and $NaNO_2$ to the acid solution produces a fluctuating effect on the rate of hydrogen evolution as shown in figure 4.4. Chromates and nitrites are anodic inhibitors (Cohen, 1979) and they achieve inhibition by anodic polarization. That is causing a potential shift of the metal electrode to the positive or nobler direction (Reference Antropov, 1967). Inhibition of a metal under this condition occurs when a passivating film is formed.

When the potential of a metal is shifted to more electropositive values (with respect to stationary corrosion potential), the rate of anodic reaction (which is equivalent to the corrosion rate) increases as indicated by $i_a = i_{corr}$ while the rate of cathodic reaction falls. As the potential of the metal is increased further due to an increase in salt concentration, the rate of cathodic process reduces and that of the anodic process increases up to a salt concentration of 0.80% and 1.00% for $Na_2Cr_2O_7$ and $NaNO_2$ respectively, where as the inability of these salts to aid the steel samples in forming a passivating film, there is a breakdown in the entire inhibition process. Thus, rate of cathodic reaction begins to increase.

### 4.2.5. Effect of Time on the Volume of Hydrogen Evolved by Low Carbon Steels In HCl Solution

Figures 4.7 to 4.11 indicate that the reaction of hydrogen evolution is not accomplished at a steady rate. The curve of volume of hydrogen evolved Vs time for the steel sample corroding in uninhibited acid solution shows that the rate of hydrogen evolution is relatively small (as shown by the slope of the curve), at the first hour of the experiment and, thereafter, increases with time as indicated by the steepening of the curve. This suggests that the material initially resists attack by the acid. The addition of aldehydes considerably reduces the rate of hydrogen evolution as represented by the shallower slopes of the curves. This indicates that the aldehydes stifle hydrogen evolution reaction. However, sodium dichromate and sodium nitrite cause an increase in the volume of hydrogen evolved - suggesting that they ($Na_2Cr_2O_7$ and $NaNO_2$) stimulate the reaction of hydrogen evolution.

### 4.2.6 Effects of Time on the Corrosion of Low Carbon Steels in Inhibited Hydrochloric Acid Pickling Solution

Having established that acetaldehyde showed the highest inhibition efficiency when compared with formaldehyde and benzaldehyde (Figures 4.5 and 4.6), experiments were further carried out to investigate the effect of variation of time on the corrosion rate of low carbon steels in hydrochloric acid solution with the addition of varying concentrations of acetaldehyde.

As shown in Figure 4.12, the corrosion rate of the low carbon steel samples in hydrochloric acid solution with the addition of varying concentrations of acetaldehyde increases initially with time, reaches a peak and then decreases as the time of immersion was increased. It could also be deduced from Figure 4.12 that corrosion inhibition was

initially low (prior to the peak of the curve) and later increases as the time of exposure was increased. This could be attributed to adsorption mechanism which may be accomplished in two stages: physical and chemisorption stages. Inhibition of the low carbon steel coupons, before the corrosion peak could be attributed to physical adsorption while chemisorption was probably responsible for inhibition after the peak.

Results obtained from Figures 4.1 and 4.5 show that increasing the concentration of the aldehydes beyond 0.2% did not appreciably affect the corrosion rate and inhibition efficiency of the aldehydes. Furthermore, it is recommended that pickling time should be limited to 30 minutes in order to avoid considerable attack on the base metal.

# CHAPTER FIVE

## 5.0. CONCLUSIONS AND RECOMMENDATIONS

### 5.1. CONCLUSIONS

The following inferences are made from the results of weight loss and hydrogen evolution measurements carried out to investigate the effects of inhibitors on corrosion of Low Carbon Steel in HCl Pickling Solution.

1. Formaldehyde, acetaldehyde and benzaldehyde inhibit both the corrosion and hydrogen evolution reactions of low carbon steels in HCl solution to a varying degree implying that they are both anodic and cathodic inhibitors.
2. The corrosion rate P, of the steel samples is inversely proportional to the concentration C, of the aldehydes according to the following empirical equations:

   $P = 0.00964\ C^{-0.5965}$ (Formaldehyde)

   $P = 0.0102\ C^{-0.4325}$ (Acetaldehyde)

   $P = 0.01901\ C^{-0.3596}$ (Benzaldehyde).
3. The inhibition efficiency of the aldehydes increases with the aldehyde concentration at constant acid concentration according to the following sequence: Benzaldehyde < Formaldehyde < Acetaldehyde.
4. Corrosion inhibition of low carbon steels in hydrochloric acid solution by acetaldehyde is initially low, and later increases with time.
5. Sodium dichromate and sodium nitrite stimulate the corrosion of low carbon steels in HCl Solution and the degree of stimulation increases with salt concentration.
6. The corrosion rate P, of the steel samples increases linearly with $Na_2Cr_2O_7$ and $NaNO_2$ concentration according to the regressional equations:

$$P = 0.1300 + 0.1694\ C \quad (Na_2Cr_2O_7)$$

$$P = 0.1600 + 0.1417\ C \quad (NaNO_2).$$

7. Inhibitor concentration of 0.20% and time of 30 minutes is recommended for hydrochloric acid pickling of low carbon steels.

## 5.2. RECOMMENDATIONS

By considering the shortcomings of this investigation, the following recommendations are prescribed:

1. Potentiokinetic studies of the corrosion of the steel samples in HCl solution is recommended so that the exact mechanism of corrosion inhibition may be better understood.
2. The effect of inhibitors on the kinetics of pickling should be investigated.
3. The effect of acid concentration on corrosion inhibition should be studied.

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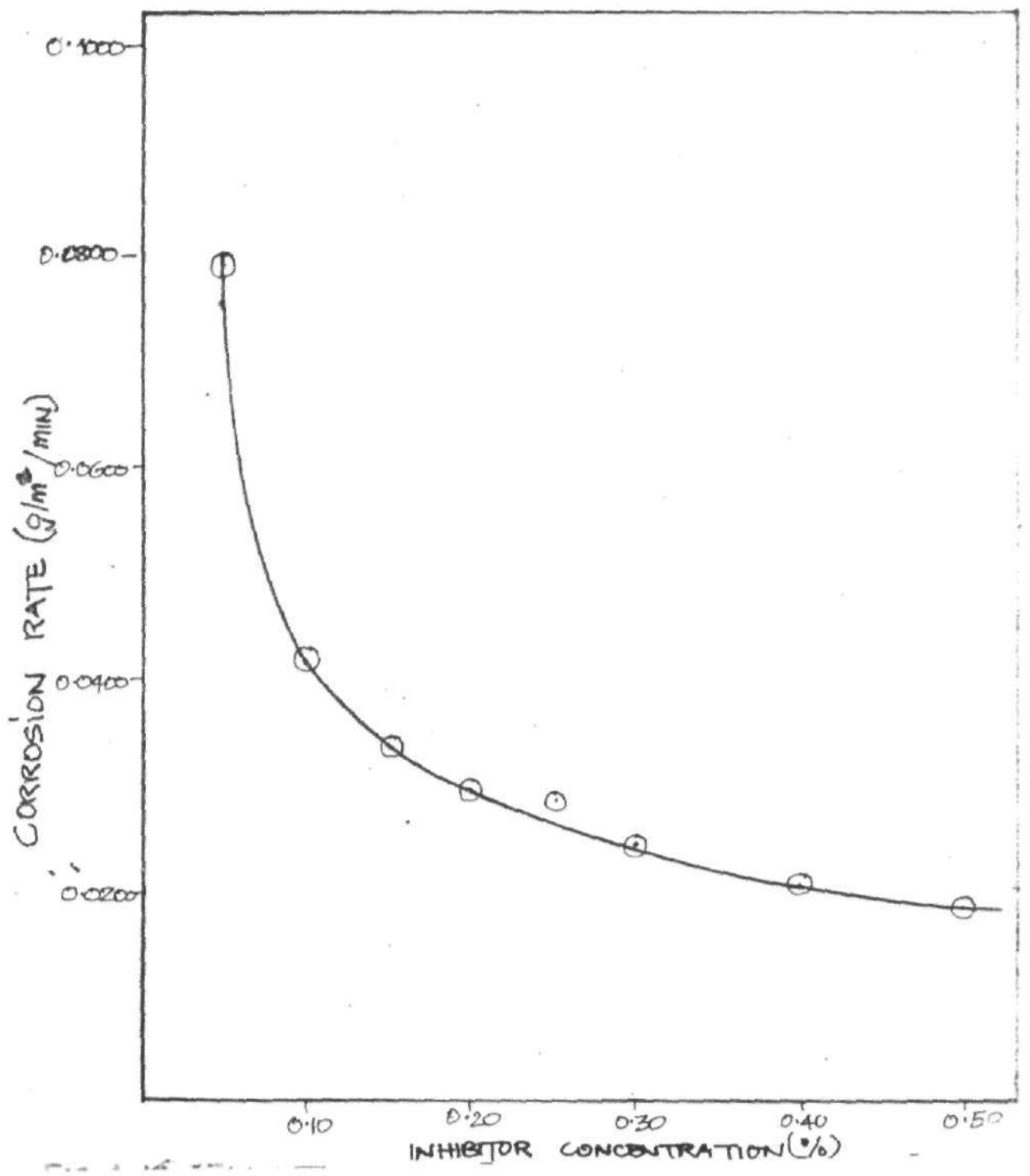



FIGURE 4.13: THE EFFECT OF FORMALDEHYDE CONCENTRATION ON THE CORROSION RATE OF THE STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION

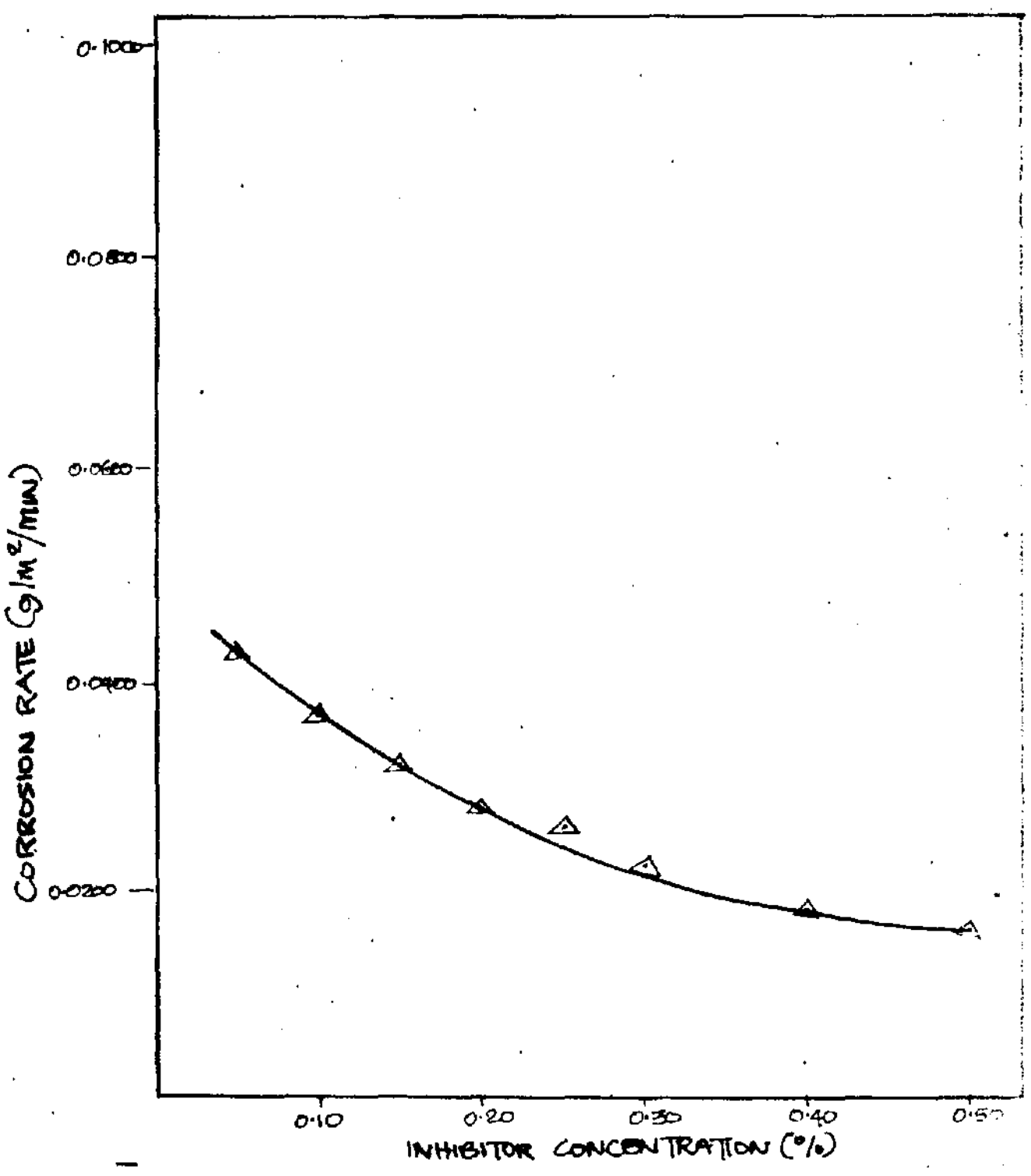



**FIGURE 4.14:** THE EFFECT OF ACETALDEHYDE CONCENTRATION ON THE CORROSION OF THE STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION

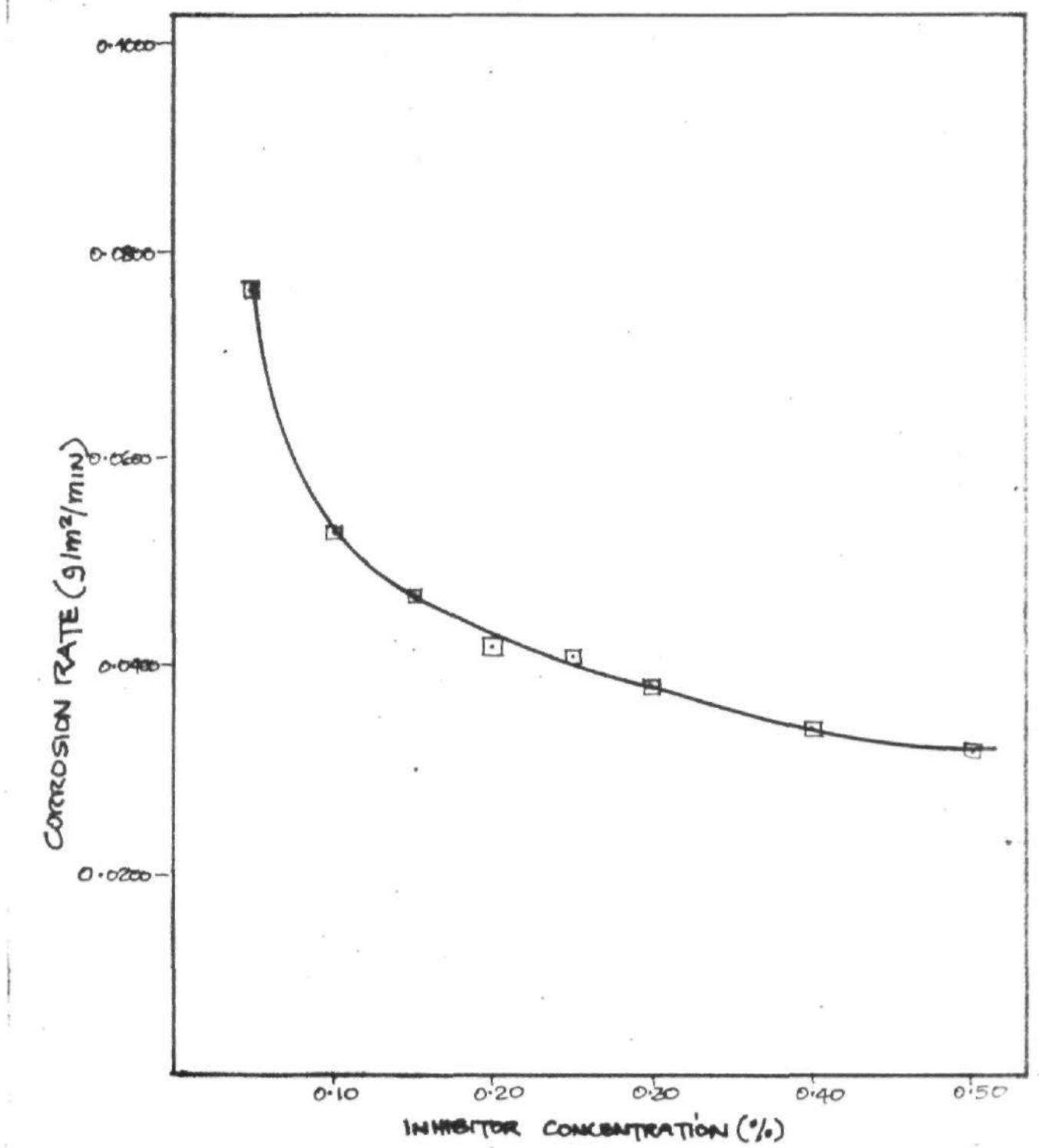



FIGURE 4.15: THE EFFECT OF BENZALDEHYDE ON THE CORROSION OF THE STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION

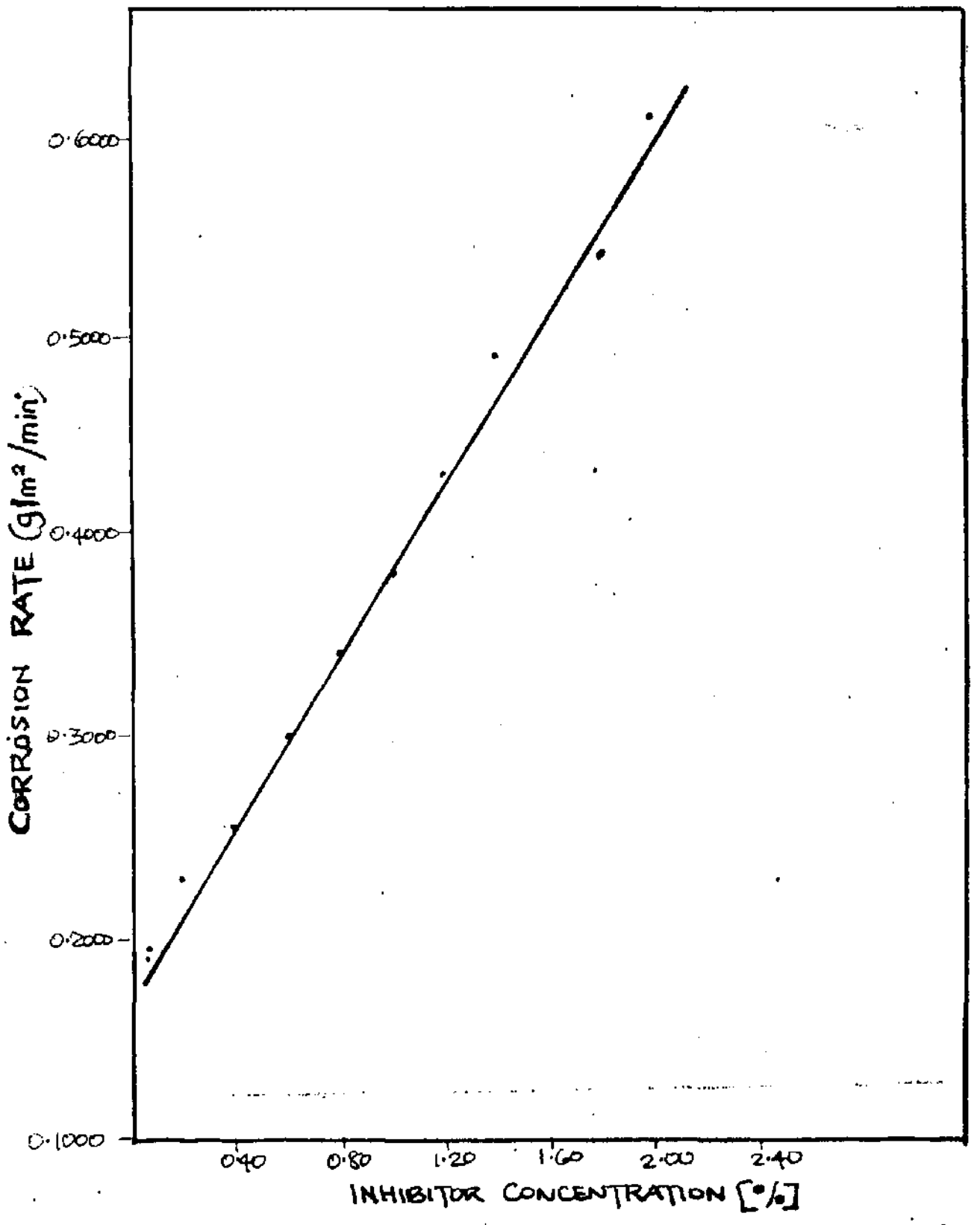



**FIGURE 4.16:** THE EFFECT OF SODIUM DICHROMATE CONCENTRATION ON THE CORROSION RATE OF THE STEEL SAMPLES IN HCl PICKLING SOLUTION

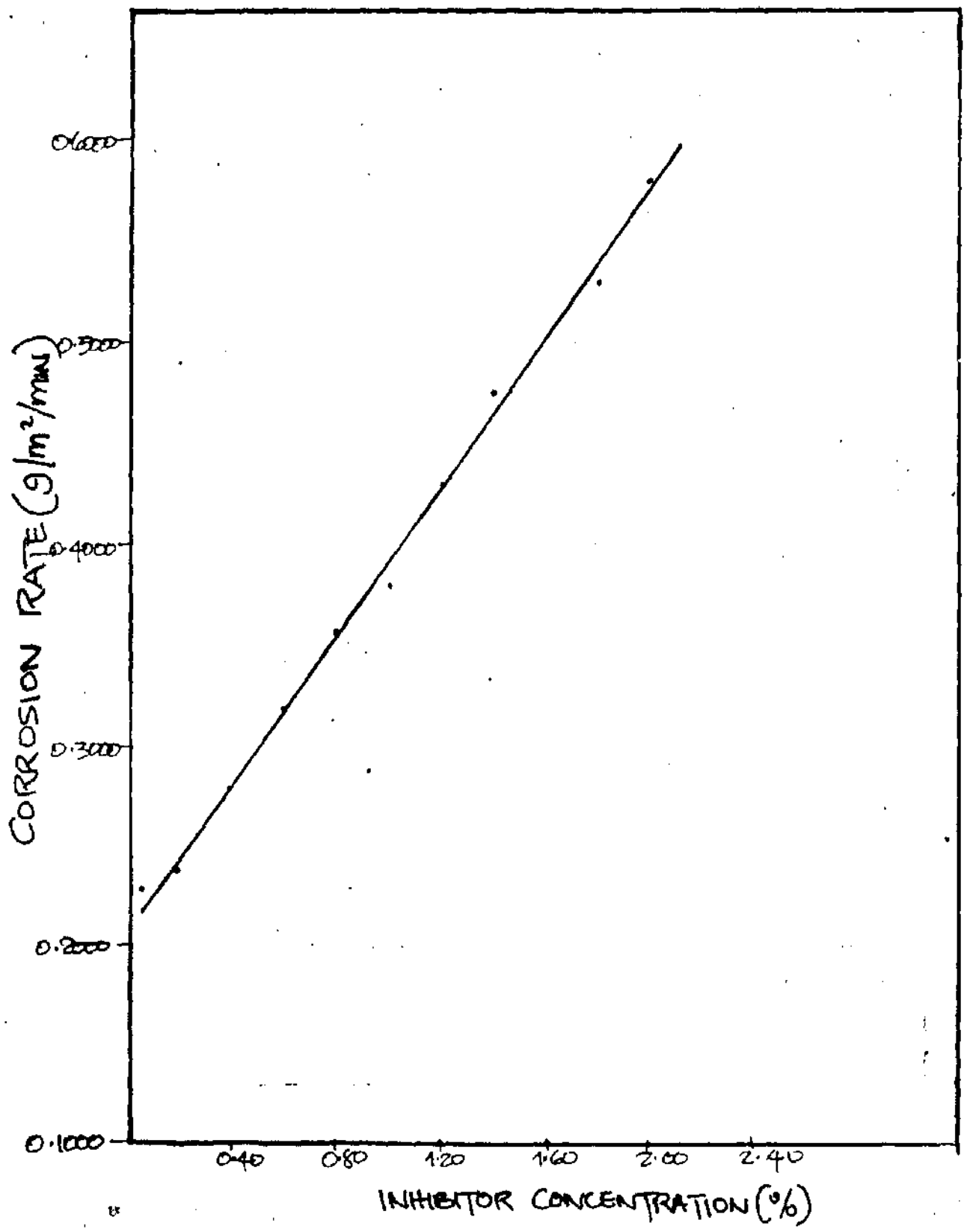



FIGURE 4.17: THE EFFECT OF SODIUM NITRITE CONCENTRATION ON THE CORROSION RATE OF THE STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION

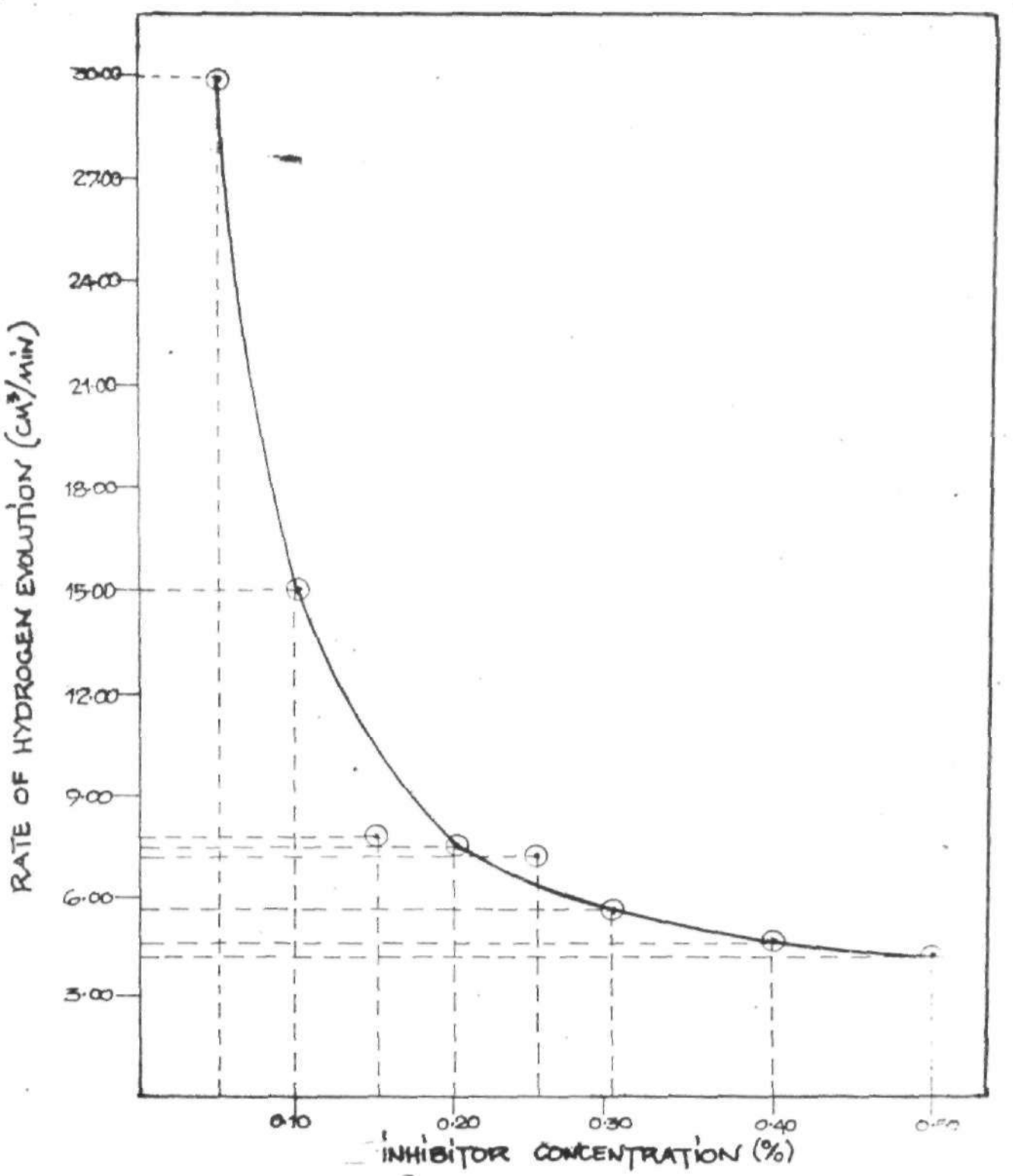



FIGURE 4.18: THE EFFECT OF FORMALDEHYDE CONCENTRATION ON THE RATE OF HYDROGEN EVOLUTIONS OF THE STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION

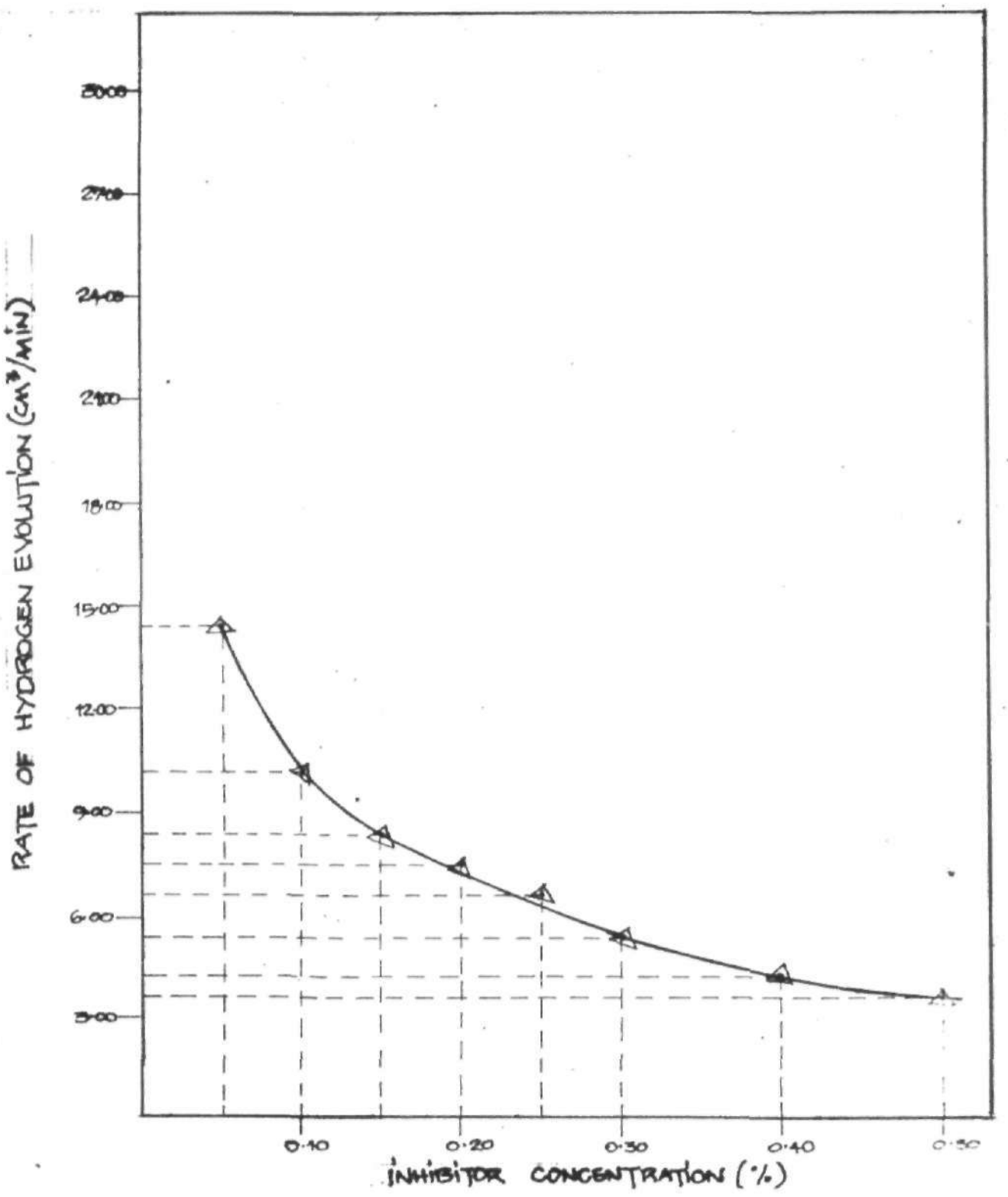



FIGURE 4.19: THE EFFECT OF ACETALDEHYDE CONCENTRATION ON THE RATE OF HYDROGEN EVOLUTION OF THE STEEL SAMPLES IMMERSED IN HCl PICLING SOLUTION

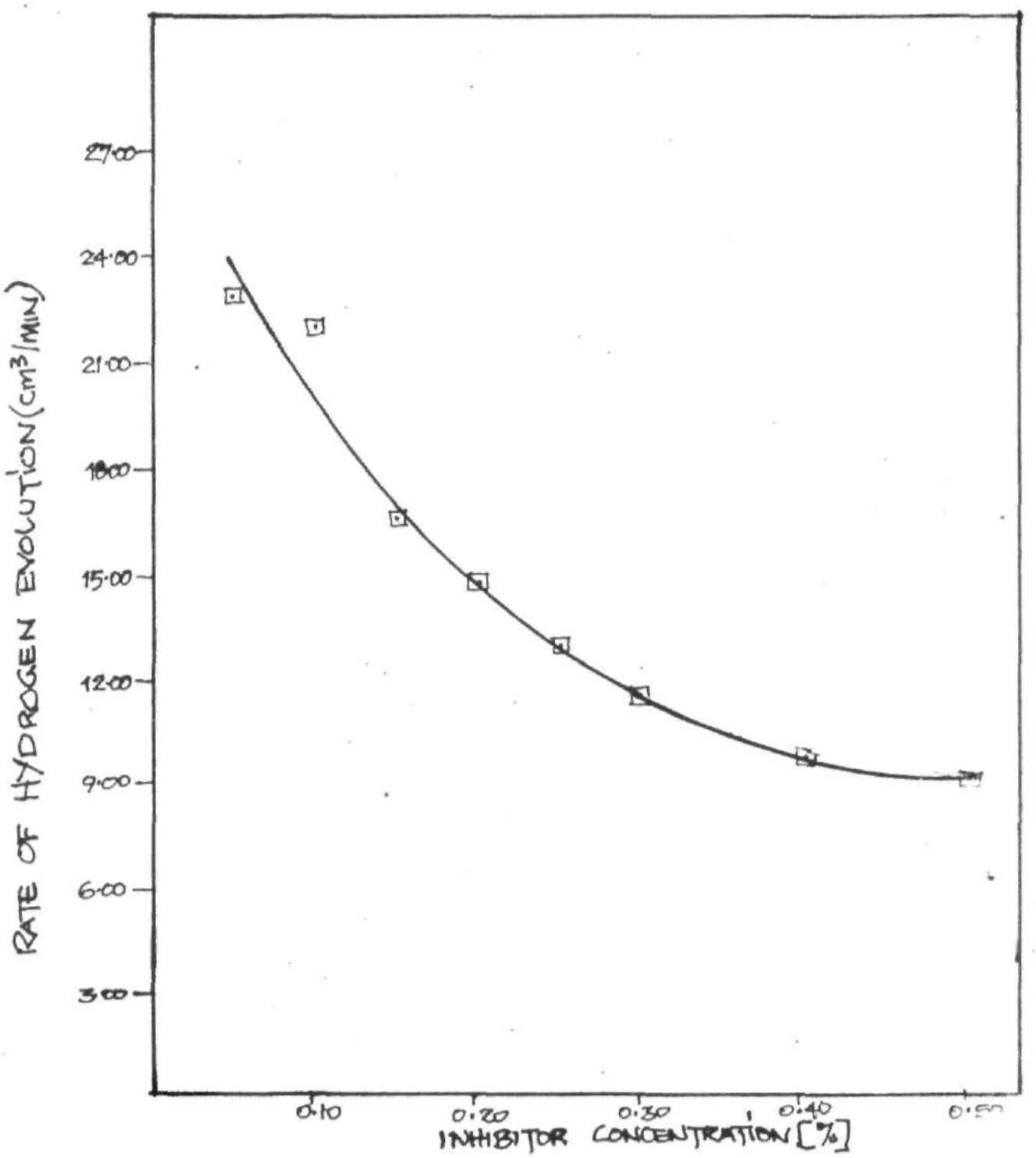



**FIGURE 4.20:** THE EFFECT OF BENZALDEHYDE CONCENTRATION ON THE RATE OF HYDROGEN EVOLUTION OF THE STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION

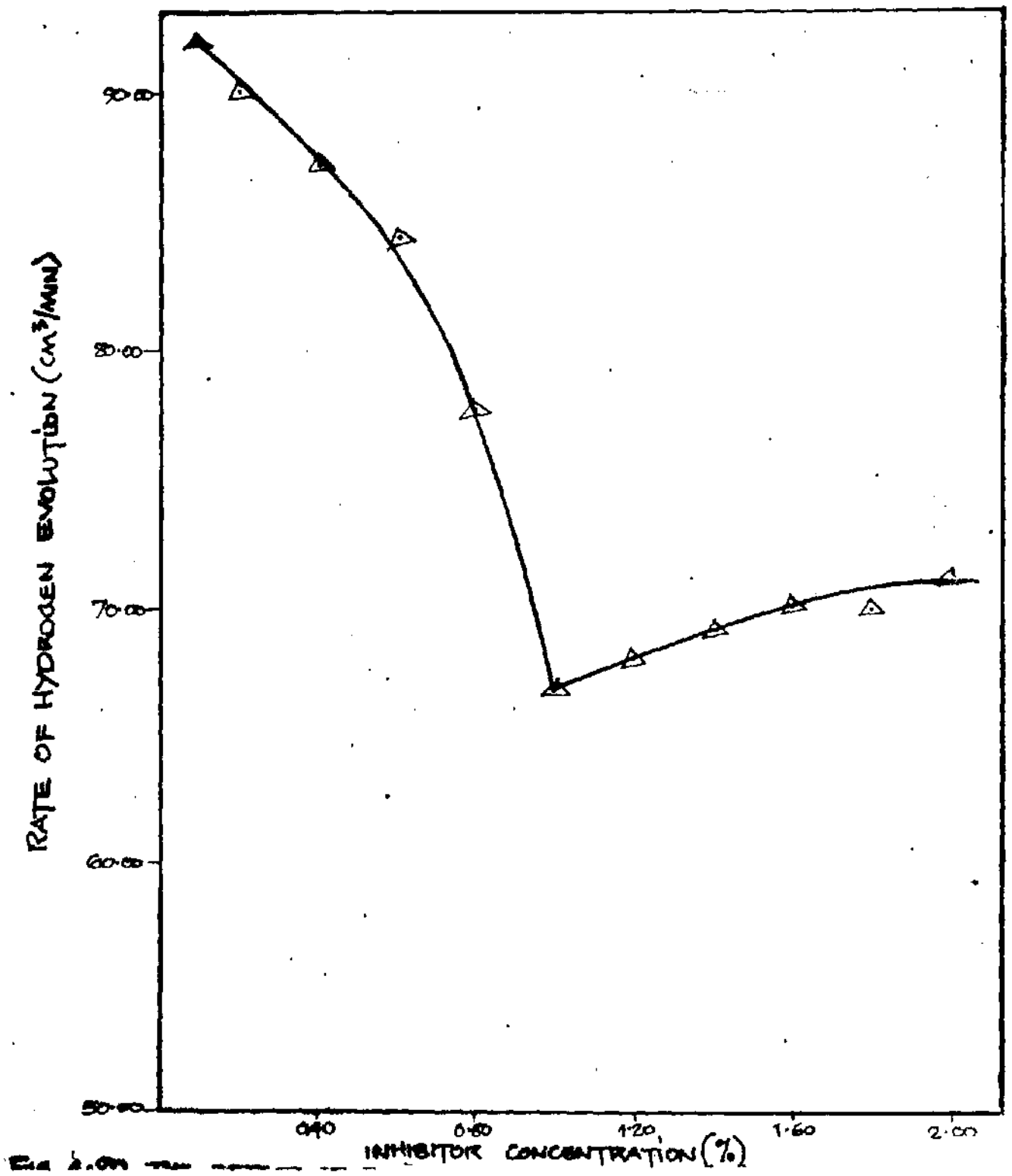



FIGURE 4.21: THE EFFECT OF SODIUM NITRITE CONCENTRATION ON THE RATE OF HYDROGEN EVOLUTION OF THE STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION.

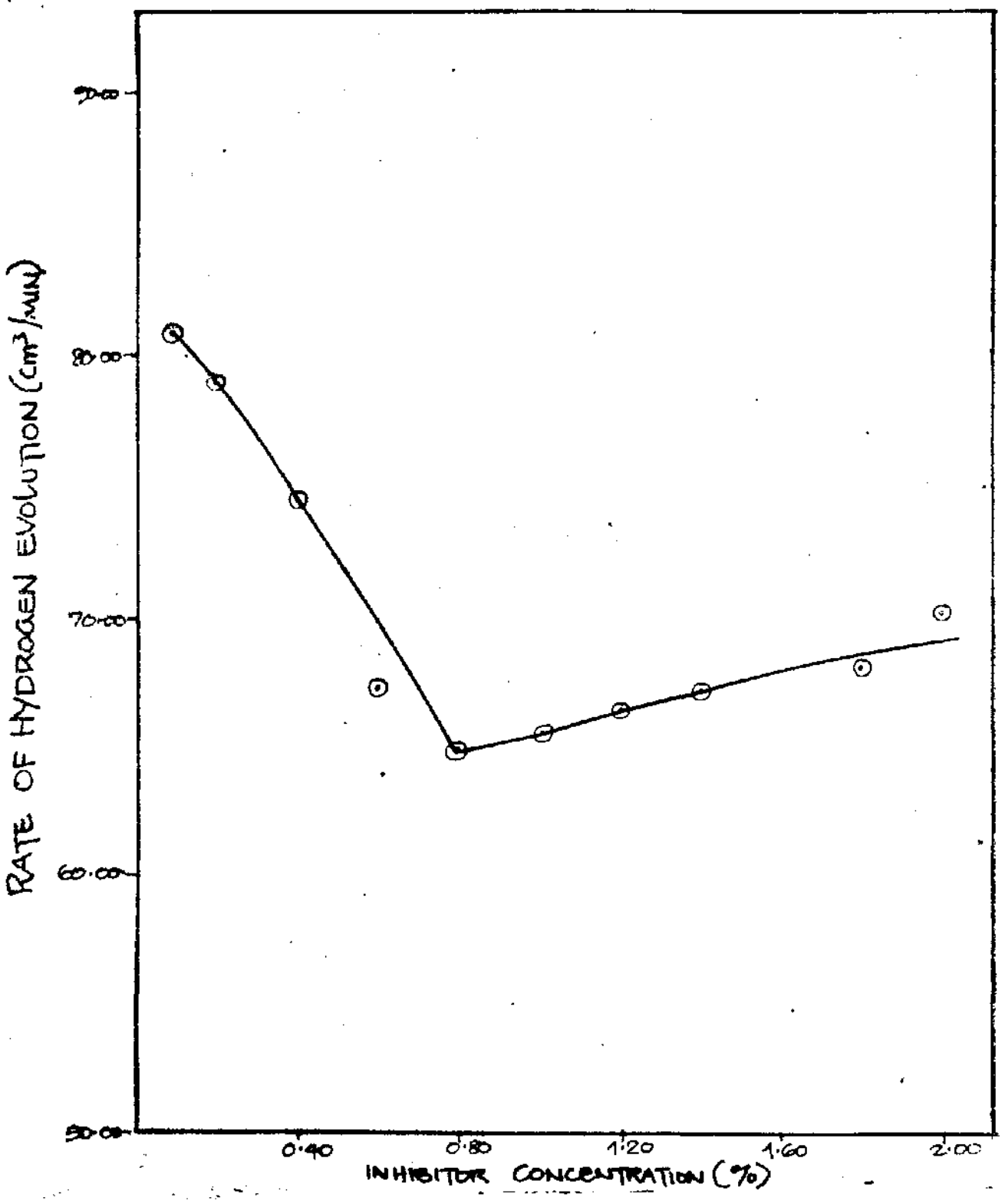



**FIGURE 4.22:** THE EFFECT OF SODIUM DICHROMATE CONCENTRATION ON THE RATE OF HYDROGEN EVOLUTION OF THE STEEL SAMPLES IMMERSED IN HCl PICKLING SOLUTION.