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Evaluation of Corrosion Rates of Mild Steel in Acidic Medium Using Different Techniques

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By

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بِسْمِ اللَّــهِ الرَّحْمَـٰنِ الرَّحِيمِ

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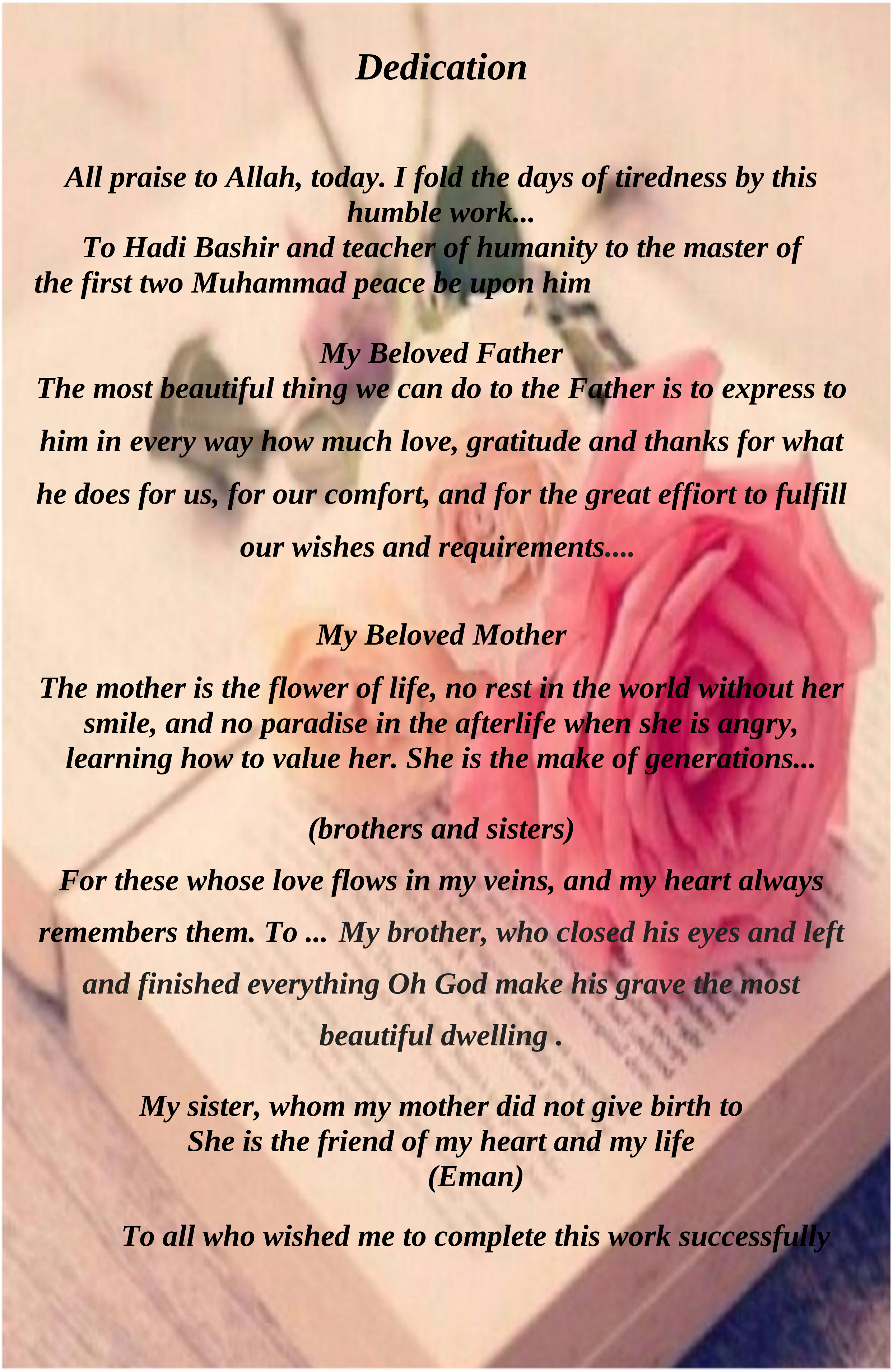

Dedication

All praise to Allah, today. I fold the days of tiredness by this humble work...
To Hadi Bashir and teacher of humanity to the master of the first two Muhammad peace be upon him

My Beloved Father
The most beautiful thing we can do to the Father is to express to him in every way how much love, gratitude and thanks for what he does for us, for our comfort, and for the great effiort to fulfill our wishes and requirements....

My Beloved Mother

The mother is the flower of life, no rest in the world without her smile, and no paradise in the afterlife when she is angry, learning how to value her. She is the make of generations...

(brothers and sisters)

For these whose love flows in my veins, and my heart always remembers them. To ... *My brother, who closed his eyes and left and finished everything Oh God make his grave the most beautiful dwelling .*

My sister, whom my mother did not give birth to
She is the friend of my heart and my life
(Eman)

To all who wished me to complete this work successfully

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WROOD.N.A

Abstract

In this work the inhibition effect of sodium iodide as an inorganic corrosion inhibitor on the corrosion of low carbon steel in hydrochloric acid solution at different a temperatures of (303.15 ,313.15 ,323.15 and 333.15) K has been studied by using weight loss and the electrochemical polarization methods . corrosion inhibition efficiency is found to increase with increasing concentration and time ,the maximum value of inhibition efficiency obtained was 96.07% at 333.15 K in presence of 2.5 mL/L inhibitor concentration and a time of 4h.The results showed that the corrosion rate in the presence and absence of (sodium iodide) as inhibitor is increased with temperature for a given inhibitor concentration,the corrosion rate decreased with increasing inhibitor concentration for a given temperature. The two mechanics were used to explain the adsorption process of corrosion inhibitors on the metal surface (Langmuir adsorption isotherm and Freundlich adsorption isotherm) . It was observed that the inhibitory substance follows the Langmuir adsorption isotherm more than the Freundlich adsorption isotherm .That is the corrosion inhibitor works according to the adsorption on the metal surface and the formation of a single layer.The values of equilibrium constants were used to evaluate standard adsorption free energy (ΔG^0_{ads}) to determine the type of adsorption (Physical, Chemical or mixed mode). In this study, adsorption involves on the predominant chemical adsorption and adsorption occurs a spontaneous on the metal surface because the adsorption free energy values are negative . Arrhenius equation and transition state equation were used to find values the (activation energy E_a, activation of enthalpy ΔH^*, and activation of entropy ΔS^*). XRD and AFM analysis were performed to study the inhibition of sodium iodide in HCl solution . XRD and AFM analyses showed that in presence of sodium iodide surface becomes smooth because of the formation of inhibitive film over metallic surface.

Corrosion rates were studied by electro-polarization under temperatures conditions (303.15 ,313.15 ,323.15 and 333.15) K and the concentration of the inhibitor substance (0, 0.5, 1, 1.5, 2 and 2.5) mL/L . The polarization curves in the presence and absence of inhibitory substances at different temperatures indicate that the values of corrosion current densities increases by increasing the temperature at any concentration of the inhibitor and also that the corrosion current densities decrease with increasing the inhibitor concentrations at any temperature .So E_{Corr} value does not change significantly in presence of NaI suggesting that it is a mixed type inhibitor. The values of cathodic slopes (βc) are larger as compared to the values of anodic slope (βa)

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Chapter Three

List of Symbols and Abbreviations

Symbol	Meaning	Units
C_R	Corrosion Rate	gmd
$C_{R\ uninh}$	Corrosion Rate without Inhibitor	gmd
C_{Rinh}	Corrosion Rate with Inhibitor	gmd
A	Frequency Factor	-------
E_a	Activation Energy	kJ. mol^{-1}
R	Gas Constant	J. mol^{-1}. K^{-1}
T	Absolute Temperature	K
N	Avogadro's Number	molecule.mol^{-1}
h	Planck's Constant	J. s
ΔS^*	Entropy of Activation	kJ. mol^{-1}. K^{-1}
ΔH^*	Enthalpy of Activation	kJ. mol^{-1}
θ	Surface Coverage	--------
IE	Inhibition Efficiency	--------
K_L	Langmuir Adsorption Constant	L / ml
C_i	Inhibitor Concentration	mL/L
$\Delta G^0{}_{ads}$	Standard Adsorption Free Energy	kJ. mol^{-1}
R^2	Correlation Coefficient	--------
K_F	Freundlich Adsorption Constant	L /mL
n''	Slope	--------
k	Rate Constant	L /mL
k_0	Rate Constant in Zero Order	g / m^2.h
k_1	Rate Constant in First Order	1/h
k_2	Rate Constant in Second Order	m^2/ g.h
n'	Order of Reaction	-------
W_1	Weigh the Sample Before Corrosion	gm
W_2	Weigh the Sample After Corrosion	gm
$t_{1/2}$	Half-Life	h
a	Initial Weight of Carbon Steel	gm
η	Over-Potential, (Polarization),	mV

	Overvoltage	
η_a	Over-Potential for Activation Polarization	mV
η_c	Over-Potential for Concentration Polarization	mV
E^0	Equilibrium Potential	-----------
E	Polarized Potential	mV
i	The Current Density	mA/cm^2
i_0	Exchange Current Density	mA/cm^2
β	Tafel Constant	-----------
F	Faraday Constant	columbs/mole
α	The Symmetry Coefficient	-----------
z	Number of Electrons	eV
i_a	Anodic Current Density	mA/cm^2
i_c	Cathodic Current Density	mA/cm^2
C	Concentration	M
ηR	Resistance Polarization	mV
δ	Diffusion Layer Thickness	cm
K	Specific Conductivity	Ω^{-1}.cm^{-1}OrS cm^{-1}
D	Diffusivity	cm / s^2
C_b	Bulk Concentration	g .mole/cm^3
C_S	Surface Concentration	g .mole/cm^3
AA	Surface Area	cm^2
i_L	Limiting Current Density	mA/cm^2
ρ	The Specific Resistance	Ω..cm
l	The Solution Gap Between the Capillary Tip and the Working Electrode	cm
i_{corr}	Corrosion Current Density	mA/cm^2
E_{corr}	Corrosion Potential	mV
b_a	Anodic Tafel Slope	mV
b_c	Cathodic Tafel Slope	mV
i_{app}	Applied Current Density	mA/cm^2
β_a, β_c	Anodic and Cathodic Tafel Constant	mV/dec

R_a	*The Roughness Average*	*nm*
R_y	*The Peak-Valley Height*	*nm*
R_q	*The Root Mean Square*	*nm*

List of Abbreviation

Meaning	*Abbreviation*
Molybdate ions	MoO_4^{-2}
Sodium Chloride	*NaCl*
Mils Per Year	*mpy*
Stainless Steel	*SS*
Polyvinylpyrollidone	*PVP*
Potassium Iodide	*KI*
Zinc Ions	Zn^{+2}
Fourier Transformed Infrared	*FTIR*
Scanning Electron Microscopy	*SEM*
Atomic Force Microscopy	*AFM*
X-ray Diffractometry	*XRD*

X-ray Photoelectron Spectroscopy	***XPS***
Attenuated Total Reflection	***ATR***
Energy Dispersive X-ray	***EDX***
Sodium Molybdate	Na_2MoO_4
Phosphoric acid	H_3PO_4
Phytic Acid	***PA***
Sulfuric Acid	H_2SO_4
Open Circuit Potential	***OCP***
Silicate	SiO_3^{-2}
Phosphate	PO_4^{-3}
Sodium Molybdate	***SM***
Impedance Spectra r	***AC***
Zink Hydroxide	$Zn(OH)_2$
Iron	Fe^{+2}
Trisodium Citrate	***TSC***

Sodium Nitrite	$NaNO_2$
L-tryptophane	***Trp***
Nitrogen Dioxide	NO_2^-
Iodide	I^-
Iron(III) Oxide	Fe_2O
Electrochemical Impedance Spectroscopy	***EIS***
Potentiodynamic Polarization	***PDP***
Hydroxypropyl Cellulose	***HPC***
2-Undecy-N-Carboxymethyl-N-Hydroxyethyl Imidazoline	***UHCI***
Tannic Acid	***TA***
Linear Polarization Resistance	***LPR***
Hydrochloric Acid	***HCl***
Sodium Citrate	***SC***
Sodium Dodecylbenzene Sulphonate	***SDBS***
Diammonium Phosphate	$(NH_4)_2HPO_4$
Sodium Vanadate	$NaVO_3$

Cydonia Vulgaris leaves	**CVL**
Sodium Molybdate	Na_2MoO_4
Central Composite Design	**CCD**
Response Surface Methodology	**RSM**

Chapter One

Introduction & Previous Studies

1.1. Introdication

Corrosion can be defined as an irreversible reaction of a material with the environment which usually (but not always) results in the degradation of the material and deterioration of a metal by chemical or electrochemical reaction with the surrounding environmen and there are several parameters that influence the rate , nature of the corrosion reactions which include the material, the properties of the material , the environment, the chemical composition, the constituents and the temperature [1,2] .Corrosion is one of the main concerns in the durability of metallic materials and their structures. Many efforts have been made to develop a corrosion inhibition process to prolong the life of existing structures and minimize corrosion damages [3].A corrosion inhibitor is a substance which when added in small concentration to an environment effectively reduces the corrosion of a metal exposed to that environment[4].The first step in the adsorption of natural or organic inhibitor molecules on the surface of metal usually involves replacement of water molecules adsorbed at the metal surface [5] .The corrosion inhibitors types can be chemicals synthetica natural. The inhibitors can be classified depending to on inhibitory factors such as the chemical kind of the inhibitors , the mechanism of activity , Oxidants or do not oxidants generally the inhibitors interact with the rust (corrosion product) initially formed resulting in a consistent and insoluble layer on the metal surface[6].Mild steel is a metal that has found high range of mechanical and industrial application world wide. It is one of the best preferred construction material for industries due to its availability and mechanical properties however, it is highly vulnerable to corrosion and pose high economic burden to replace almost all of the environments in which metals are used serve as potential hostile and aggressive medium to them their successful application depends on the protective mechanisms against corrosion,corrosion occurs when protective mechanisms have been overlooked break down or have been exhausted leaving the metal vulnerable to attack [7]. All metals have a characteristic, inherent tendency to corrode and react in aqueous environments to produce metal ions and release electrons. This inherent reactivity can be shown in terms of free-energy(ΔG).The inherent reactivity of a metal can be expressed by the magnitude of the free energy change on the metal suffering a corrosion process. The corrosion process of the metal dissolving as ions generates some electrons that are consumed by a secondary reaction; the two processes must balance their charges. The sites hosting these two processes may be located close to each other on the metals surface, or far apart depending on local circumstances. When a metal (Fe) is placed in pure water, some ions will immediately pass into solution:

$$Fe \longrightarrow Fe^{+2} + 2e^{-} \qquad E^{0} = 0.44\ V \qquad (1.1)$$

Building-up negative charge on the metal and the existence of metal ions in solution make it possible for a back-reaction to proceed:

$$Fe^{+2} + 2e^{-} \longrightarrow Fe \qquad E^{0} = -0.44\ V \qquad (1.2)$$

and ultimately the equilibrium is established:

$$Fe \longleftrightarrow Fe^{+2} + 2e^{-}$$

A steady potential difference exists between the metal and the solution.The magnitude of this potential difference depends on the metal type and composition of the solution [8].

Corrosion of metallic materials can be divided into two main groups:

- ☐ ***Wet Corrosion*** **:** It occurs when the corrosive environment is a liquid such as water with dissolved species. The liquid is an electrolyte and the process is typically electrochemical in nature; also corrosion may occur in other fluids such as fused salts and molten metals.

- ☐ ***Dry Corrosion :*** It occurs when the corrosive environment is a dry gas and the corrosion is also repeatedly called chemical corrosion and the best-known example is a high- temperature corrosion [9].

1.2. Importance of Corrosion Studies

The importance of corrosion studies is twofold.The first is economic, including the reduction of material losses resulting from wasting away or sudden failure of piping, tanks, metal components of machines, ships hulls marine structure . The second is conservation, applied primarily to metal resources, and the wastage of which includes corresponding losses of energy and water resources accompanying the production and fabrication of metal structures. Losses sustained by industry, by amount to many billions of dollars annually [10]**.**

1.3. Types of Corrosion

a. Uniform (General) Corrosion

It is the rate of metal loss over the exposed surface, which is characterized by corrosive attack proceeding evenly over the entire surface area, or a large fraction of the total area. Uniform corrosion is the simplest form of corrosion. It is one of the most easily measured and predictable forms of corrosion, making disastrous failures relatively rare; therefore it is not always the most important in terms of cost or safety. But if surface corrosion is permitted to continue, the surface may become rough and surface corrosion can lead to more serious types of corrosion [11,12].

b. Pitting Corrosion

Pitting corrosion is characterized by a highly localized loss of metal. It appears as a deep tiny hole on the metal. The width of the pit may increase with time but not to the extent to which the depth increases. Most often, the pit opening remains covered with the corrosion product, making it difficult to detect during inspection [11,12].

c. Crevice Corrosion

This is localized corrosion concentrated on crevices in which the gap is sufficiently wide for liquid to penetrate into the crevice and sufficiently narrow for the liquid in the crevice to be stagnant. Various metals Al,Fe,Cr,and Ni may suffer from crevice corrosion (CC). which is affected by several factors; of a metallurgical, environmental, electrochemical, surface physical and last but not least, a geometrical nature. crevice corrosion occurs beneath flange gaskets nail,screw heads, and paint coating edges in overlap joints between tubes, and tube plates in heat exchangers etc. The same form of corrosion develops beneath deposits.corrosion products, dirt, sand, leaves, and marine organisms, hence it is called deposit corrosion in such cases. It comprises mechanisms, modelling, test methods and results, practical experience, protective measures, and monitoring [11].

d. Intergranular Corrosion

Intergranular corrosion is a localized attack on or at grain boundaries with insignificant corrosion on other parts of the surface. This is a dangerous form of corrosion because the cohesive forces between the grains may be too small to withstand tensile stresses.The toughness of the material is seriously reduced at a relatively early stage, and fracture can occur without warning [12].

e. *Stress Corrosion Cracking* (SCC)

Stress corrosion cracking (SCC) is a process involving the initiation of cracks and their propagation, possibly up to complete failure of a component, due to the combined action of tensile mechanical loading and a corrosive medium. This stress can either be applied (external load), or can be residual stress in the metal (e.g. due to production process or heat treatment) [11].

f. Erosion Corrosion

The term "erosion" applies to deterioration due to mechanical force. Erosion corrosion is usually caused by a gaseous or corrosive liquid flowing over the metal. It is affected by velocity, turbulence, impingement, the presence of suspended solids and temperature. Turbulence phenomena can destroy protective films and cause very high corrosion rates in materials, therefore all equipment exposed to flowing fluid is subject to erosion corrosion [12].

g. *Selective Corrosion*

It is also called selective leaching or de metal it implies the selective dissolution of one of the components of an metal that forms a solid solution. It leads to the formation of a porous layer made of the more noble metal [13] .

h. *Galvanic Corrosion*

It is also called bimetallic corrosion it results from the formation of an electrochemical cell between two metals. The corrosion of the less noble metal is thus accelerated [13].

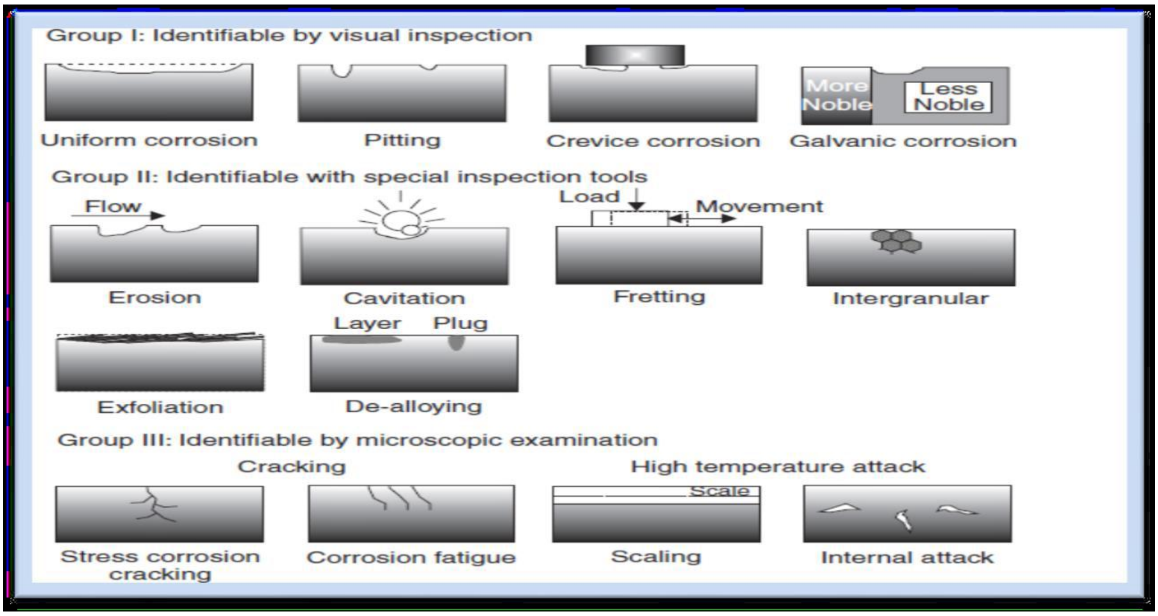


Figure (1.1) Types of Corrosion [14]

1.4. Corrosion Inhibitors

An inhibitor is a substance which retards or slows down the rate of chemical reaction. Thus, a corrosion inhibitor is a substance which, when added to an environment, decreases the rate of attack by the environment on a metal. Corrosion inhibitors are usually added in small amounts to acids, cooling waters, steam, and other environments, either continuously or intermittently to prevent serious corrosion [15].

Inhibitors decrease or prevent the reaction of the metal with the media. They reduce the corrosion rate by [16] :

(i) adsorption of ions/molecules onto metal surface,

(ii) increasing or decreasing the anodic and/or cathodic reaction,

(iii) decreasing the diffusion rate for reactants to the surface of the metal,
(iv) decreasing the electrical resistance of the metal surface.
(v) Using inhibitors that are often easy to apply and have in situ application advantage.

1.5. Inhibitors Classifications

The corrosion inhibitors can be chemicals either synthetic or natural and could be classified by:

- the chemical nature as organic or inorganic;

In general the inorganic inhibitors have cathodic actions or anodic. The organics inhibitors have both actions, cathodic and anodic and the protective by a film adsorption.

- the mechanism of action as anodic, cathodic or a anodic-cathodic mix and by adsorption action or as oxidants or not oxidants [17].

The classification of the inhibitors is shown in the following scheme :-

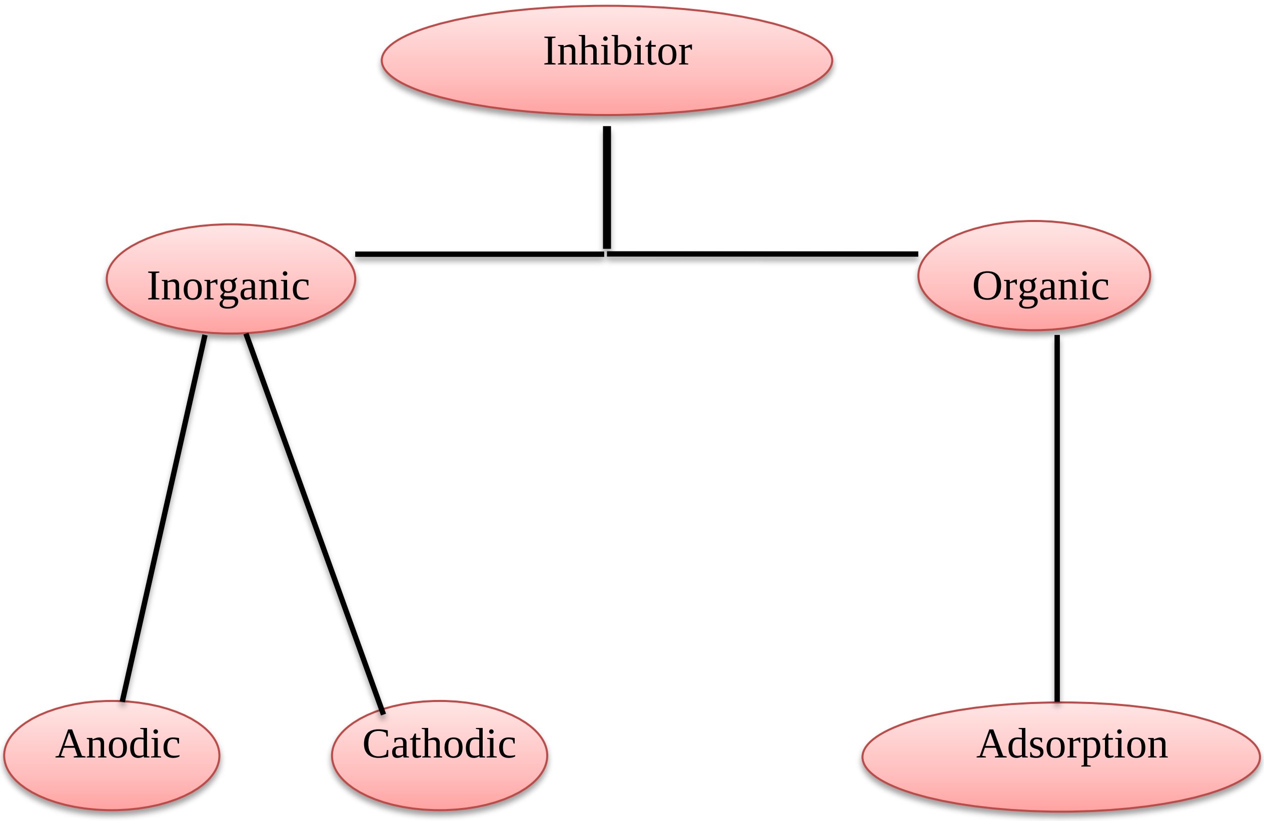


Figure (1.2) Scheme Classification of Inhibitors.

1.5.1. Inorganic Inhibitor

1.5.1.1. Anodic Inhibitors

Anodic inhibitors (also called passivation inhibitors) act by a reducing anodic reaction, that is, blocks the anode reaction and supports the natural reaction of passivation metal surface, also, due to forming a film adsorbed on the metal. In general, the inhibitors react with the corrosion product, initially formed, resulting in a cohesive and insoluble film on the metal surface [17,18] .Fig (1.3) shows a potentiostatic polarization diagram of a solution with behavior inhibitor anodic. The anodic reaction is affected by the corrosion inhibitors and the corrosion potential of the metal is shifted to more positive values. As well, the value of the current in the curve decreases with the presence of the corrosion inhibitor.

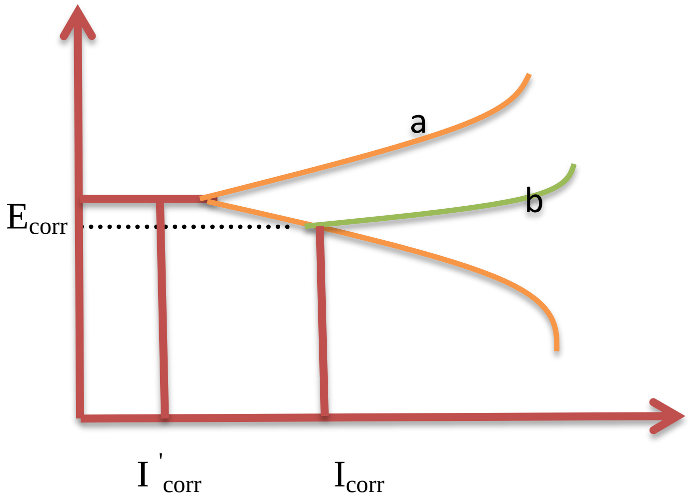


Figure (1.3) Potentiostatic polarization diagram: electrochemical behavior of a metal in a solution with anodic inhibitor (a) versus without inhibitor (b).

1.5.1.2. Cathodic Inhibitors

During the corrosion process, the cathodic corrosion inhibitors prevent the occurrence of the cathodic reaction of the metal. These inhibitors have metal ions able to produce a cathodic reaction due to alkalinity thus producing insoluble compounds that precipitate selectively on cathodic sites. Deposit over the metal a compact and adherent film restricting the diffusion of reducible species in these areas. Thus increasing the impedance of the surface and the diffusion restriction of the reducible species that is the oxygen diffusion and electrons conductive in these areas.

These inhibitors cause high cathodic inhibition [17,18,19] .Fig (1.4) shows an example of a polarization curve of the metal on the solution with a cathodic inhibitor. When the cathodic reaction is affected the corrosion potential is shifted to more negative values.

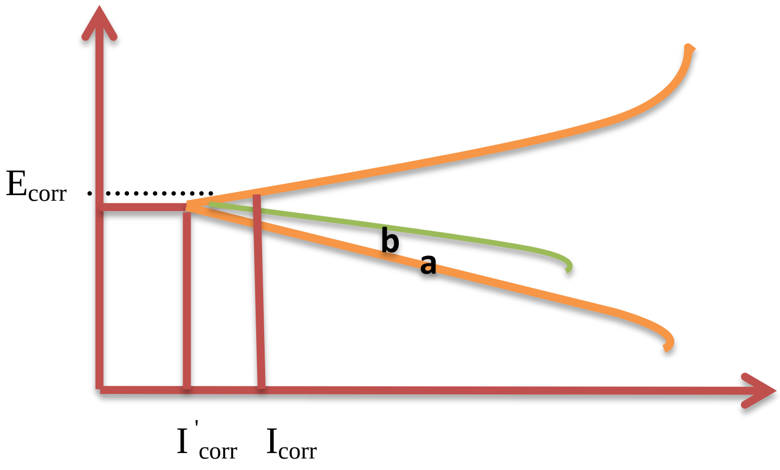
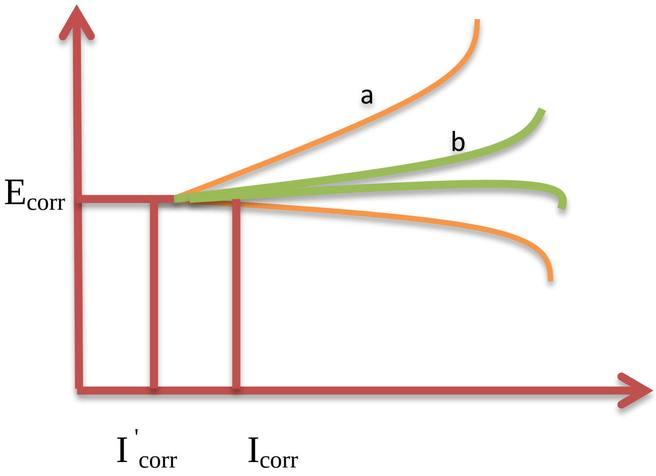


Figure (1.4) Potentiostatic polarization diagram: electrochemical behavior of the metal in a cathodic inhibitors solution (a) as compared to the same solution without inhibitor (b).

1.5.2. Organic Inhibitor

Organic compounds are used as inhibitors .Occasionally they act as cathodic,anodic or together as cathodic and anodic inhibitors nevertheless .As a general rule they act through a process of surface adsorption designated as a film forming. Naturally the occurrence of molecules exhibits a strong affinity for metal surfaces compounds showing good inhibition efficiency and low environmental risk [20]. These inhibitors build up a protective hydrophobic film adsorbed molecules on the metal surface which provides a barrier to the dissolution of the metal in the electrolyte.They must be soluble or dispersible in the medium surrounding the metal [17].In Fig(1.5) which shows a theoric potentiostatic polarization curve, it can be seen that the effect of the solution containing organic inhibitor on the metal presents an anodic and cathodic behavior. After the addition of the inhibitor, the corrosion potential remains the same, but the current decreases from *Icor* to *I'cor*.



Figure(1.5) Theoretical potentiostatic polarization diagram: electrochemical behavior a metal on a solution containing a cathodic and anodic inhibitor (a) compared to the same solution without the inhibitor (b).

1.6. Effect of Operating Conditions

1.6.1 Effect of Temperature

Temperature increases the rate of almost all chemical reactions, which leads to increase in corrosion rate. Like most chemical reactions, the rate of corrosion of iron and steel in aqueous acid solutions increases with increasing temperature [21]. This effect can be expressed by Arrhenius equation in which the rate of corrosion change with temperature [22].

$$C_R = A\ exp\left(\frac{-Ea}{RT}\right) \qquad (1.3)$$

Where A is Frequency factor, Ea is Activation energy (kJ/mole), R is Gas constant (8.314 J/mole.K), T is Absolute temperature (K). From Arrhenius equation, activation energy and frequency factor can be calculated by taking the natural (ln) of the previous in the equation:-

$$Ln\ C_R = ln\ A - \frac{E_a}{R} \cdot \frac{1}{T} \qquad (1.4)$$

So, ln (C_R) can be plotted against (1/T) with a slope of (-Ea / R) and intercept of ln A. Temperature changes have the greatest effect when the rate determining step is the activation process. It is therefore not surprising that the activation energy of inhibited reactions at high coverages can be either larger or smaller than that of uninhibited reactions. Information contained in the literature shows that the relationship ln (C_R) = f (1/ T) is quite frequently, although not always linear in the presence of inhibitor. While equation of transition state can be used to calculate enthalpy and entropy of activation as [23].

$$C_R = \frac{RT}{Nh}\ exp\left(\frac{\Delta S^*}{RT}\right)\ exp\left(\frac{-\Delta H^*}{R}\right) \qquad (1.5)$$

$$\frac{C_R}{T} = \frac{R}{Nh} exp\left(\frac{\Delta S^*}{R}\right)\ exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (1.6)$$

$$ln\left[\frac{C_R}{T}\right] = ln\left(\frac{R}{Nh}\right) exp\left(\frac{\Delta S^*}{R}\right)\ exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (1.7)$$

$$ln\left[\frac{C_R}{T}\right] = ln\left(\frac{R}{Nh}\right) + ln\ exp\left(\frac{\Delta S^*}{R}\right) + ln\ exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (1.8)$$

$$ln\ \left[\frac{C_R}{T}\right] = ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^*}{R}\right) - \left(\frac{\Delta H^*}{R}\right) \cdot \frac{1}{T} \qquad (1.9)$$

Where; h is the Planck's constant (6.62×10^{-34} J.s), N is the Avogadro's number (6.02×10^{23} molecule.mol^{-1}), ΔS* is the apparent entropy of activation ($kJ.mol^{-1}.K^{1}$), ΔH* is the enthalpy of activation ($kJ.mol^{-1}$).From equation (1.9) we can plot ln (C_R/T) against 1/T and the slope of the straight line shows a value ($- \Delta H^*/R$) and intercept shows a value of ($\Delta S^*/R + \ln R / N h$) from which ΔH^* and ΔS^* can be calculated.

1.6.2 Effect of Inhibitor Concentration

Investigators of acid corrosion soon learn that there is a characteristic relation between inhibitor concentration and loss in weight of the metal specimen . As the concentration of inhibitor increases the weight loss decreases and tends to approach a low constant value which depends on the properties of particular inhibitor [21].The inhibitor concentration can be related to amonut of inhibitors adsorbed on metal surface by adsorption isotherm. The most frequently used isotherms are Langmuir, Freundlich and Kinetic-thermodynamic models [24]. To obtain the adsorption isotherm the degree of surface coverage (θ) for various concentrations of the inhibitor must be calculated and the various models must be tested to show the compatibility of the model with the data through the equations following.

$$\boldsymbol{\theta} = \frac{\boldsymbol{IE}}{\mathbf{100}} \qquad \textbf{\textit{(1.10)}}$$

Where

θ is the Surface coverage and IE is the inhibitor efficiency.

a . Langmuir Adsorption Isotherm

The model for the Langmuir isotherm is a set of uniform adsorption sites and many cases of strong adsorption do not fit this isotherm. Mathematically, this isotherm is given as:

$$\boldsymbol{\theta} = \frac{K_L . C_i}{1+K_L\, C_i} \qquad \textbf{\textit{(1.11)}}$$

Where K_L is the equilibrium constant (L/mL) for the Langmuir adsorption isotherm representing the degree of adsorption (i.e., the higher the value of K_L indicates that the inhibitor is strongly adsorbed on the metal surface, C_i is the inhibitor concentration (mL/L), and θ is the surface coverage [21]. Rearranging equation (1.11) will give:

$$\frac{C_i}{\theta} = \frac{1}{K_L} + C_i \qquad (1.12)$$

$$K_L = \frac{1}{55.5}\, exp\left(\frac{-\Delta G^0_{ads}}{RT}\right) \qquad (1.13)$$

$$\Delta G^{0}_{ads} = -\, RT\ ln\ 55.5\ K_L \qquad (1.14)$$

Where (55.5) is the water concentration in solution expressed in M. Equation (1.12) can be plotted as C_i / θ against C_i from intercept the values of K_L. Can be calculated behavior of equilibrium constant of adsorption (K_L) was noticed to increased with increase in temperature [25].

b . Freundlich Adsorption Isotherm

This isotherm can be represented by the equation (1.15).

$$\Theta = K_F\ C_i^{n''} \qquad (1.15)$$

Where K_F and n'' are constant for a given system at a given temperature [25]. This isotherm can be written as:

$$Ln\ \Theta = ln\ (K_F\ C_i^{n''}) \qquad (1.16)$$

$$Ln\ \Theta = ln\ K_F + n''\ ln\ C_i \qquad (1.17)$$

Where; θ is surface coverage, K_F is the equilibrium constant for the Freundlich adsorption constant (L/mL), n'' is slope. Equation (1.17) can be plotted as ln θ against ln C_i , where slope and intercept yield the values of n" and K_F respectively.

1.7 Effect of Reaction Time

The rate of reaction can be obtained by plotting the concentration of carbon steel consumption against time and measuring the slope of the curve dw/dt (W is weight loss and t is time) at the required time. The rate of reaction obtained from such a method is known as instantaneous rate. For the determination of the instantaneous rate at any point, the slope of the curve is determined.The rate of reaction can be expressed by the following equations [26]:

$$\frac{dw}{dt} = k\, w^{n'} \qquad (1.18)$$

$$\ln\left(\frac{dw}{dt}\right) = \ln k + w^{n'} \qquad (1.19)$$

$$\int \frac{dW}{W^{n'}} = k \int dt \qquad (1.20)$$

Equation (1.20) can be integrated for different values of n`. Equations (1.21, 1.22 and 1.23) represent the rate equation for zero first and second order respectively :

$$X = k_0\ t \qquad (1.21)$$

$$W_1 = W_2\, exp\,(k_1\, t) \qquad (1.22)$$

$$k_2\, t = \frac{1}{a-x} - \frac{1}{a} \qquad (1.23)$$

Where W_1 is the weigh the sample before corrosion at t = 0 (gram) W_2 is weigh the sample after corrosion at any time (gram) ,($\Delta W = x$), x is the reaction concentration and $t_{1/2}$ is half-life (h). The half-life period is defined as the time necessary for the concentration of a reactant to decrease to half of its initial value. Half-life indicates the stability of reactants, the longer half-life the greater the stability of reactants.

1.8 Polarization

When there is no net current flows from an electrode then this electrode is at equilibrium state and its potential is the equilibrium potential (E°). When net current flows to or from its surface the potential changes from E° to Ei the electrode is then said to be polarized and the process is termed as polarization. Polarization is measured in volts as follows:

$$\eta = E_i - E^\circ \qquad (1.24)$$

Where

η = The Over-potential, (polarization), overvoltage

E_i = The polarization potential.

E^0 = Equilibrium potential

Fig (1.6) shows polarization curves (E vs. log i) for the corrosion of metal in a reducing acid in which there are two exchange processes involving oxidation of M/M^+ and reducing H^+/H_2 [27].

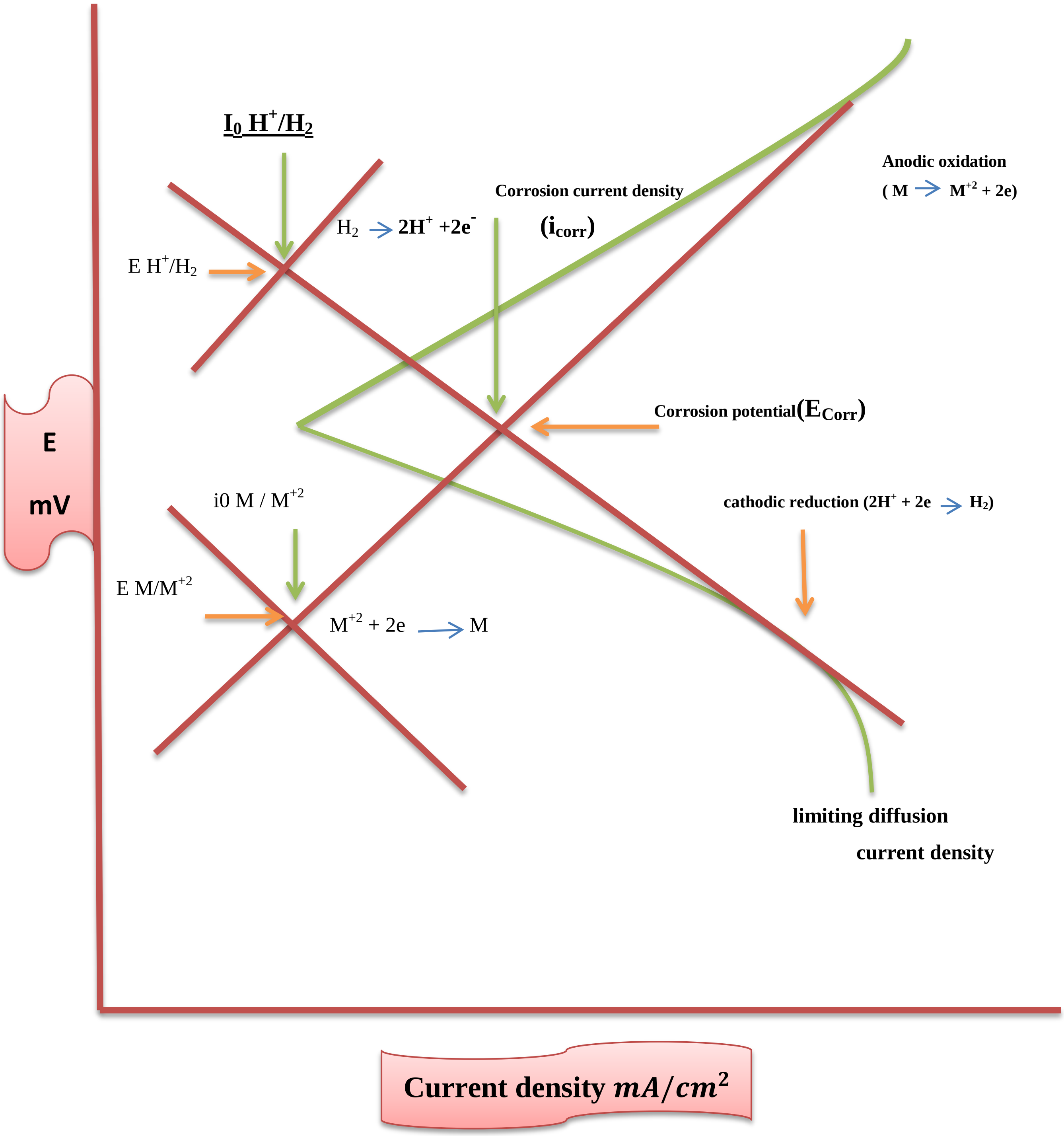
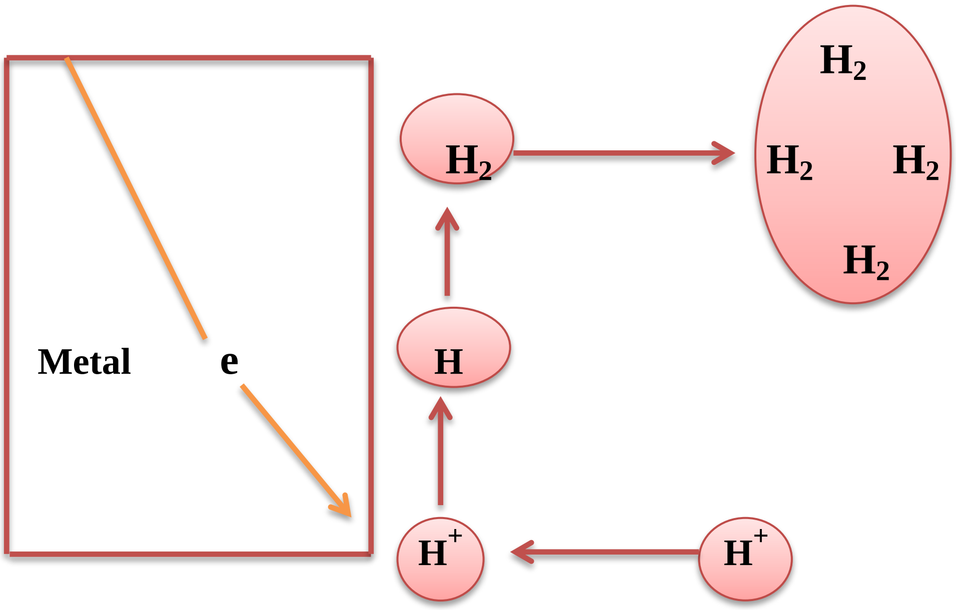


Figure (1.6) Electrode Kinetic Behavior of a Metal (M) in Reducing Acid.

1.8.1. Polarization types :

1.8.1.1. Activation Polarization (ηA):

This polarization is caused by a slow electrode reaction or stated in another way. The reaction at the electrode requires activation energy in order to go. The most important point is that of hydrogen ion reduction at the cathode [28] reaction might be considered as :-



$$2H^+ + 2e \longrightarrow 2H \longrightarrow H_2 \qquad (1.25)$$

Ions Stage (1) Absorbed on Metals Stage (2) Gas

Stage (1) occurs rapidly, whereas stage (2) is generally the slower and rate-controlling step [21].

The activation is overpotential, and hence the activation energy varies exponentially with the rate of charge transfer per unit area of electrode surface, as defined by the well-known Tafel equation [21]:

$$\eta A = \pm \beta \log \left(\frac{i}{io} \right) \qquad (1.26)$$

Where

i = The current density

β = The Tafel constant being equal to ($2.303 \frac{R\,T}{\alpha Z\,F}$)

i_0 = Exchange current density

η_a = Over-potential for activation polarization

The Tafel constant (β) varies with the nature of the electrode process and ,Faraday constant (F) and with the nature of the solution. Thus (ηA) will be linearly related to (log i) at overpotential greater than 0.05 V [21].The position of the curve will be dependent on the equilibrium exchange current density (i_0) the symmetry coefficient (α) and the number of electrons (z) involved in one act of the rate determining step. The Tafel equation for a cathodic process can be expressed in the form [21] :

$$\eta_{A,c} = \frac{R\,T}{\alpha Z\,F} \ln i_0 - \frac{R\,T}{\alpha Z\,F} \ln i_c \qquad (1.27)$$

Similarly for the anodic process:

$$\eta_{A,a} = -\frac{R\,T}{(1-\alpha)Z\,F} \ln i_0 + \frac{R\,T}{(1-\alpha)Z\,F} \ln i_a \qquad (1.28)$$

It is evident from these expressions that since in the Tafel region (i) must be greater than (i_0) and the signs of the overpotential will be negative for ηA,c and positive for ηA,a.

1.8.1.2. Concentration Polarization (ηC):

Concentration polarization is obtained when the rate of an electrode reaction is dependent on mass transfer, i.e. the rate at which the reactant is transported to the surface of the electrode and the rate at which the product is transported away from the electrode. Transport through the solution to and from the metal surface occurs by diffusion, ionic migration (transport of electrical charge through the solution) and convection of these diffusion through the thin static layer of solution adjacent to the metal surface. The diffuison layer (δ) is usually of greatest significance. However, this is not always the case in practical systems, particularly, where dissolved oxygen is the cathodic reactant. In certain circumstances the rate of diffusion through the bulk solution to the metal-solution interface may be rate determining [21]. For concentration polarization reaction current is given by Fick's law [29]:

$$| I_L | = Z\ F\ D\ A\ \frac{d\,C}{d\,X} \tag{1.29}$$

Or its equivalent

$$| I_L | = Z\ F\ D\ A\ \frac{C_b - C_s}{\delta} \tag{1.30}$$

The limiting current the maximum current under diffusion control is obtained when $C_S = 0$

$$| I_L | = Z\ F\ D\ A\ \frac{C_b}{\delta} \tag{1.31}$$

Or

$$| I_L | = Z\ F\ D\ A\ C_b \tag{1.32}$$

Where the mass transfer coefficient is defined as:

$$K = \frac{D}{\delta} \tag{1.33}$$

The concentration polarization can also be expressed as [21].

$$\eta_C = \frac{R\,T}{Z\,F} \ln \frac{C_s}{C_b} \qquad (1.34)$$

Or

$$\eta_C = \frac{R\,T}{Z\,F} \ln 1 - \frac{1}{i_L} \qquad (1.35)$$

Where

i_L= Limiting current density

F = Faraday's constant (columbs/mole).

D = Diffusivity (cm/s^2)

δ = Diffusion layer thickness

Cb = Bulk concentration (g mole/cm^3)

Cs = Surface concentration (g mole/cm^3)

A = Surface area (cm^2)

K = Specific conductivity

From equation (1.35) it an be seen that :-

1. The term **(1- $\frac{1}{i\,L}$)** is equivalent to the term **($\frac{C_s}{C_b}$) in** equation (1.34).

2. When I is very small in comparison with I_L, the concentration polarization is negligible.

3. When I approaches I_L in magnitude, concentration polarization approaches infinity.

1.8.1.3. *Resistance Polarization* (η_R)*:*

The resistance polarization is the ohmic potential drop through a portion of the electrolyte surrounding the electrode, through a metal reaction product film on the surface or both. An ohmic potential drop always occurs between the working electrode and the capillary tip of reference electrode. The ohmic (i.e., solution) IR drop is given by [21]:

$$IR_{soln.} = i\,\rho\,l = i\,.\,\frac{1}{K} \qquad (1.36)$$

Where

ρ = The specific resistance (Ω.cm)
k = The conductivity ($\Omega^{-1}.cm^{-1}$) or ($S.cm^{-1}$) S = Siemens
l = The solution gap between the capillary tip and the working electrode (cm)

Resistance polarization is important only at high current densities or in high resistance electrolyte solution [34]. All of these three types of polarization will be present to a greater or less extent in most corrosion reactions.

$$\eta_{Total} = \eta_A + \eta_C + \eta_R \qquad (1.37)$$

But if one is more influential than the others, then it will control the reaction rate.

Where
η = Over-potential, (polarization), overvoltage
η_A = Over-potential for activation polarization
η_C = Over-potential for concentration polarization
η_R = Over-potential for *resistance polarization*

1.9 Linear Polarization Technique:

The linear polarization technique in principle is a convenient and rapid way for determining corrosion rates [30] . Although this technique was developed by Wanger and Traud [31].Who stated that the corrosion process with two coupled electrochemical reactions under activation control can be represented by:

$$I = icorr \,.\, \left[exp\left(\frac{\eta}{ba}\right) - exp\left(\frac{\eta}{bc}\right)\right] \qquad (1.38)$$

But it lay dormant until the early nineteen-fifties when it was used by Stern and Geary [32,33].In various studies of metal dissolution in acids. Briefly their method rests on the mathematical consequence of expanding two exponential functions around the rest potential equation, (1.38) for relatively small increment of the exponent (i.e. for potential within about 10 mV of the corrosion potential). It is observed that the applied current density is a linear function of the electrode potential. The slope of this linear polarization is related to the kinetic parameters of the system as follows:

$$\frac{\Delta E}{\Delta i_{app}} = \frac{\beta a\, \beta c}{2.303\, icorr\, (\beta a + \beta c)} \qquad (1.39)$$

Where βa and βc are the anodic and cathodic Tafel slopes respectively. was unreasonable to treat polarization curve in the region near the corrosion potential as a straight line , inflection point of the polarization curve did not coincide with the point ΔE = 0 except in the case where Tafel slopes of anodic and cathodic reactions of the corrosion process where equal ($\beta_a = \beta_c$) In addition, it was unsuitable to take (10 mV) as the confines of linearization because in most cases polarization curves would obviously deviate from the straight line before ΔE reached (10 mV). Thus equation (1.39) will bring a high percent of error because there is no linearity near the corrosion potential

1.10 Previous Studies

Corrosion of mild steel has been a subject of numerous studies due to its high technological value and its uses in a wide range of industrial applications

Majed (2009) studied the effect of molybdate ions ($MoO_4^{=}$) on corrosion behavior of SS 304 in 0.1M NaCl solution with six different concentration of molybdate ion in the range (0.01 – 0.3M) at room temperature. Corrosion parameters such as open circuit potential (E_{ocp}), corrosion potentials (E_{Corr}), corrosion current density (i_{corr}), and Tafel slops (bc & ba)were measured and discussed. The polarization resistance (Rp) and rate of the corrosion in (mpy) values were calculated. All these parameters showed the role of molybdate as inhibitor material of corrosion SS 304 in NaCl solution and exhibit that the 0.03M MoO_4^{-2} has the best values of Rp, rate (mpy) and % P. The inhibition by molybdate was observed through adsorption process and formation of oxide layer on surface of stainless steel [34].

Umoren et al.(2009) studied the effect of iodide ions on the corrosion inhibition of aluminium in 2M HCl in the presence of polyvinylpyrollidone (PVP) using gasometric (hydrogen evolution) technique at 30-60 ^{0}C. The results obtained showed that PVP effectively reduces the corrosion rates of aluminium in the acid medium. Inhibition efficiency (% IE) increases with increase in concentration of PVP. Increase in temperature increases corrosion rate but decreases inhibition efficiency. The addition of iodide ions enhanced the inhibition efficiency of PVP considerably. Adsorption of PVP and PVP + KI followed Temkin adsorption isotherm. Phenomenon of physical adsorption is proposed from the obtained E_a and ΔG^0_{ads} values[35].

Sherine et al .(2010) studied the inhibition efficiencies of inhibitor systems constituting various combinations of hydroquinone and zinc ions(Zn^{+2}) in controlling corrosion of carbon steel immersed in well water have been by weight loss method.It was found that 100 ppm of zinc has 50% inhibition efficiency (Immersion period =7 days). When 150 ppm of hydroquinone is added, the IE increases to 97%. The nature of the protective film formed on the metal surface has been analyzed by FTIR spectra, SEM, and AFM analysis [36].

Deng et al.(2011) studied the inhibition effect of sodium molybdate (Na_2MoO_4) on the corrosion of aluminium in 1.0 M H_3PO_4 solution by weight loss, potentiodynamic polarisation curves.The results show that Na_2MoO_4 is a good inhibitor, and the inhibition efficiency obtained by three methods is higher than 84% at 20 mM. The adsorption of Na_2MoO_4 obeys Freundlich isotherm at lower concentrations (1–7 mM), while Langmuir isotherm at higher concentrations (7–20 mM). Polarisation curves indicate that Na_2MoO_4 acts as an anodic inhibition[37].

Chidiebere et al .(2014) studied the inhibition properties of phytic acid (PA) on Q235 mild steel corrosion in 0.5 M H_2SO_4 which was estimated using electrochemical techniques. Polarization results revealed PA to be a mixed-type inhibitor in 0.5 M H_2SO_4 with a more pronounced cathodic effect. The values of the synergistic factor with KI were higher than unity indicating that both additives act cooperatively to improve inhibition performance. The adsorption of PA followed the Langmuir adsorption isotherm. The mechanism of chemical adsorption is proposed on the basis of the trend of inhibition efficiency with temperature and the calculated values of the activation energy (E_a) [38] .

Al-Otaibi et al .(2014) studied the alcoholic extracts of eight plants namely Lycium shawii, Teucrium oliverianum, Ochradenus baccatus, Anvillea garcinii, Cassia italica, Artemisia sieberi, Carthamus tinctorius, and Tripleurospermum auriculatum grown in Saudi Arabia.They were studied their corrosion inhibitive effect on mild steel in 0.5 M HCl media using the open circuit potential (OCP), Tafel plots method. All the plant extracts inhibited the corrosion of mild steel in acidic media through adsorption and act as mixed-type inhibitors [39].

Anaee (2014) studied two inorganic inhibitors to protect mild steel in cooling water system (single and binary sodium silicate and phosphate). Four different concentrations of silicate and phosphate ions were used (1×10^{-3}, 5×10^{-3}, 1×10^{-2} and 0.2M) and (1×10^{-3},5×10^{-3}, 1×10^{-2} and 0.1M), respectively, in addition to two mixtures of SiO_3^{-2} and PO_4^{-3}.Corrosion parameters were measured by electrochemical method using potentiostate such as corrosion potentials, corrosion current densities and Tafel slopes and were used to calculate polarization resistance. These results indicate that the best concentration of SiO_3^{-2} and PO_4^{-3} is 1×10^{-2} M that gave % P 74.088 and 95.494, respectively, while PO_4^{-3} gave better protection than SiO_3^{-2} and its mixtures.The adsorption of SiO_3^{-2} and PO_4^{-3} on the steel surface in simulated cooling water obeys the Langmuir adsorption isotherm model [40].

Epshiba *et al .(2014)* studied the inhibition efficiency of sodium molybdate (SM) in controlling corrosion of carbon steel in well water, in the presence of sodium molybdate (SM) ,and Zn^{+2} by the weight loss method. The formulation consisting of 250 ppm of SM and 50 ppm of Zn^{+2} offers 92% inhibition efficiency to carbon steel. A synergistic effect exists between SM and Zn^{+2}. Polarization study reveals that SM-Zn^{+2} system functions as an anodic inhibitor, and the formulation controls the anodic reaction predominantly. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{+2}- MoO_4^{-2} complex and $Zn(OH)_2$ [41].

Deepa et al.(2015) studied the inhibition efficiency (IE) of Trisodium Citrate (TSC) in controlling corrosion of carbon steel in RO water in the absence and presence of Zn^{+2} .It has been evaluated by weight-loss method. The formulation consisting of 150 ppm TSC and 10 ppm Zn^{+2} has 72.5% IE. It is found that the inhibition efficiency of TSC increases with the addition of Zn^{+2} ion. Polarization study and characterization surface analysis studies confirm the protection of the carbon steel surface by inhibitive film. A suitable mechanism for corrosion inhibition has been proposed based on the results obtained from the above studies [42].

Kwolek et al .(2016) studied corrosion rates of aluminum in phosphoric acid solutions gravimetrically in a presence of sodium molybdate which acts as an inhibitor. Inhibition efficiencies were calculated. The most effective corrosion inhibition was observed for 0.5 M H_3PO_4 and 100 mM of Na_2MoO_4. Since insoluble corrosion products precipitated onto specimens and influenced the determined corrosion rates, an analysis of a morphology of the specimens was performed by using a scanning electron microscope [43].

Yaro et al .(2016) studied the inhibition of mild steel corrosion in 1M HCl by 1-propanol and the synergistic effect of potassium iodide (KI) was investigated using weight loss and polarization techniques in the temperature (30 and 50) °C. The results confirmed using electrochemical polarization measurements. Experimental results showed that the inhibition efficiency (IE%) increases with increase in concentration of inhibitor and with increase in temperature as well. The addition of iodide ions to alcohol (inhibitor) enhanced the inhibition efficiency due to synergistic effect. Potentiodynamic polarization studies showed that the studied compound is mixed-type inhibitor causing blocking of active sites on the mild steel surface .The adsorption of the inhibitor and its combination with iodide ions on mild steel surface followed Langmuir adsorption isotherm via physisorption mechanism, which was proposed based on values of adsorption Gibbs free energy difference ΔG_{ads}.. Statistically, the multi-variable regression equation describes the behavior of the corrosion inhibition process with high accuracy (correlation coefficient R^2 between 0.974 and 1)[44].

Eyu et al.(2016) studied the effect of potassium iodide (KI) and sodium nitrite ($NaNO_2$) inhibitors on the corrosion inhibition of mild steel in chloride bicarbonate solution using electrochemical techniques. Potentiodynamic polarisation data suggest that, when used a combination of KI and $NaNO_2$) function together to inhibit reactions at both the anode and the cathode Predominantly anodic KI/NO_2^- concentration ratios varied from 2:1 to 2:5 and inhibition efficiency was optimized for a ratio of 1:1. The surface morphology and corrosion products were analysed using scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The latter shows that the addition of I^- to NO_2 facilitates the formation of a passivating oxide (Fe_2O_3) as compared to NO_2^- alone, decreasing the rate of metal dissolution observed in electrochemical testing [45].

Guo et al .(2017) studied the inhibition effects of L-tryptophane (Trp) and its synergistic effect with KI on the corrosion of mild steel in 1.0 M HCl solution.They have been investigated using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) measurements. The results show that the inhibition efficiency increases with the concentration of Trp and increases further when KI exists. The synergistic effect between Trp and KI was discussed by calculating the synergism parameter, which suggests that there is a cooperative mechanism between iodide anion and Trp cation. [46].

Nwanonenyi et al.(2016) studied the inhibitive performance of hydroxypropyl cellulose (HPC) and and its combination with potassium iodide (KI) on mild steel corrosion in 0.5 M H_2SO_4 acid solution using potentiodynamic polarization, gravimetric measurement technique and theoretical computations.Weight loss results obtained indicate that the HPC and its combination with KI functioned as a good inhibitor in sulphuric acid environment with inhibition efficiency of 76.43% and 89.73% respectively, and inhibition efficiency increased with concentration. Changes observed in polarization parameters suggest the adsorption of HPC on the mild steel surface, leading to the formation of protective films. The adsorption characteristics of the inhibitor were approximated by Langmuir isotherm. Synergistic effect increased the inhibition efficiency in the presence of halide additives and the values of the synergistic factor with KI were higher than unity indicating that both additives act cooperatively to enhance inhibition performance [47].

Mu et al. (2017) studied the mixture of 2-undecyl-*N*-carboxymethyl-*N*-hydroxyethly imidazoline (UHCI) with potassium iodide (KI) as a corrosion inhibitor for carbon steel in 8% amidosulfuric acid solution was investigated by weight loss test and electrochemical methods. Results show that the combined inhibitor strongly inhibits the corrosion of 20 carbon steel in amidosulfuric acid solution, and the mixture with the mass ratio (UHCI:KI) of 9:1 has the best corrosion inhibition at a total concentration of 0.4%. The impedance spectra of carbon steel electrodes change from one time constant into two time constants when the mixture inhibitor adds into the blank solution, while the polarization curves indicate that the mixture behaves as a mixed type inhibitor. The mixture is found to follow the Langmuir adsorption isotherm, and the mechanism is chemisorption [48].

Ajeel (2017), studied corrosion inhibition of mild steel in 1M H_2SO_4 solution by rosmarinus officinalis Leaves extract by weight loss and potentiostatic methods. Increasing acid concentration leads to an increase in the corrosion rate of the electrode. The variable conditions used in this investigation are (100 to 1000 ppm at 25 °C). Rosmarinus Officinalis Leaves extract for mild steel. It has been found that the concentrates as a compelling consumption inhibitor for gentle steel in acidic medium. The hindrance process is credited to the development of an adsorbed film of inhibitor on the metal surface which secures the metal against corrosion. The inhibition efficiency was observed to increase with increasing inhibitor concentration up to maximum 92% for 1000 ppm at 25 °C. The results show that the corrosion rate without inhibitor was 5.6 mpy while with inhibitor was 0.43 mpy, which means that corrosion rate was improved more than 90%.The effects of immersion time (2h) at 25 °C on the inhibition of corrosion have also improved corrosion resistance. The results obtained show that Rosmarinus Officinalis Leaves Extract could serve as an excellent friendly green corrosion inhibitor [49].

Yousif (2017) studied the corrosion inhibition effects of cefixima and aminobenzylpenicillin drug inhibitors in 0.05 M deaerated sulfuric acid solution for carbon steel by using electrochemical techniques and quantum chemical calculations as well as scanning electron microscope (SEM). It is observed from the experimental findings that both compounds perform as good inhibitors and behave according to mixed type inhibitor in terms of their inhibitory action. Additionally, it was found the percentage of corrosion inhibition become maximam when the concentrations of the cefixima and aminobenzylpenicillin inhibitors are increased. The influence of temperature on the corrosion of carbon steel has been investigated and the activation energy values were estimated. The corrosion efficiency decreases with increasing the temperature range. The parameters of thermodynamic have been determined and they indicate that the adsorption mechanism follows the Langmuir isotherm model and forms a protective layer on carbon steel surface electrode, which was characterized by scanning electron microscope measurements [50].

Abdullah (2017), studied Pomegranate shells as green inhibitors for steel 44-2 in 0.1M HCl at various temperatures (30, 40, 50, and 60) °C using electrochemical technique. Five concentrations of inhibitor were added 4, 8, 12, and 16 ppm. Corrosion tests were performed by Potentiostat at 5 mV.sec^{-1} scan rate and the data measured by Tafel extrapolation method Tafel slopes, corrosion current density and corrosion potential. inhibition efficiencies were calculated and indicated that 8 ppm was the best concentration for inhibition especially at 60℃, which was 96.47%. Pomegranate Shells behaves as anodic inhibitor type and obeys Langmuir adsorption isotherm. The equilibrium constant of the adsorption-desorption process and the apparent free energy of adsorption confirm the physicsorption of pomegranate shells [51].

Usman et al.(2017) studied the corrosion inhibition performance of tannic acid (TA) on API 5L X60 pipeline steel in CO_2-saturated with 3.5% NaCl solution using two electrochemical techniques namely linear polarization resistance (LPR).The effect of KI addition on the inhibitive performance was assessed. The results obtained showed that TA moderately inhibited the steel corrosion in the studied medium. Addition of KI synergistically enhanced the inhibitive performance of TA. Corrosion inhibition performance of TA alone and on addition of KI was influenced by concentration and immersion time. Excellent inhibition with protection efficiency of about 90% was achieved on addition of KI to TA at longer immersion time up to 24 h. Surface characterization techniques namely Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS),and Fourier Transformed Infrared (FTIR) spectroscopy were employed to elucidate the mechanism of the inhibition. [52] .

Haruna et al .(2018) studied corrosion inhibition performance of an environmentally benign compound gelatin on X60 steel in 15% hydrochloric acid (HCl) at 25℃. The inhibition efficiency of the gelatin was examined using weight loss, potentiodynamic polarization (PDP). Both the weight loss and the electrochemical results showed that the gelatin exhibits high inhibition efficiency and the inhibition efficiency increases with increasing gelatin concentration. The addition of low concentration potassium iodide improves the inhibition efficiency of gelatin considerably. The ATR-FTIR and SEM/EDX surface morphology analyises provide evidence of formation of protective gelatin film on the metal surface[53].

Liu et al .(2018) studied the inhibition effect of four inhibitors of sodium citrate (SC), sodium dodecylbenzene sulphonate (SDBS), diammonium phosphate ($(NH_4)_2HPO_4$) and sodium vanadate ($NaVO_3$) on the corrosion behaviour of AM60 magnesium alloy in 0.1 M sodium chloride (NaCl) solution by immersion and electrochemical tests, surface morphology and chemical composition analyses. The results show that AM60 suffers severe attack in NaCl solution in long-term immersion. When inhibitors are added, its corrosion resistance is improved. All these inhibitors can form a barrier to inhibit the corrosion process and especially, the barrier becomes more protective after longer time of immersion. [54].

Awad et al.(2018) studied corrosion inhibition of aluminum in ($1M$ H_3PO_4) in absence and presence of Cydonia Vulgaris leaves (CVL) extracts as friendly corrosion inhibitors. The effect of temperature and inhibitor concentration at immersion time of ($3h$) was studied using weight loss method. The obtained results revealed that cydonia vulgaris leaves(CVL) extracts inhibited aluminum in (H_3PO_4) and decreased the rate of corrosion. By increasing the concentration and temperature of the inhibitor, its efficiency increased. Higher inhibition efficiency for aluminum corrosion of (95.51%) was obtained at a higher level of inhibitor concentration and temperature. The adsorption of Cydonia Vulgaris leaves(CVL) extracts was found to obey Langmuir adsorption isotherm model. The values of the free energy of adsorption were more than (−20 kJ/$m$ol) which was indicative of a mixed mode of physical and chemical adsorption. Activation enthalpy (ΔH^*), and activation entropy (ΔS^*) of aluminum corrosion was found to be (43.7254 kJ/mol $^{-1}$) , (−0.1804 kJ mol^{-1}K^{-1}) and (20.2732 kJ mol $^{-1}$), (−0.1921 kJ mol $^{-1}K^{-1}$) in the absence and presence of the extract respectively [55].

Khadom et al.(2018) studied Corrosion inhibition of mild steel in 1 M HCl in the absence and presence of potassium iodide (KI) as a corrosion inhibitor. The effects of temperature and inhibitor concentration were studied using weight loss technique. The result obtained shown that KI act as an inhibitor for mild steel in HCl and decreases the corrosion rate. The inhibition performance was found to increases with increase in inhibitor concentration and temperature. Higher inhibition efficiency was 94% at higher level of inhibitor concentration and temperature. The adsorption of KI on mild steel surface was found to fellow Langmuir adsorption isotherm. The values of the free energy of adsorption were between − 20 and − 40 kJ/mol that is indication of mixed mode of physical and chemical adsorption. Mathematical models were also suggested to correlate the corrosion rate data with independent variables [56].

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Cao et al .(2019) studied Corrosion inhibition of carbon steel in 0.5 M HCl solution by novel ionic liquid (IL), 1,1′-(1,4-phenylenebis (methylene))bis(3-(carboxymethyl)-1H-imidazol-3-ium) chloride with and without KI by electrochemical tests, surface and solution analysis as well as theoretical calculation. Results showed that IL can suppress anodic and cathodic reaction by adsorption onto the steel surface and follows Langmuir adsorption isotherm. The inhibition efficiency increases with increasing IL concentration. Addition of KI to IL increases the maximum inhibition efficiency form 94.8 % to 96.2 % when using IL:KI of 1:1. Theoretical inhibition-efficiency results correlate well with experimental observations [57].

Rashid and Khadom (2019) studied the performance of sodium molybdate (Na_2MoO_4) as a corrosion inhibitor for medium carbon steel corrosion in saline water containing nitrate and chloride ions was at various inhibitor concentrations, temperatures, exposure times and rotational velocities. Mass loss and electrochemical techniques were used to evaluate the corrosion rates. The individual and interactive effects of these four parameters were optimized for minimum response of corrosion rate using central composite design (CCD) with response surface methodology (RSM) [58].

1.11 The Aim of Work

The subject of this work included a number of important aims ,which may by summarized as:

1. Studying the corrosion rates of mild steel in HCl at different concentrations of sodium iodide and temperatures.

2. Studying the surface morphology by X-ray diffraction and atomic force microscopy.

3. Studying the kinetics of reaction of mild steel in HCl solutions at different operating conditions.

4. Studying the mechanism adsorption of corrosion inhibitors on the surface of mild steel .

5. Investigating the polarization curves using potentiostatic technique of the sodium iodide concentrations (0, 0.5, 1, 1.5, 2 and 2.5) mL/L at different temperatures (303.15, 313.15, 323.15 and 333.15) K.

Chapter Two

Experimental Part

2.1 Chemicals and Materials

2.1.1. Chemicals Used

Sodium iodide is used as a corrosion inhibitor for mild steel in HCl through this investigation. The used sodium iodide has the properties shown in the following table :

Table (2.1) The Properties of Sodium Iodide

Description	**Colorless or white granules**
Formula	**NaI**
Molecular weight	**149.89 g/mol**
Melting point	**661 °C**
Boiling point	**1304 °C**
Density	**3.68 gm/cm^3**
Max. Limits of Impurities (%)	
Potassium (K)	**0.1%**
Sulfate (SO_4)	**0.01%**
Heavy metals (as pb)	**0.001%**
Iron (Fe)	**0.002%**

2.1.2. Materials Used

The used materials are shown in the following table:

Table (2.2) Used Materials

	Materials	**Origin**	**Function**	**Purity**
1.	**Hydrocloric acid**	**Europe**	**Corrosion medium**	**37 %**
2.	**Benzene**	**Europe**	**Grease removal**	**99.7 %**
3.	**Acetone**	**Europe**	**Cleaning and drying**	**99.9 %**

2.2. Apparatues

In this study the apparatues used is shown in Table (2.3) with their models and locations.

Table (2.3) The Apparatus Used in this Study.

NO.	Apparatues	Model	Location
1.	Thermostatic Water Bath	YCW-01, 220V/50Hz ,4.8A	Laboratories of Chemistry Department, College of Science, University of Diyala, Iraq
2.	Electronic Balance	KERN & Shone GmbH, Type ACS 120-4, NO. WB12AE0308,CAPA CITY 120g, READABILITY 0.1mg.	
3.	AFM	Nano compact (PHYWE)	(College of Education for pure Science/ Ibn Al-Haitham/university of Baghdad)
4.	XRD	Shimadzu X-ray Diffractometer (XRD – 6000)	
5.	Potentiostatic Polarization	Germany	University of Technology/ Iraq

2.3. Preparation of Corrosive Solution

The solution of (1M HCl) was prepared by dilution of the (37%) by using distilled water. The test solutions were freshly prepared before every experience by directly adding the inhibitor to the corrosion solution . A solution of the corrosion inhibitor was prepared by dissolving 40 g of sodium iodide in 25 mL of water at room temperature and adding to 1M

HCl at several concentrations of 0.5, 1, 1.5, 2 and 2.5 mL/ L as shown in Fig (2.1) .

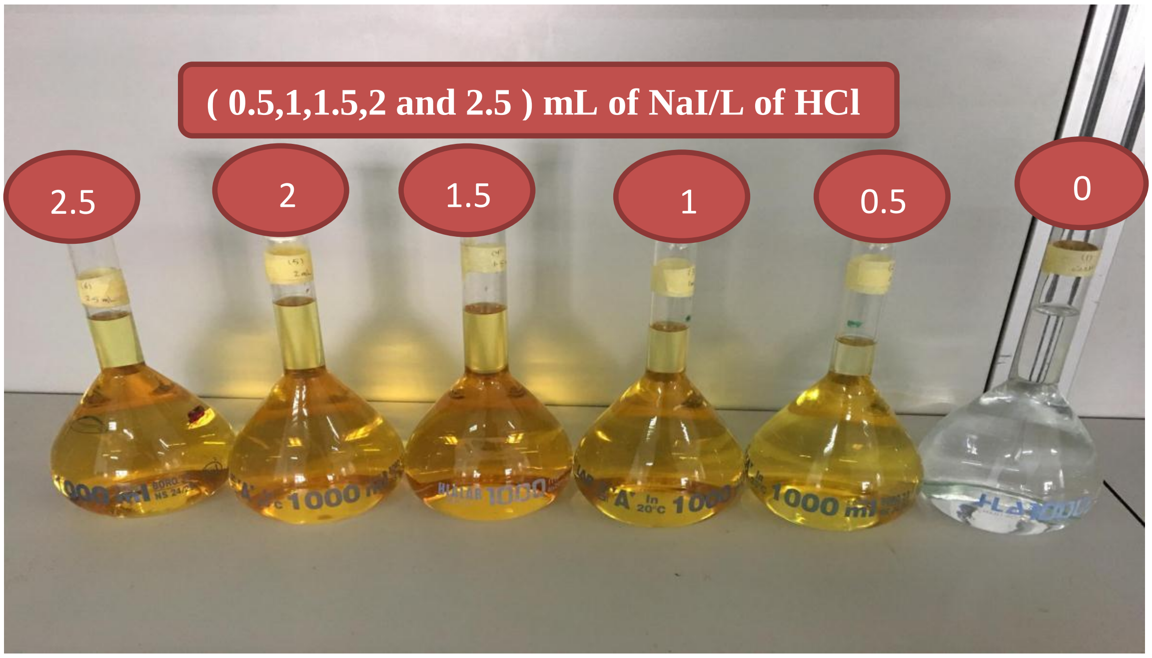


Figure (2.1) The preparation of hydrochloric acid (1M HCl) corrosion solution.

2.4. Corrosion Specimen Preparation

Specimens of dimensions 3 x 1 x 0.1cm were used .The samples were abraded with emery paper of grade number,60,120, 320,400,600,800,900,1000,and 1200 (Fig 2.2.a), then washed with flow tap water followed by distilled water. It is dried with cleaning tissue, immersed in benzene and acetone and dried again . The samples were weighted by 4-digits electronic balance, and the dimensions were measured by an electronic vernier, as shown in (Fig 2.2.b and 2.2.c) respectively, they were completely immersed in corrosion solution and transferred to water bath as in (Fig 2.2.d) respectively.

Figure 2.2 (a-d) Instruments and Steel Samples .

a. Steel Samples . b. Electronic Balance c. Electronic Vernier
d. Water Bath

2.5. Weight Loss Measurement and Kinetic Measurement

For weight loss measurements and kinetics studies the metal samples were completely immersed in 200 mL corrosion solution of (1M HCl) in beaker then transferred to water bath, as in (Fig 2.2.d). They were exposed for a period of (1h,2h,3h and 4h) at the desired temperature and inhibitor concentration. Then the metal samples were cleaned, washed with flow tap water followed by distilled water ,dried with clean tissue, immersed in benzene and acetone ,and dried again. Weight losses were determined in the presence and absence of inhibitor at (303.15,313.15,323.15 and 333.15) K and (0.5,1,1.5,2 and 2.5) mL/L inhibitor concentration as shown in Fig (2.3) .

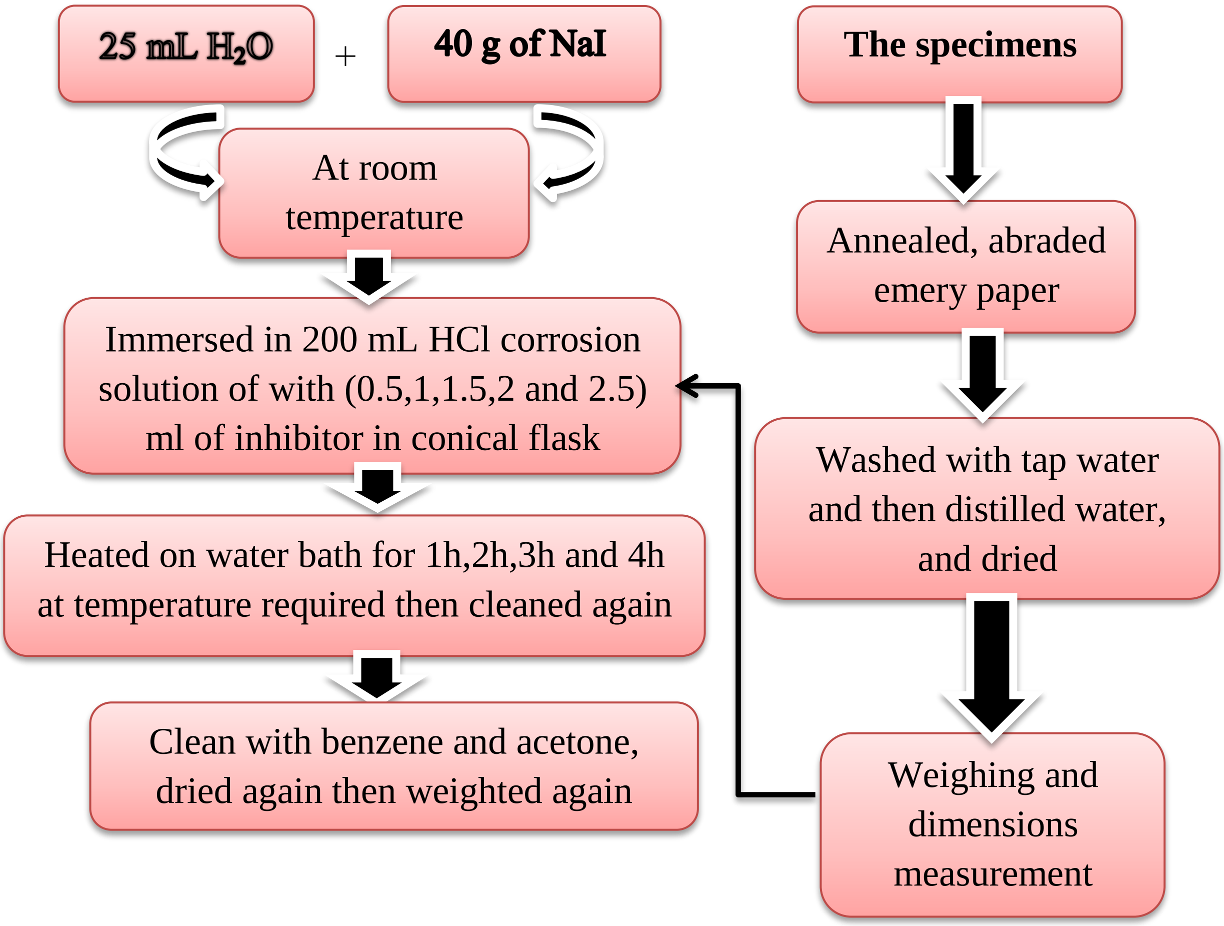


Figure (2.3) The experimental set up of corrosion study.

2.6. Diagnostic Techniques

2.6.1. Atomic Force Microscopy

Atomic force microscopy is arguably the most versatile and powerful microscopy technology for studying samples at nanoscale. It is versatile because an atomic force microscope can not provide only image in three-dimensional topography, but it also provides various types of surface measurements according to the needs of scientists and engineers. It is powerful because an AFM can generate images at atomic resolution with angstrom scale resolution height information, with minimum sample preparation as shown in Fig **(2.4)** .

Figure (2.4) Atomic force microscopy .

2.6.2. X-ray Diffraction Technique

X-ray diffraction techniques are used for the identification of crystalline phases of various materials and the quantitative phase analysis subsequent to the identification. X-ray diffraction techniques are superior in elucidating the three-dimensional atomic structure of crystalline solids. The properties and functions of materials largely depend on the crystal structures. X-ray diffraction techniques have, therefore, been widely used as an indispensable means in materials research, development and production as shown in Fig **(2.5)** .

Figure (2.5) X-ray diffraction technique.

2.7. Potentiostatic Polarization and Description of the System

Tests were carried out in cell as shown in Fig (2.6). The cell was equipped with three electrods : the working electrode, reference electrode, and auxiliary electrod .

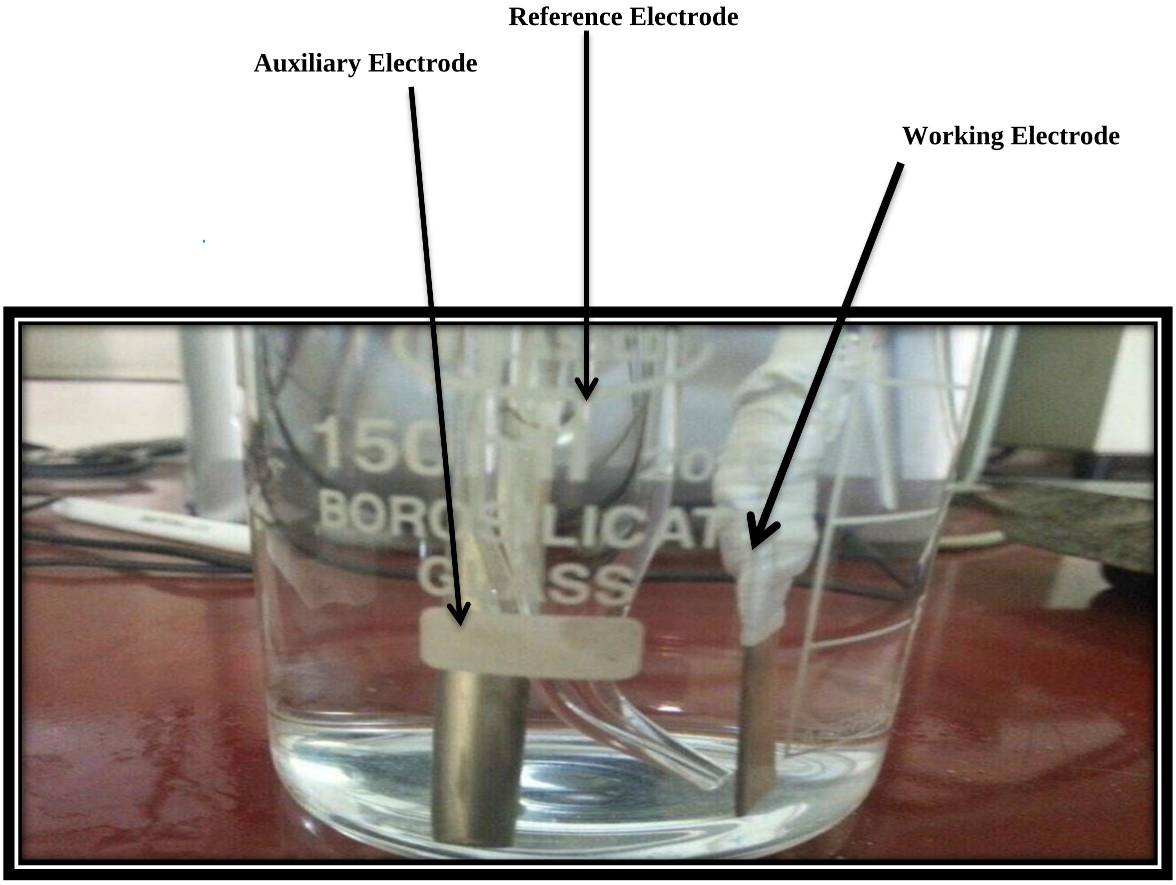


Figure (2.6) Electrochemical corrosion cell .

2.8. Electrodes of the Corrosion Cell

2.8.1. The Working Electrode:

The working electrode was (1× 2 cm) carbon steel flat specimen, 0.1cm thick, with small hole of about 1 mm diameter near the end of specimen. The sample was suspended from the hole by a copper wire. The contact point has been isolated to prevent any effect that may result in association with one side coating of the sample and the survival of one side whose area has been measured . Point of connection was insulated in order to prevent any effect that may yield from coupling [59].

2.8.2. Auxiliary Electrode

Platinum electrode was used , and the platinum connected to a plastic plate with epoxy .Platinum electrode was used in this research as an auxiliary electrode due to its large surface area and high catalytic activity. It passes the electrical current which is necessary to produce the wanted potential difference [60] .

2.8.3. The Reference Electrode

Saturated Calomel Electrode (SCE) was used as a reference electrode.Silver-silver chloride electrode was used owing to its simplicity and high reproducibility .This electrode consists of silver wire, silver chloride ,and chloride icons ."Luggin capillary" .As shown in Fig (2.7) the tip of the luggin capillary is placed as closed as possible to the surface of the working electrode in the corrosion cell .This potentiostate was connected to voltmeter and ammeter to read voltage and current respectively [60] .

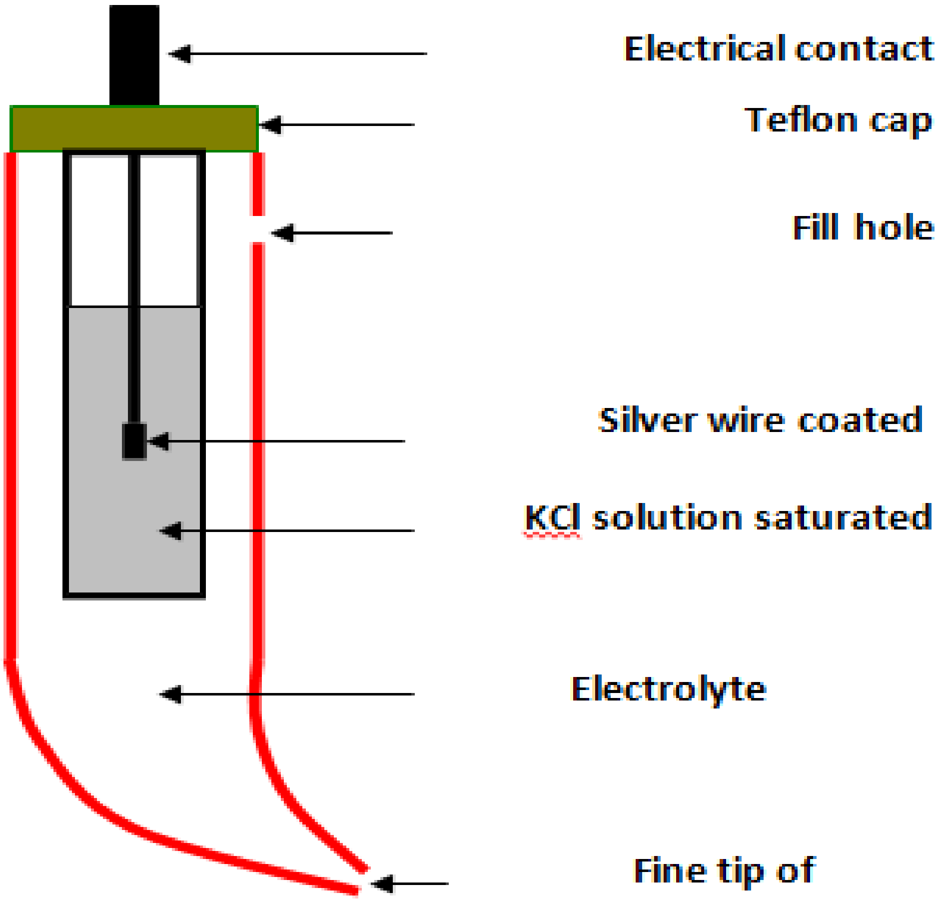


Figure (2.7) Schematic diagram of the reference electrode with luggin capillary [60].

Chapter Three

Results & Discussion

3.1. Weight Loss Measurements

Corrosion rates (C_R) were determined in presence and absence of inhibitor using the following formula [61]:

$$\boldsymbol{C_R} = \frac{\Delta \boldsymbol{W}}{\boldsymbol{A\,t}} \qquad \textit{(3.1)}$$

Where ΔW is weight loss in grams, A is area of specimen in m^2, and t is exposure time in days. Corrosion rates were obtained in term of g/m^2 day (gmd).

gmd = grams per square meter per day .

Inhibition efficiency was calculated using the equation:-

$$\%\,\boldsymbol{IE} = \frac{\boldsymbol{C_{R\,uninh}} - \boldsymbol{C_{R\,inh}}}{\boldsymbol{C_{R\,uninh}}}\ \textit{x 100} \qquad \textit{(3.2)}$$

Where $C_{R\ uninh}$ and $C_{R\ inh}$ are the corrosion rates in the absence and presence of various concentrations of inhibitor respectively. Corrosion rate and inhibitor efficiency were evaluated at different operating conditions and the results were collected in table (3.1). It is clear that corrosion rate increased with temperature and decreased with inhibitor concentration.

Table (3.1) Effect of temperature on the corrosion rate of mild steel in (HCl) in absence and presence of sodium iodide (NaI) as a corrosion inhibitor.

Time (4h)				
C_{inh} / (mL/L)	**Temperature /°C)**	**C_R /(gmd)**	**% IE**	**θ (surface coverage)**
Blank	**30**	**36.3240**	**0**	**0**
	40	**48.6984**	**0**	**0**
	50	**98.7960**	**0**	**0**
	60	**266.5776**	**0**	**0**
0.5	**30**	**13.3176**	**63.33**	**0.6333**
	40	**17.6352**	**63.78**	**0.6378**
	50	**21.5280**	**78.20**	**0.7820**
	60	**40.9176**	**84.65**	**0.8465**
1	**30**	**12.2376**	**66.30**	**0.6630**
	40	**14.4312**	**70.36**	**0.7036**
	50	**19.6968**	**80.06**	**0.8006**
	60	**26.3016**	**90.13**	**0.9013**
1.5	**30**	**10.8888**	**70.02**	**0.7002**
	40	**12.6048**	**74.11**	**0.7411**
	50	**17.8728**	**81.90**	**0.8190**
	60	**20.4696**	**92.32**	**0.9232**
2	**30**	**9.6048**	**73.55**	**0.7355**
	40	**9.9912**	**79.48**	**0.7948**
	50	**16.9656**	**82.82**	**0.8282**
	60	**18.6960**	**92.32**	**0.9232**
2.5	**30**	**7.8402**	**78.41**	**0.7841**
	40	**8.2656**	**83.02**	**0.8302**
	50	**9.5784**	**85.90**	**0.8590**
	60	**10.4568**	**96.07**	**0.9607**

3.2. Effect of Different Conditions on Corrosion Rate

3.2.1. Corrosion Rates in the Absence of Inhibitor

Weight loss measurements were used to calculate the rates of corrosion in uninhibited acid solutions at different temperatures after (4h) immersion time for mild steel in (IM HCl). It was found that the corrosion rate increased in case of temperature increasing at (303.15,313.15,323.15 and 333.15) K .

3.2.2- Corrosion Rates in the Presence of Inhibitor

It is clear that the addition of sodium iodide (NaI) reduces the corrosion rate markedly ,as show in Table (3.1). Generally, for mild steel, corrosion rate was found to increase with temperature. The higher NaI concentration added the lower was corrosion rate in (1M HCl). Therefore, NaI decreased the mild steel corrosion rate in (1M HCl) which indicates that it can be used as a corrosion inhibitor for that metal as shown in Fig (3.1) [62] .The effect of temperature on corrosion rate at different inhibitor concentration is expressed in Fig (3.2).These Figures show that the corrosion rate increases with increasing in temperature at all studied inhibitor concentration. At inhibitor concentration of (0.5 mL/L) the corrosion rate increases significantly when the temperature increased from (303.15 to 333.15) K . The effect of (1mL /L) inhibitor concentration is higher that of (0.5 mL/L). While at the inhibitor concentration of (1.5 , 2 and 2.5 mL/L) the temperature increases corrosion rate slightly. This may be due to the partial desorption of the inhibitor from mild steel surface with temperature and at a higher inhibitor concentrations [63].

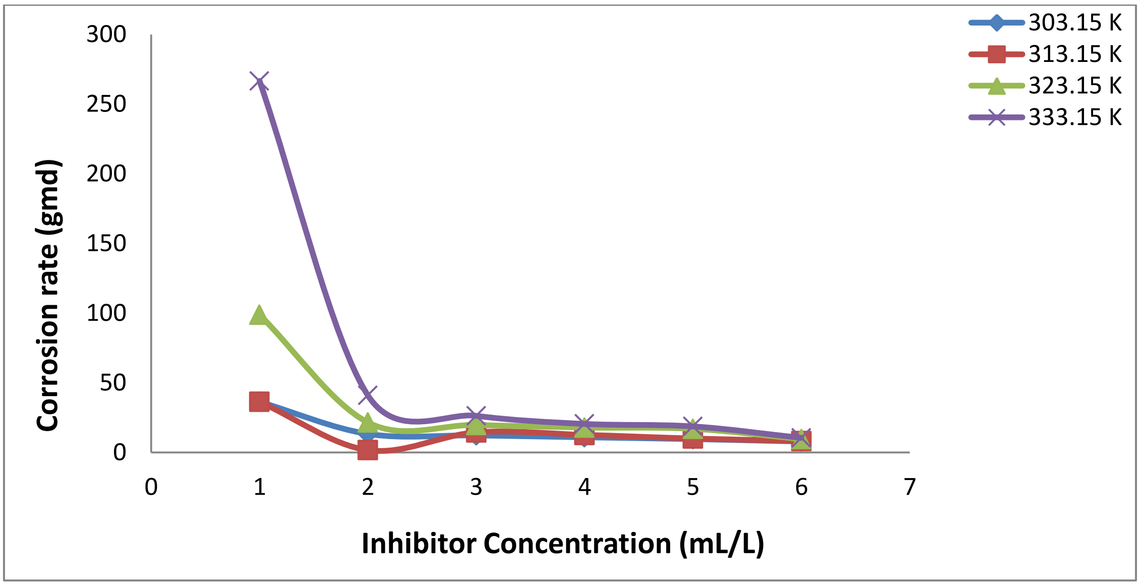


Figure (3.1) The effect of inhibitor concentration (NaI) on the corrosion rate of mild steel immersed in (1M HCl) at different a temperature at (4h) .

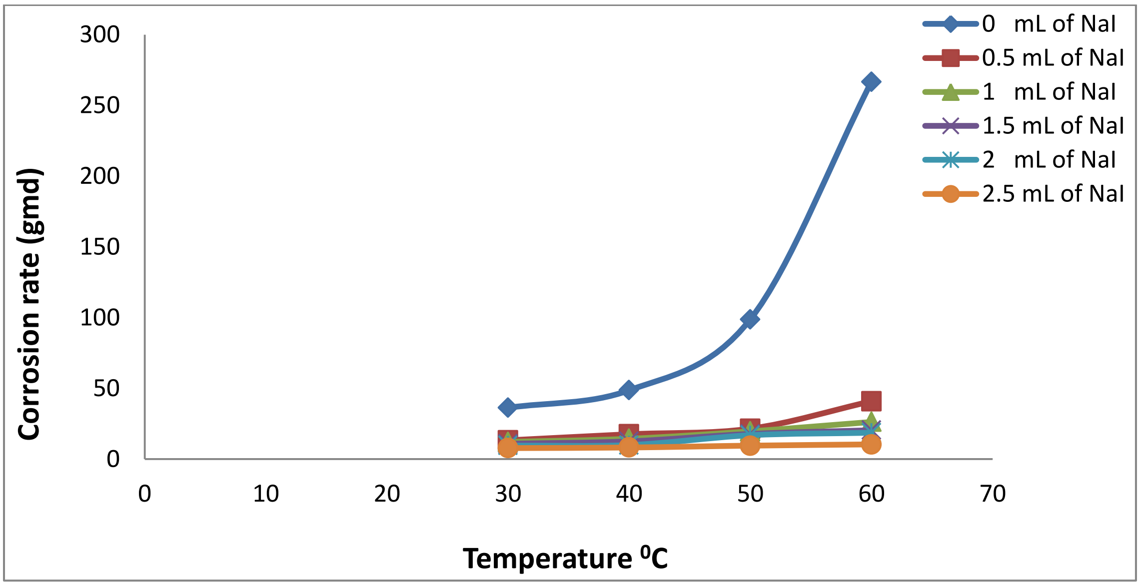


Figure (3.2) The effect of temperature on the corrosion rate of mild steel after immersion in (1M HCl) at different concentration at (4h) .

The values of inhibitor efficiency increase with the increasing of inhibitor concentration. Fig (3.3) shows the variation of inhibitor efficiency with inhibitor concentration. It was (63.33 - 96.07) % for (0.5 - 2.5) mL/L of (NaI) in (1M HCl) for mild steel respectively [64]. Fig (3.4) show the effect of temperature on inhibitor efficiency.

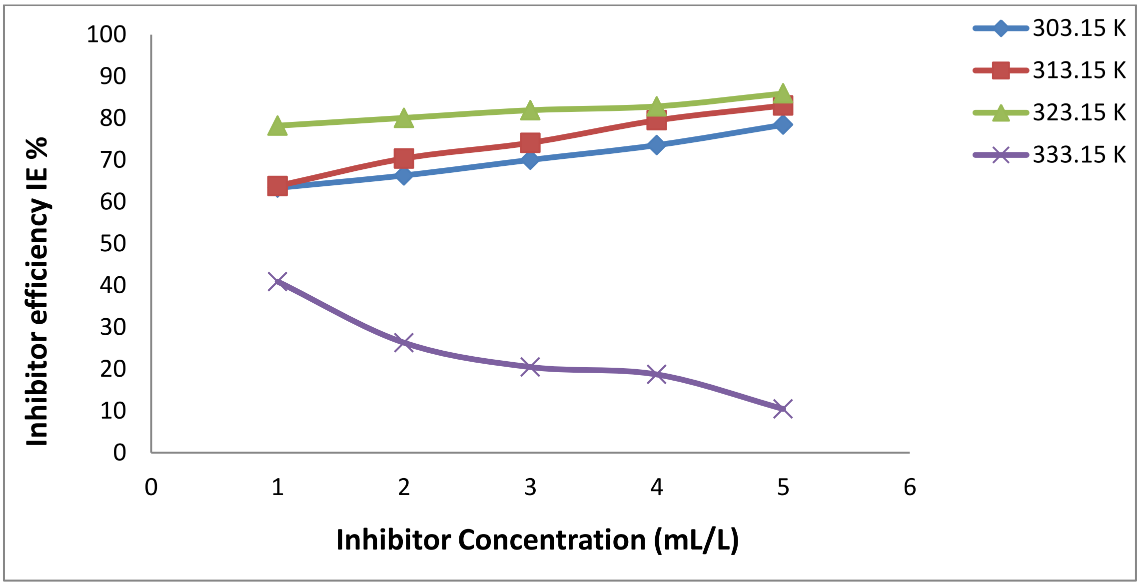


Figure (3.3) The effect of concentration of (NaI) inhibitor on inhibitive efficiency of mild steel corrosion in (1M HCl) and at different a temperature.

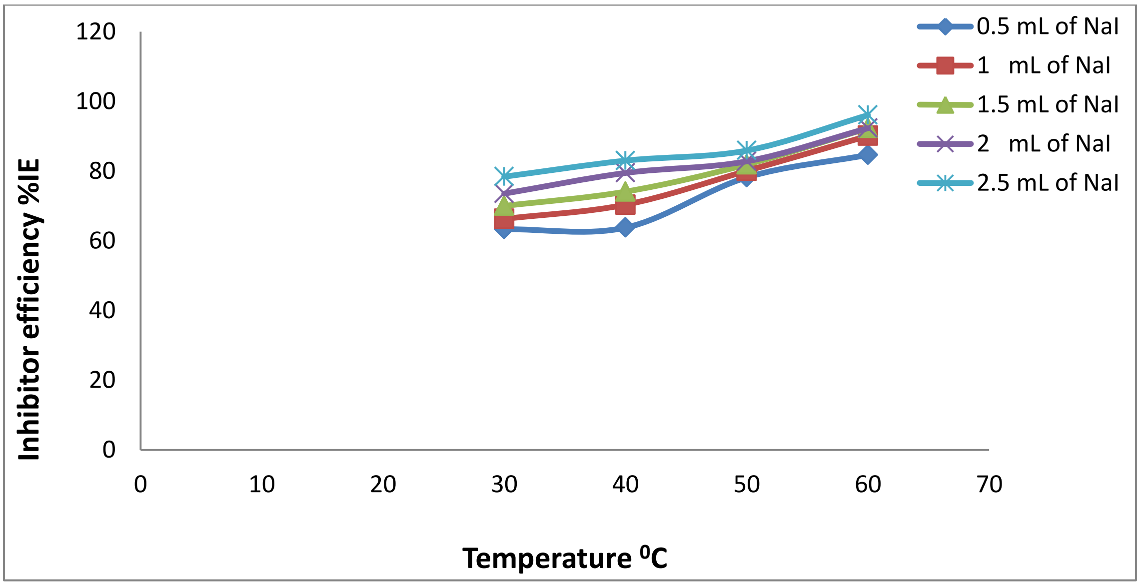


Figure (3.4) The effect of temperature on inhibitive efficiency of (NaI) inhibitor for mild steel corrosion in (1M HCl) at different concentration.

3.3. Inhibitor Performance and Adsorption Studies

It was shown that increasing the inhibitor concentration from (0.5 to 2.5) mL/L decreases the corrosion rate to very low values. Fig(3.1) shows this situation clearly. It is clear from this figures that the corrosion rate approaches its minimum value when the inhibitor concentration is (2.5mL/L). This might be due to that (2.5 mL/L) inhibitor concentration is enough to cover the metal surface at the temperature from (303.15 to 333.15)K. For (2 mL/L) inhibitor concentration the effect of inhibitor concentration will be less than in (2.5 mL/L). The increase in temperature from(303.15 to 313.15)K does not lead to significant change in the corrosion rate values but when the temperature increased to (323.15 - 333.15) K the corrosion rate values changed markedly. At inhibitor concentration of 0.5 and 1.5 mL/L as, shown in Fig (3.1) and Table (3.1).The surface coverage (θ) data are very useful while discussing the adsorption characteristics. The surface coverage of inhibitor at a given concentration is calculated by using equation (1.10)[65].

3.3.1- Langmuir Adsorption Isotherm

It is calculated by using equation (1.12). Figure (3.5) shows plots of (C_i/θ) versus (C_i) for NaI inhibitor in (IM HCl) at different temperatures (303.15,313.15,323.15 and 333.15) K according to equation (1.12). The data fit straight lines indicating that inhibitors are adsorbed according to the Langmuir adsorption isotherm it can also explain the increase in inhibition efficiency with increasing the concentration of the inhibitor as an indication of the increase in the number of inhibitor molecules that adsorb on the surface of the mild steel and block active sites from direct acid attacks and then protect metals from corrosion [66]. From the intercept of the straight line K_L , values can be evaluated which can be then substituted in Equation (1.13) to calculate ΔG^{0}_{ads}. Table (3.2) shows the values of K_L and ΔG^{0}_{ads}. The equilibrium constant of the inhibitor adsorption K_L values increase with increasing temperature in the range (303.15-333.15) K . The higher K_L values clearly proved the strong adsorption of (NaI) inhibitor molecules on mild steel surfaces [67].The negative values of (ΔG^{0}_{ads}) indicate that the inhibitors are adsorbed spontaneity on the metal surface and that (ΔG^{0}_{ads}) change values is associated with the efficiency of inhibition and (ΔG^{0}_{ads}) values increasing with temperature increase. It is well known that the value of (ΔG^{0}_{ads}) in the order of (-20 kJ/mol) or less negative are associated with an electrostatic interaction between the charged inhibitor molecules and the charged metal surface (physical adsorption) process those of (-40 kJ/mol) or more negative involves charge sharing or transferring from the inhibitor molecules to the metal surface to form a coordinate covalent bond (chemical adsorption) process [68]. The free energy of adsorption (ΔG^{0}_{ads}) for the studied inhibitor lies between (-20.9034) and (-25.6038) in Table (3.2),which mean it is between (-20 -40 kJ/mol) that adsorption is neither physical nor chemical but of a mixed type.Adsorption of inhibitor molecules on the surface of mild steel involves both physical adsorption and chemical adsorption (Comprehensive adsorption) but the first adsorption one is the predominant mode this assumption is supported b data obtained depending on the temperature of the inhibition process reported in Table (3.1) which shows that the calculated inhibitory efficiency increases with increasing temperature [66].

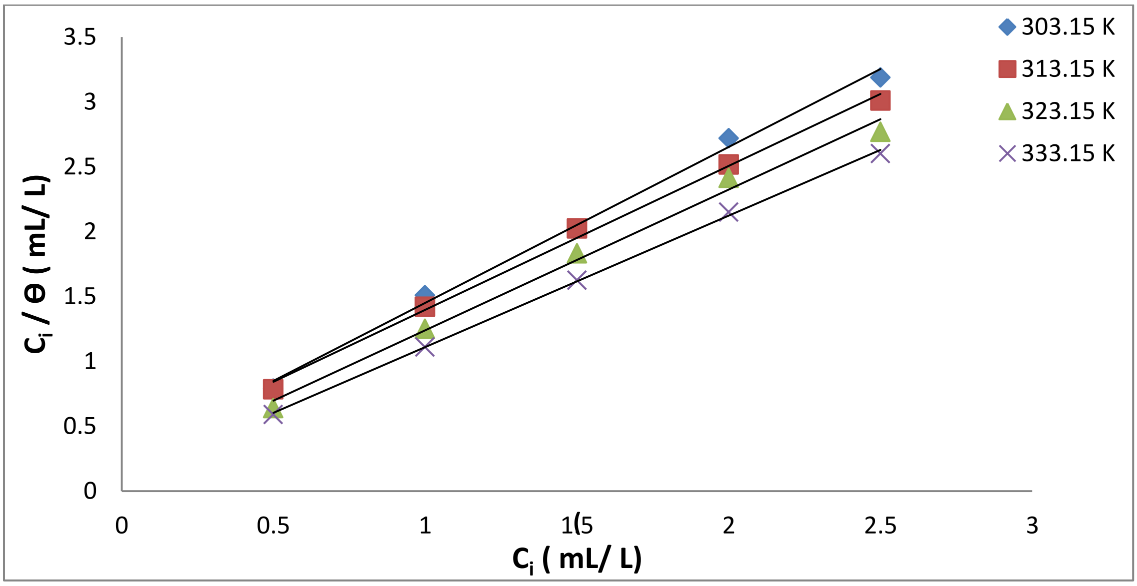


Figure (3.5) Langmuir adsorption isotherm of corrosion inhibitor for mild steel corrosion in (1M HCl) by (NaI) at different temperature .

Table (3.2) Equilibrium constant (K_L), standard adsorption free energy ($\Delta G^0{}_{ads}$), and correlation coefficient (R^2) for langmuir type adsorption isotherm of the inhibitor (NaI) for mild steel corrosion in (1M HCl) at different temperatures.

Temperature/ (K)	K_L /(L/mL)	$\Delta G^0{}_{ads}$ /(kJ/mol)	R^2
303	4.0192	-20.9034	0.9957
313	3.4916	-21.2271	0.9962
323	6.5189	-23.5819	0.9920
333	10.3950	-25.6038	0.9993

3.3.2- Freundlich Adsorption Isotherm

It is calculated by using equation (1.17) Fig (3.6) that produced by plotting (ln Ө) against (ln C_i) with slope and intercept yield values of ($n^{"}$) and (K_F) respectively with data given in Table (3.3).Freundlich does not seem to apply well to this system because correlation coefficient values are low however, Langmuir isotherm applies and gives more fitness to the adsorption isotherm system because the correlation coefficient values are high [69] .

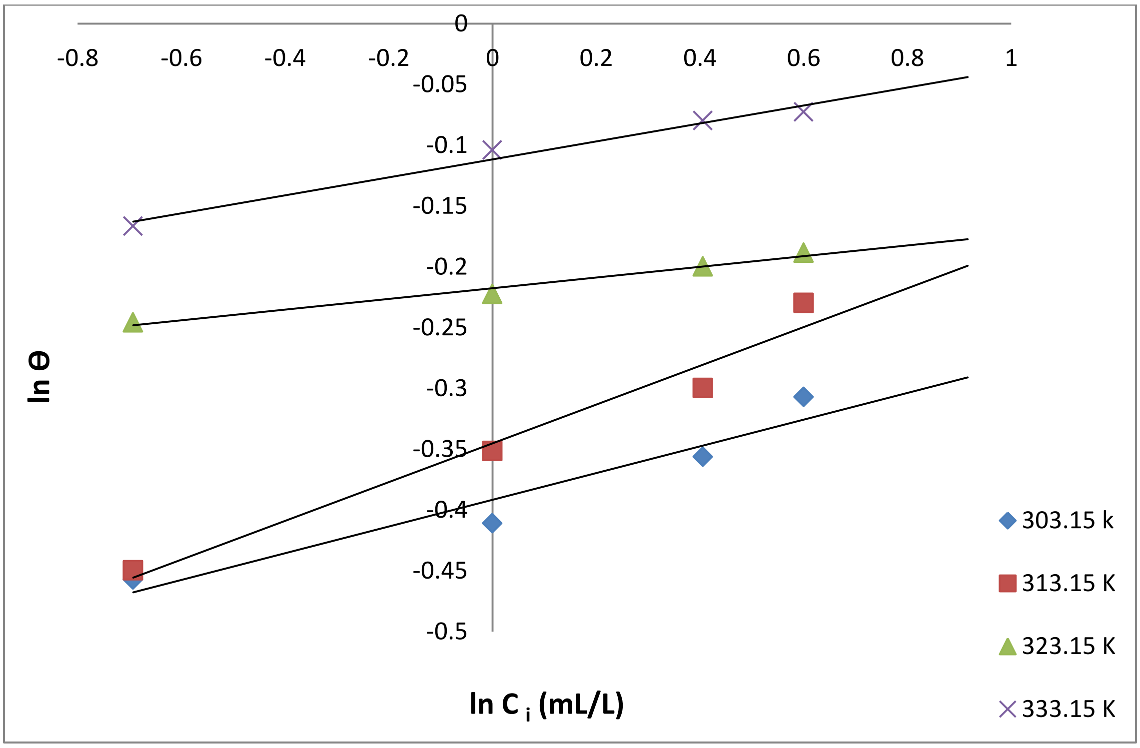


Figure (3.6) Freundlich adsorption isotherm of (NaI) for mild steel corrosion in (1M HCl) by (NaI) at different temperature .

Table (3.3) Equilibrium constant (K_F), slope (n''), and correlation coefficient (R^2) for Freundlich type adsorption isotherm of the inhibitor (NaI) for mild steel corrosion in (1M HCl) at different temperatures.

Temperature/ (K)	K_F /(L/mL)	n''	R^2
303	0.6760	0.1099	0.9284
313	0.7089	0.1651	0.9786
323	0.8044	0.0441	0.9819
333	0.8947	0.0756	0.9872

3.4. Effect of Temperature and Activation Studies

Values of apparent activation energy of corrosion (E_a) for mild steel corrosion process in (1M HCl) in the presence and absence of NaI was calculated by using equation (1.4). By plotting the Arrhenius plots of (ln C_R) versus (1 / T) data given in Table (3.1) which give straight lines with slopes equal to (- E_a / R) as in Fig (3.7) . The estimated values of (E_a) for mild steel corrosion in the presence of NaI in (1M HCl) are listed in Table (3.4) . Activation energy of mild steel was found to be (55.69216 kJ/mol) in the absence of the inhibitor and decreases to (8.45783 kJ /mol) in the presence of it. It is showed that the value of (E_a) for uninhibited solution is higher than of inhibited solution suggesting that dissolution of mild steel is slow in the presence of inhibitor and can be interpreted as due to (chemical adsorption). With temperature increase, some chemical changes occur in the inhibitor molecules leading to increased electron density at the adsorption center of inhibitor molecules and then improve the inhibition efficiency.It is clear that the inhibitor concentration plays a role in reducing the activation energy values indicating the more inhibitory effect, so (E_a) is less in the presence of inhibitor in general [70,71].

Table (3.4) Values of activation energies for the corrosion of mild steel in presence and absence (NaI) inihibitor as the corrosion inhibitor.

C_i /(mL/L)	E_a /(kJ / mol)
Blank	**55.69216**
0.5	**29.71589**
1	**21.78517**
1.5	**18.80709**
2	**12.15580**
2.5	**8.45783**

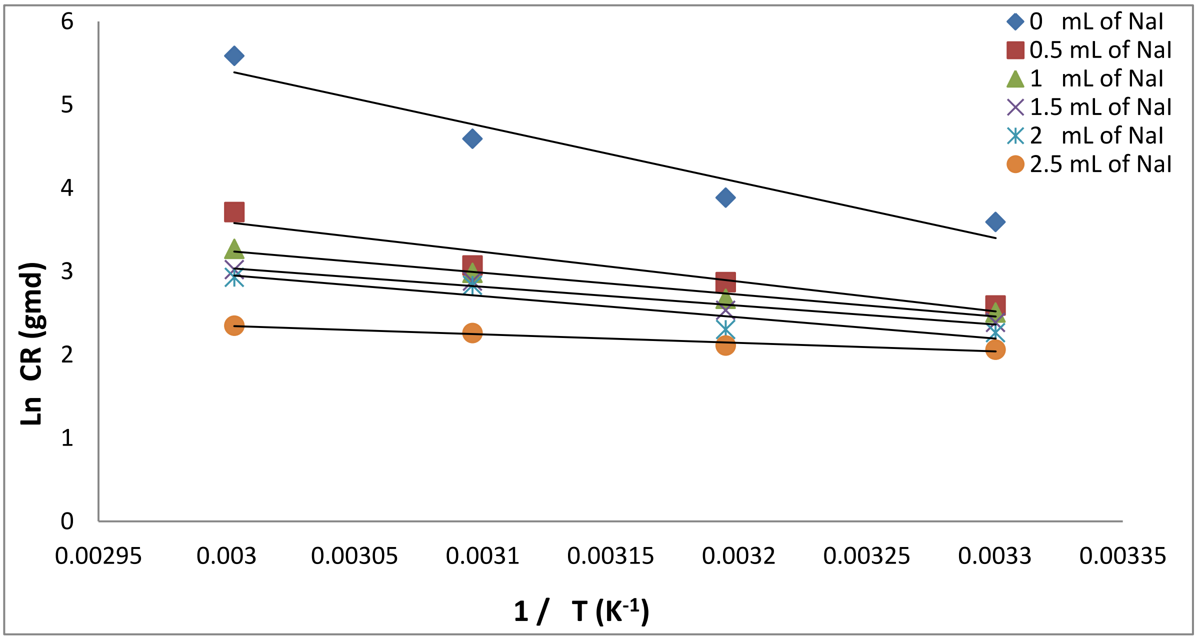


Figure (3.7) Arrhenius plot of mild steel corrosion in (1M HCl) containing various concentrations of NaI inhbitor at different temperatures .

Experimental corrosion rates values calculated from weight loss measurements for mild steel corrosion in (1M HCl) in absence and presence of NaI inihibitor were used to determine the enthalpy of activation, (ΔH^*) and entropy of activation (ΔS^*) for the formation of the activated complex from the transition state equation. The enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) were calculated by using equation (1.9) By plotting ln (C_R / T) versus (1/ T) as shown in Fig (3.8) where straight lines obtained with slopes of ($-\Delta H^* / R$) and intercepts of ln(R / N h) + ($\Delta S^* / R$) from which (ΔH^*) and (ΔS^*) were calculated and listed in Table (3.5) . The ΔH^* values are positive and this show an endothermic nature of the activated step of the corrosion process [72,73].Large and negative values of ΔS^* in the uninhibited and inhibited solutions imply that the activation complex in the rate determining steps represents association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [74-76] .Generally positive value of ΔH* means endothermic process while negative value implies exothermic process [75]. In an endothermic adsorption process ΔH* > 0 infers chemical adsorption while $\Delta H^* < 0$ indicates physical adsorption [75,77,78].

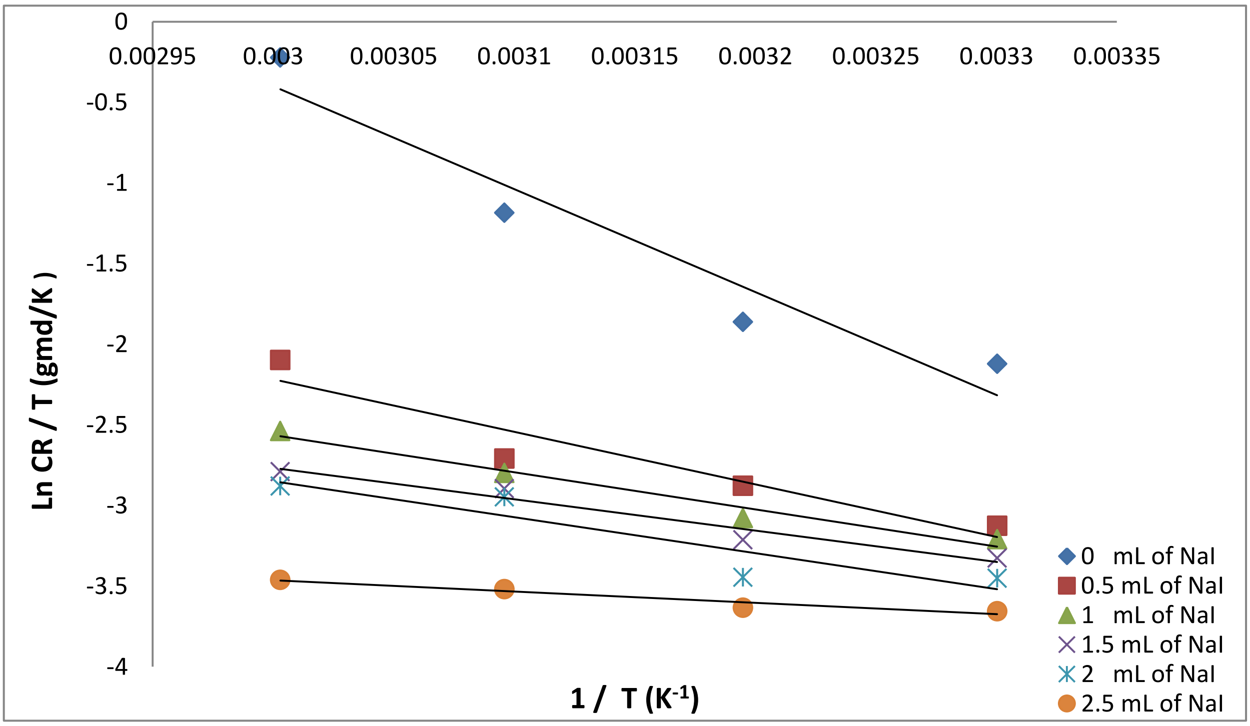


Figure (3.8) Transition state plot for mild steel corrosion in (1M HCl) in absence and presence of different concentrations of NaI inhibitor .

Table (3.5) Enthalpy and entropy of activation values of the mild steel corrosion reaction with various concentrations of NaI inhibitor in (1MHCl) .

C_i /(mL/L)	ΔS^* /(kJ / mol . K)	ΔH^* /(kJ / mol)
Blank	**-0.04170**	**53.05329**
0.5	**-0.13474**	**27.07620**
1	**-0.16141**	**19.14547**
1.5	**-0.17203**	**16.16740**
2	**-0.16568**	**18.51694**
2.5	**-0.18620**	**5.81871**

3.5. Kinetics Interpretation

In order to determine the order of the corrosion reaction of carbon steel in HCl ,equations (3.3 and 3.5) were used for the zero and first model respectively. In addition equations (3.4 and 3.6) were used to calculate the half-life of the corrosion reaction for the same models. Tables (3.6),(3.7),(3.8) and (3.9) show the results of the first order kinetic at different temperature (30,40 ,50 and 60) °C in presence and absence of inhibitor solution at different times (1, 2, 3, and 4h).

$$\Delta W = k_0 . t \qquad (3.3)$$

$$t_{1/2} = a / 2 k_0 \qquad (3.4)$$

$$\ln (W_1 / W_2) = k_1 . t \qquad (3.5)$$

$$t_{1/2} = 0.693 / k_1 \qquad (3.6)$$

Where ΔW is weight loss in grams, a is initial weight of carbon steel (gm), k_o and k_1 are rate constant in (g / h and 1/h) respectively, $t_{1/2}$ is half –life in h. From equation (3.5) a plot of $\ln W_1/W_2$ against (t) is shown in figures (3.9), (3.10) ,(3.11) and (3.12) with slope yields the value of k_1 and tables (3.6), (3.7) ,(3.8) and (3.9) shows values of k_1, $t_{1/2}$ and correlation coefficient R^2 in first order. The reaction rates can also be expressed in terms of half-life period $t_{1/2}$. Since that values of $t_{1/2}$ increase with increases of temperature and increases with inhibitor concentration the dissolution rate of the metal in the solution decreases with increase in concentration of the inhibitor [79,80].

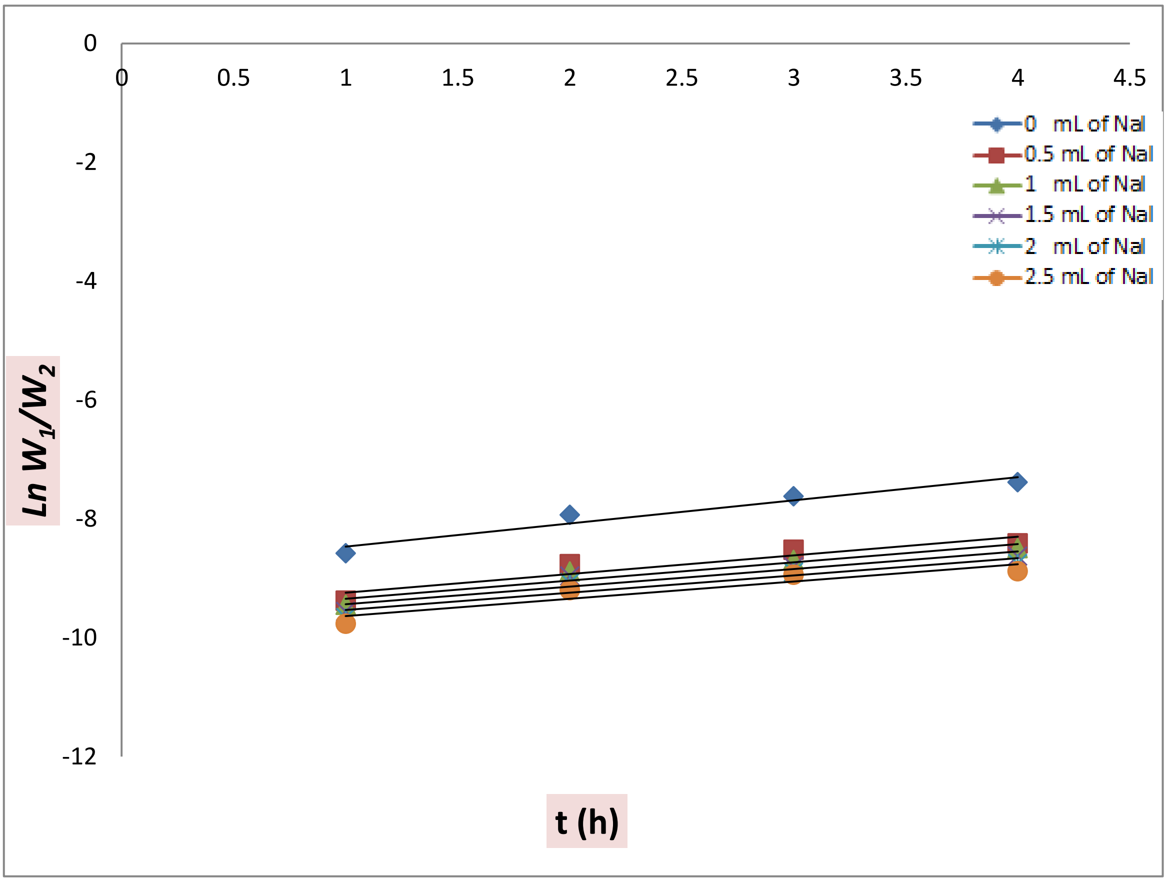


Figure (3.9) ($\ln W_1/W_2$) against time for carbon steel corrosion in 1 M HCl in presence and absence of (NaI) inhibitor at (30°C).

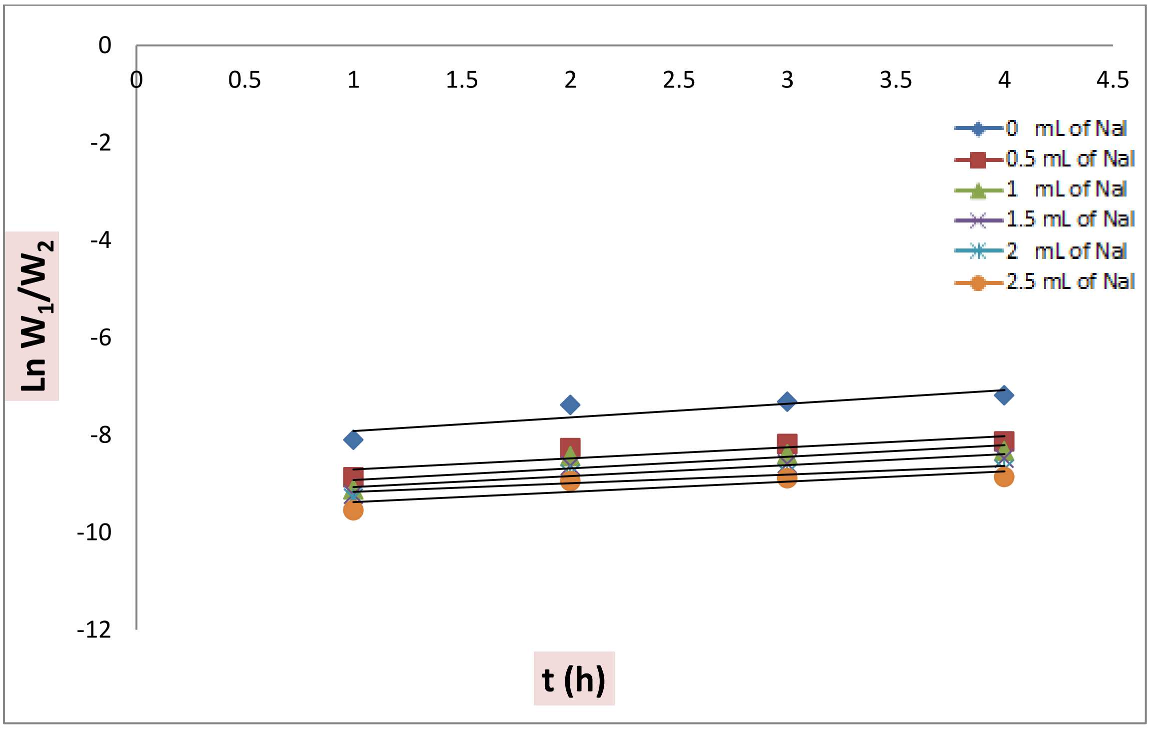


Figure (3.10) ($\ln W_1/W_2$) against time for carbon steel corrosion in 1 M HCl in presence and absence of (NaI) inhibitor at (40°C).

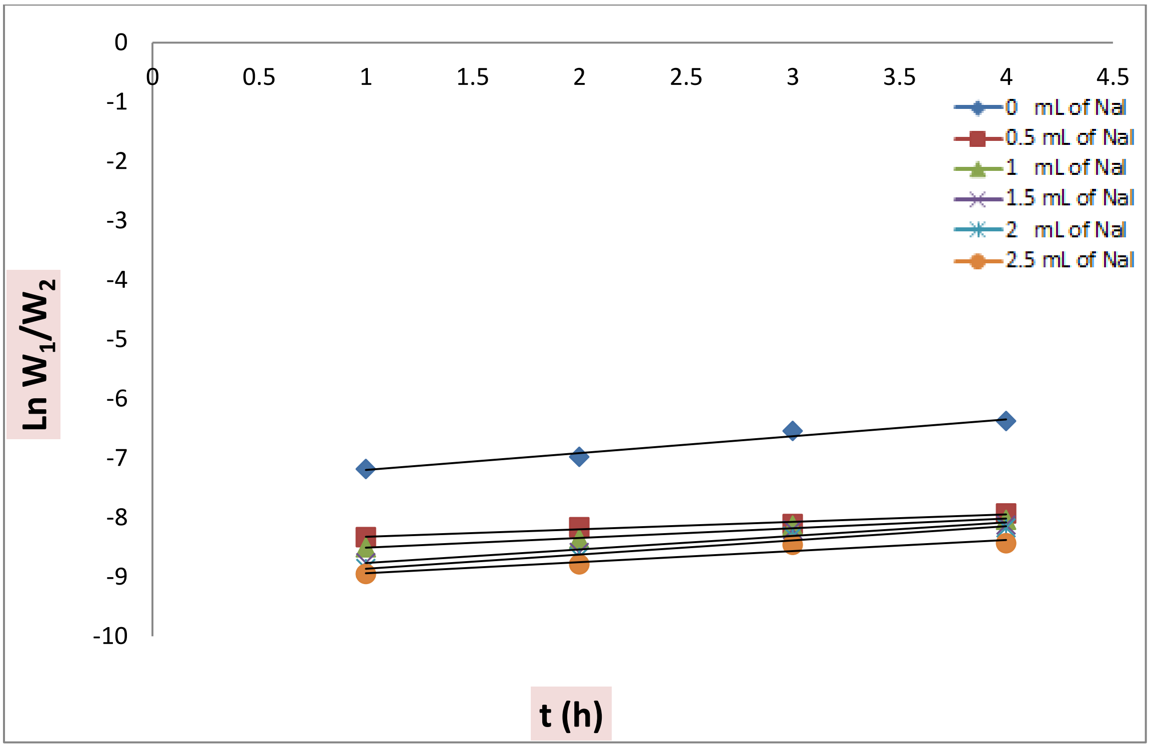


Figure (3.11) ($\ln W_1/W_2$) against time for carbon steel corrosion in 1M HCl in presence and absence of (NaI) inhibitor at (50°C).

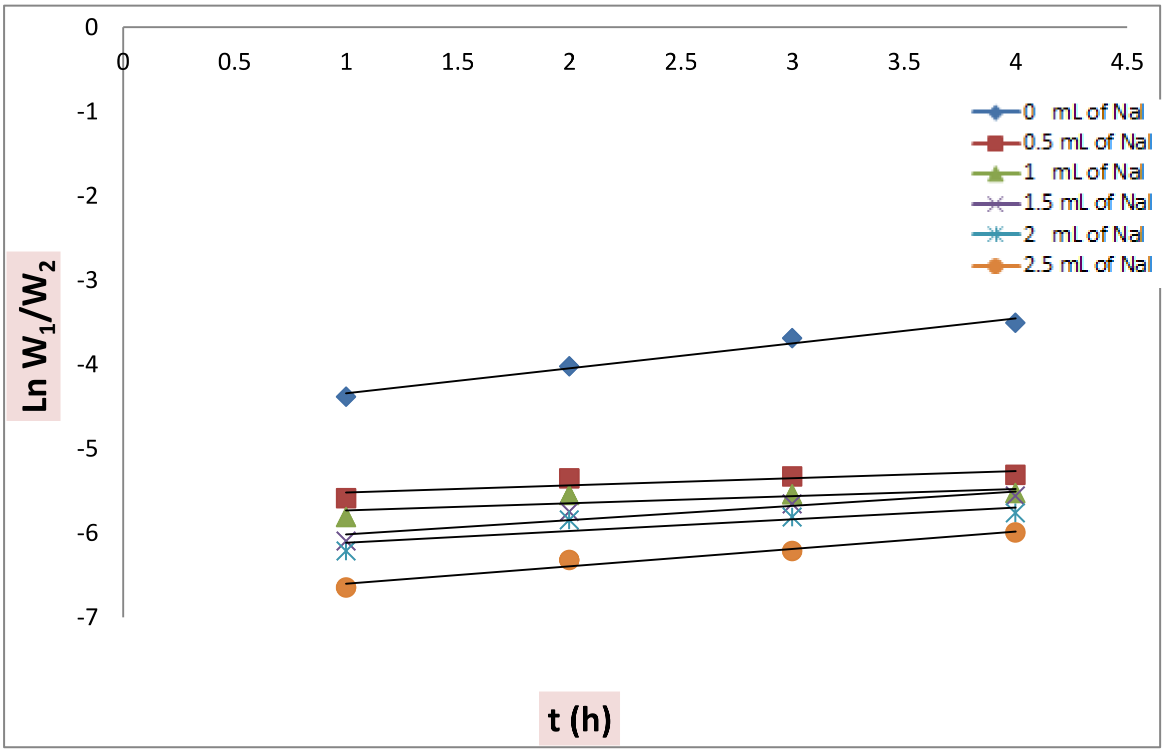


Figure (3.12) ($\ln W_1/W_2$) against time for carbon steel corrosion in 1M HCl in presence and absence of (NaI) inhibitor at (60°C).

Table (3.6) Rate constant values of first order, half-life and correlation coefficient (R^2) at different temperatures in presence and absence of inhibitor concentrations in 30°C in (1M HCl) .

Concentrations (mL/L)	k_1 (1/h)	$t_{1/2}$ (h)	R^2
Blank	0.3901	1.7764	0.9426
0.5	0.3143	2.2048	0.8806
1	0.3059	2.2654	0.9233
1.5	0.2961	2.3404	0.8890
2	0.2905	2.3855	0.8857
2.5	0.2904	2.3863	0.8648

Table (3.7) Rate constant values of first order, half-life and correlation Coefficient (R^2) at different temperatures in presence and absence of inhibitor concentrations in 40 °C in (1M HCl) .

Concentrations (mL/L)	k_1 (1/h)	$t_{1/2}$ (h)	R^2
Blank	0.2895	2.3937	0.7794
0.5	0.2399	2.8887	0.7546
1	0.2390	2.8995	0.7079
1.5	0.2265	3.0596	0.7735
2	0.2253	3.0758	0.7375
2.5	0.2103	3.2952	0.6994

Table (3.8) Rate constant values of first order , half-life and correlation coefficient (R^2) at different temperatures in presence and absence of inhibitor concentrations in 50 °C in (1M HCl) .

Concentrations (mL/L)	k_1 (1/h)	$t_{1/2}$ (h)	R^2
Blank	0.2850	3.7459	0.9699
0.5	0.1752	3.9554	0.9649
1	0.1632	4.2463	0.9798
1.5	0.1484	4.6698	0.9444
2	0.1404	4.9358	0.9750
2.5	0.1273	5.4438	0.9204

Table (3.9) Rate constant values of first order, half-life and correlation coefficient (R^2) at different temperatures in presence and absence of inhibitor concentrations in 60 °C in (1M HCl) .

Concentrations (mL/L)	k_1 (1/h)	$t_{1/2}$ (h)	R^2
Blank	0.1760	3.9375	0.9807
0.5	0.1701	4.0740	0.7228
1	0.1544	4.4883	0.6588
1.5	0.1397	4.9606	0.8780
2	0.1355	5.1143	0.7515
2.5	0.1133	6.1165	0.9625

3.6. Potentiodynamic Polarization Measurements

Polarization measurements were carried out in order to gain knowledge regarding the kinetics of the cathodic and anodic reactions polarization curves of the mild steel electrode in 1M HCl in absence and at different concentrations of inhibitor.Different temperatures also(30- 40- 50- 60) °C ,as shown in Figures (3.13),(3.14),(3.15) and (3.16).The corrosion current densities were estimated by Tafel extrapolation of cathodic and anodic curves to the corrosion potentials. The Tafel slopes were estimated as well.

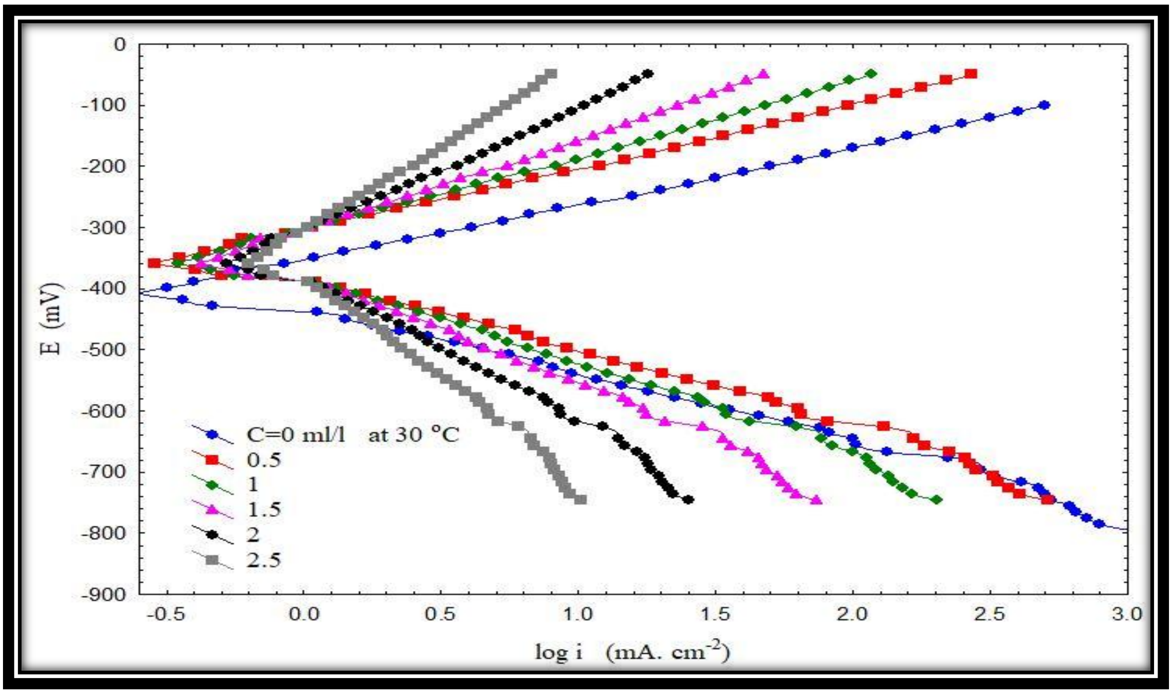


Figure (3.13) Tafel polarization curves for corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of NaI at 30 °C.

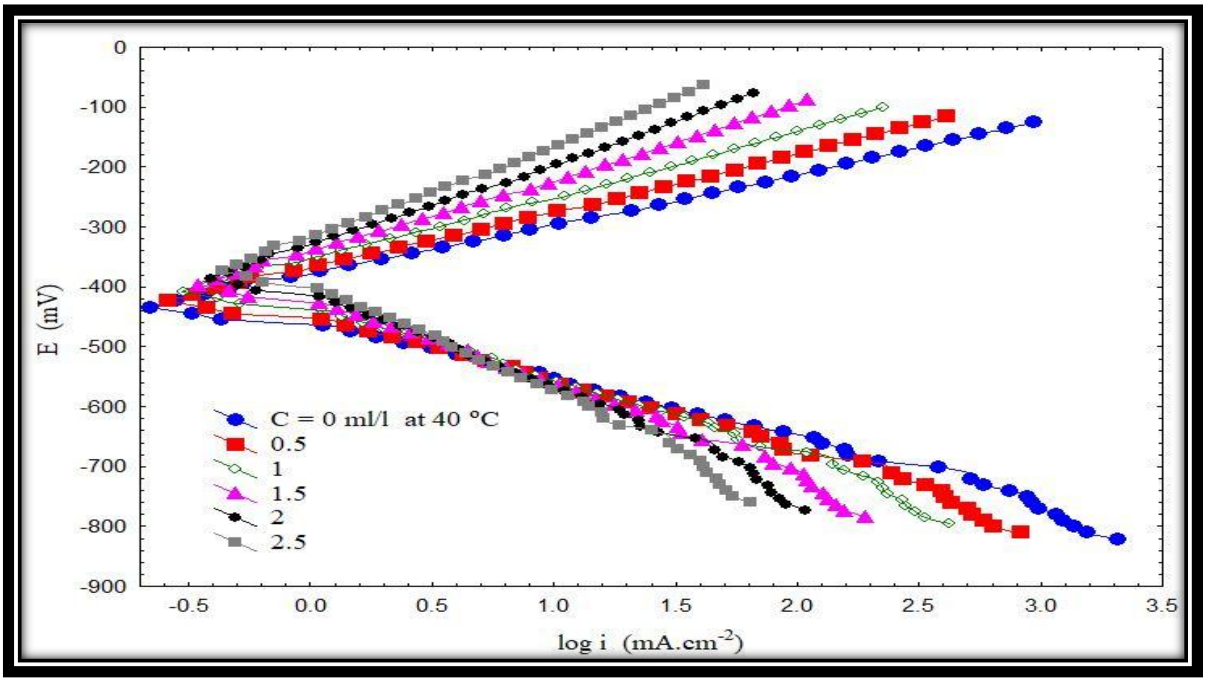


Figure (3.14) Tafel polarization curves for corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of NaI at 40 °C.

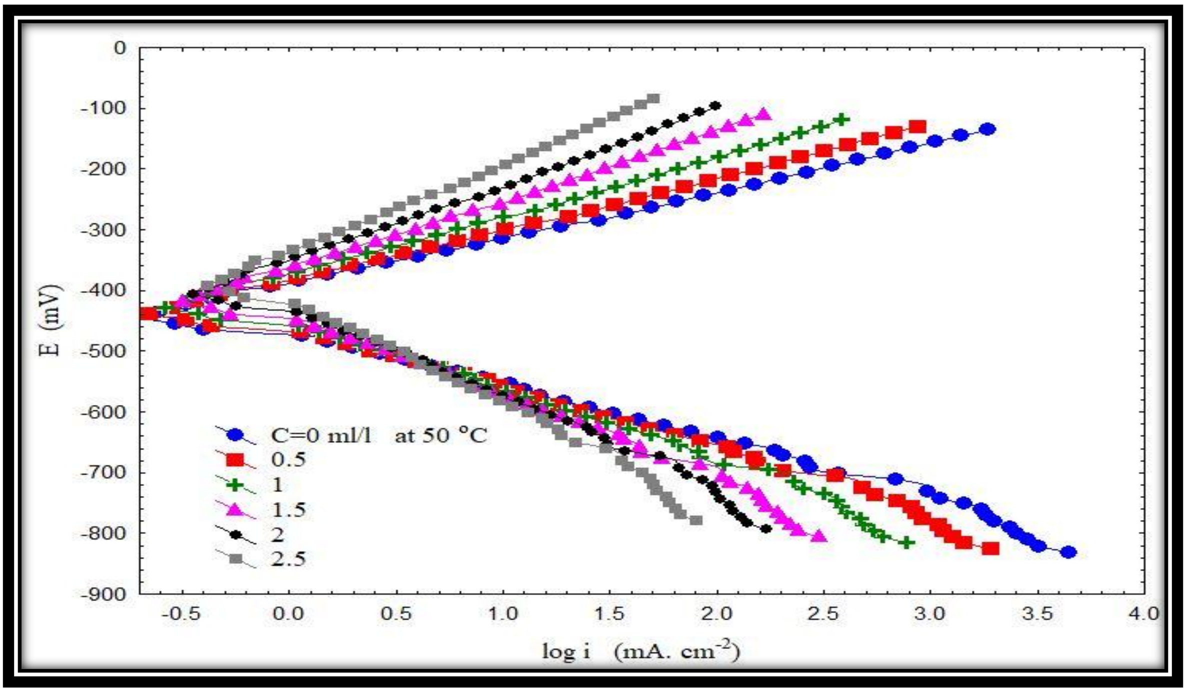


Figure (3.15) Tafel polarization curves for corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of NaI at 50 °C.

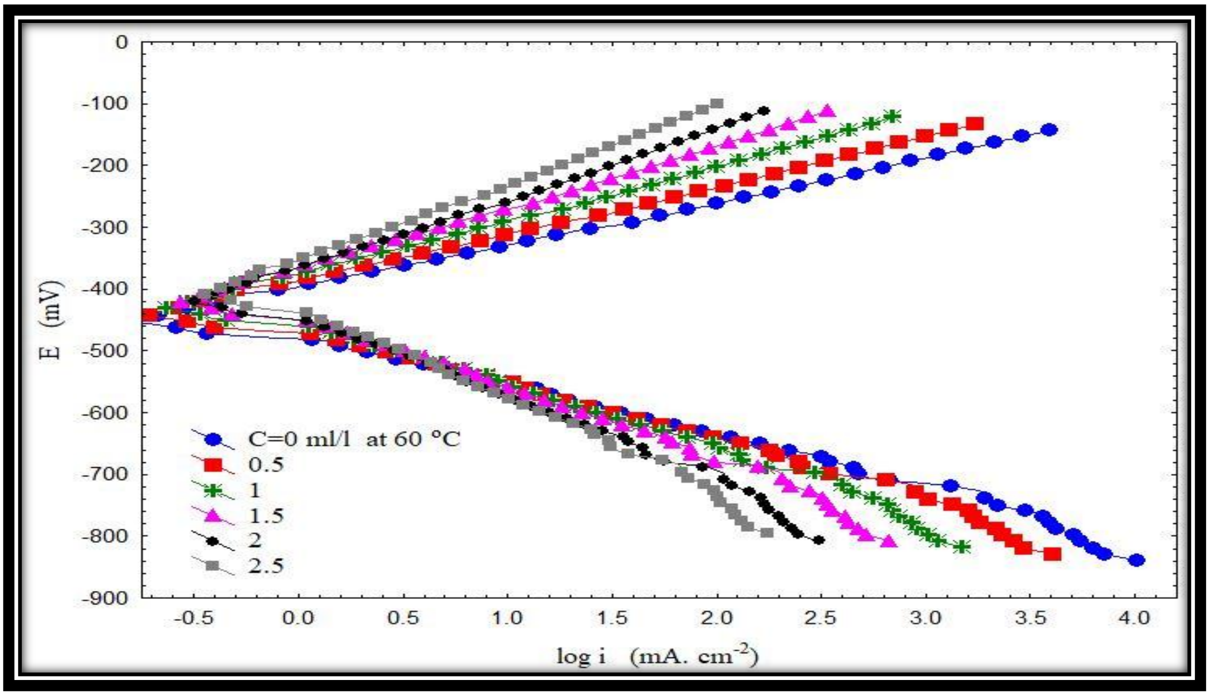


Figure (3.16) Tafel polarization curves for corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of NaI at 60 °C.

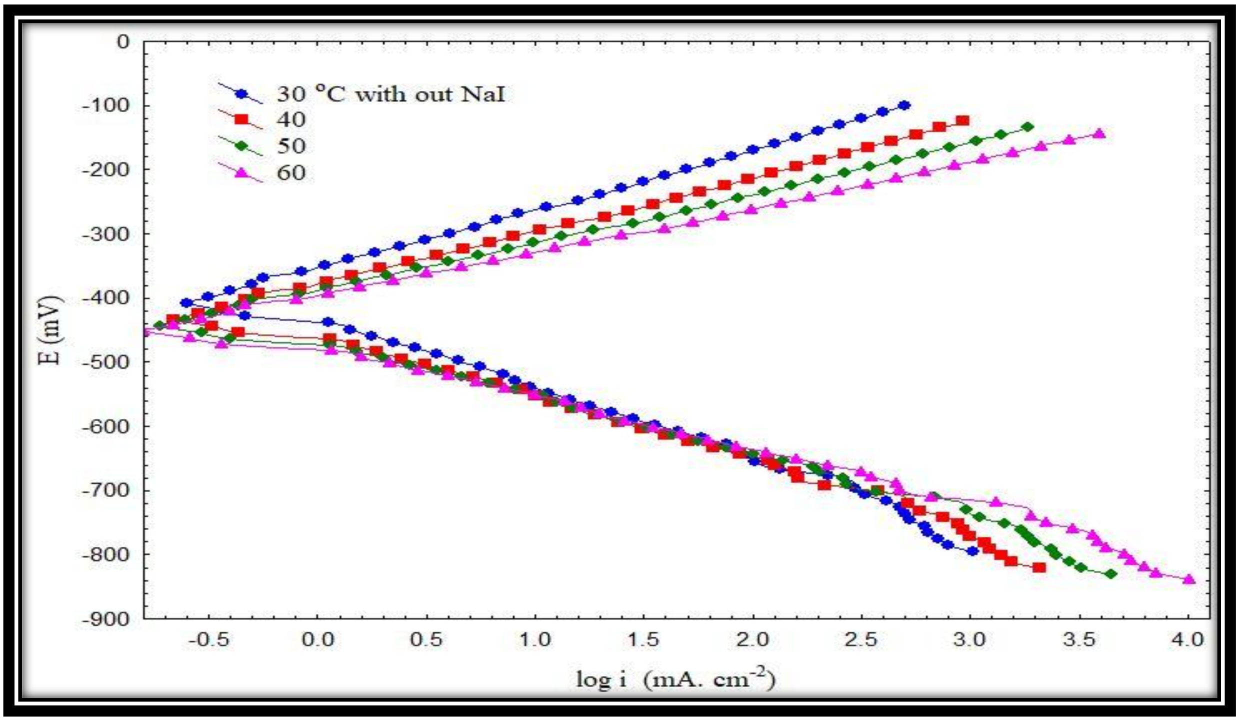


Figure (3.17) Tafel polarization curves for corrosion of mild steel in 1M HCl at 30,40,50.and 60°C with out NaI .

The Tafel polarization curves for inhibited and uninhibited mild steel specimens are shown in Fig (3.13),(3.14),(3.15) and (3.16) .Several electrochemical polarization parameters were calculated and tabulated in Table (3.10) including anodic and cathodic Tafel slopes (βa, and βc) corrosion potential (E_{corr}) corrosion current density (i_{corr}).Inhibition efficiency was derived using following equation :-

$$IE\ \% = \frac{i_{corr\ (Blank)} - i_{corr\ (Inhibitor)}}{i_{corr (Blank)}} \times 100 \qquad (3.7)$$

Where i_{corr} *(Blank)* and i_{corr} (Inhibitor) are corrosion current density without and with presence of NaI, respectively. It has been reported that (i) if the displacement in E_{corr} is >85 *mV* of inhibitor with respect to E $_{corr}$ of blank acid solution, the inhibitor could be recognized as cathodic or anodic type and (ii) if displacement in E_{corr} is < 85 the inhibitor can be considered as mixed type [81,82,83]. The inspection of Table(3.10) reveals that E_{corr} value does not change significantly in presence of NaI suggesting that it is a mixed type inhibitor. Table (3.10) shows that the values of corrosion current densities increase with increasing in temperatures in both the absence and presence of inhibitors. It is also shown that the corrosion current densities decrease with increasing the inhibitor concentrations at any temperature that NaI inhibits corrosion by blocking the active sites present on the metallic surface without changing the mechanism of corrosion.The same behavior was obtained from weight loss technique. The values of cathodic slopes (βc) are larger as compared to the values of anodic slope (βa) [84,85].

Table (3.10) Polarization Data for Corrosion of low Carbon Steel in Acidic Solution in Absence and Presennce of NaI .

Conc. mL / L	Temp. °C	E_{corr} mV	i_{corr} mA/cm^2	$-b_c$ (mV.dec^{-1})	$+b_a$	% IE
Blank	30	-439	3.16	123	85	00
	40	-464	4.24	126	87	00
	50	-474	8.59	130	88	00
	60	-482	23.19	128	82	00
0.5	30	-389	1.16	125	88	63
	40	-454	1.53	128	90	64
	50	-459	1.87	132	91	78
	60	-472	3.56	130	85	85
1	30	-385	1.06	130	90	66
	40	-439	1.26	133	92	70
	50	-448	1.71	137	93	80
	60	-461	2.29	135	87	90
1.5	30	-377	0.95	135	86	70
	40	-427	1.10	138	88	74
	50	-436	1.55	142	89	82
	60	-451	1.78	140	83	92
2	30	-375	0.84	122	75	74
	40	-416	0.87	125	77	79
	50	-423	1.48	129	78	83
	60	-451	1.63	127	72	93
2.5	30	-355	0.68	140	80	78
	40	-403	0.72	143	82	83
	50	-420	0.83	147	83	90
	60	-439	0.91	145	77	96

3.7. X-ray Diffraction Analysis

X-ray diffraction was used to study mild steel in the absence and presence of sodium iodide inhibitor [86,87].They were used for (i) a pure steel sample (ii) steel sample with the presence of hydrochloric acid (iii) steel sample with the presence of hydrochloric acid and presence of 2.5 mL/L of the sodium iodide inhibitor with the time of immersion of four hours. Fig (3.18) shows the X-ray diffraction patterns (i) pure sample due to the fact that the iron ratio is very large than other elements . Fig (3.19) shows the X-ray diffraction patterns (ii) in the presence of hydrochloric acid, a large number of peaks are observed due to the reaction of the acid solution with elements of alloy components and the appearance of new phases.Fig (3.20) shows the X-ray diffraction patterns (iii) for sample in presence of (1M) hydrochloric acid solution containing (2.5 mL /L) of sodium iodide where it's clear that identical to the pure sample . In other words, there is no effect of acid solution in the presence of inhibitor [88,89].

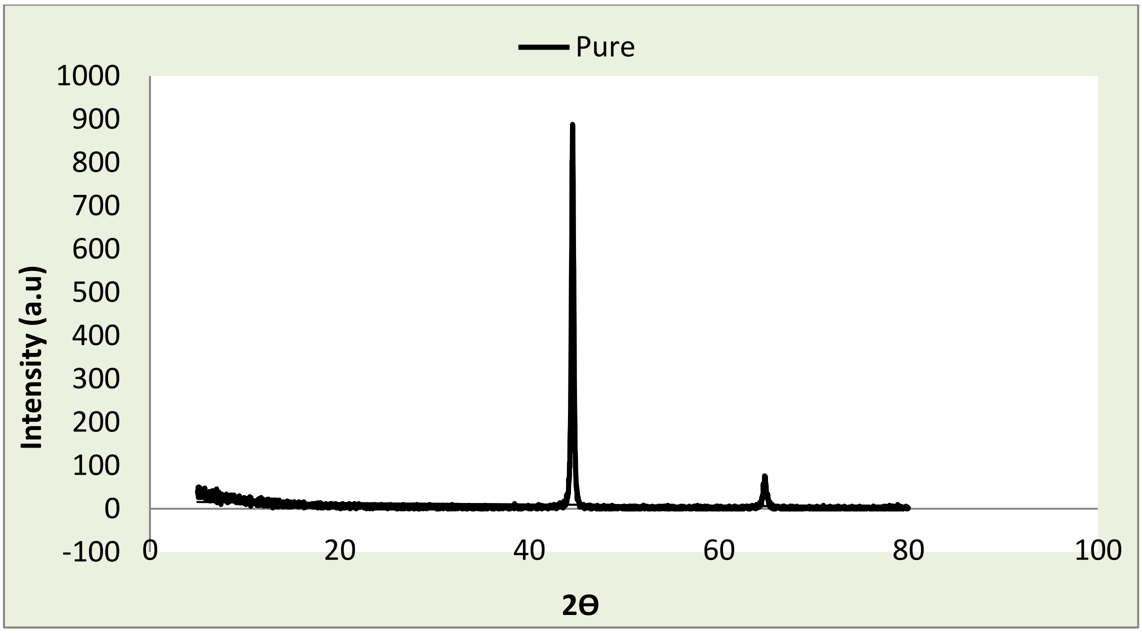


Figure (3.18) X-ray diffraction pattern of steel sample (Pure)

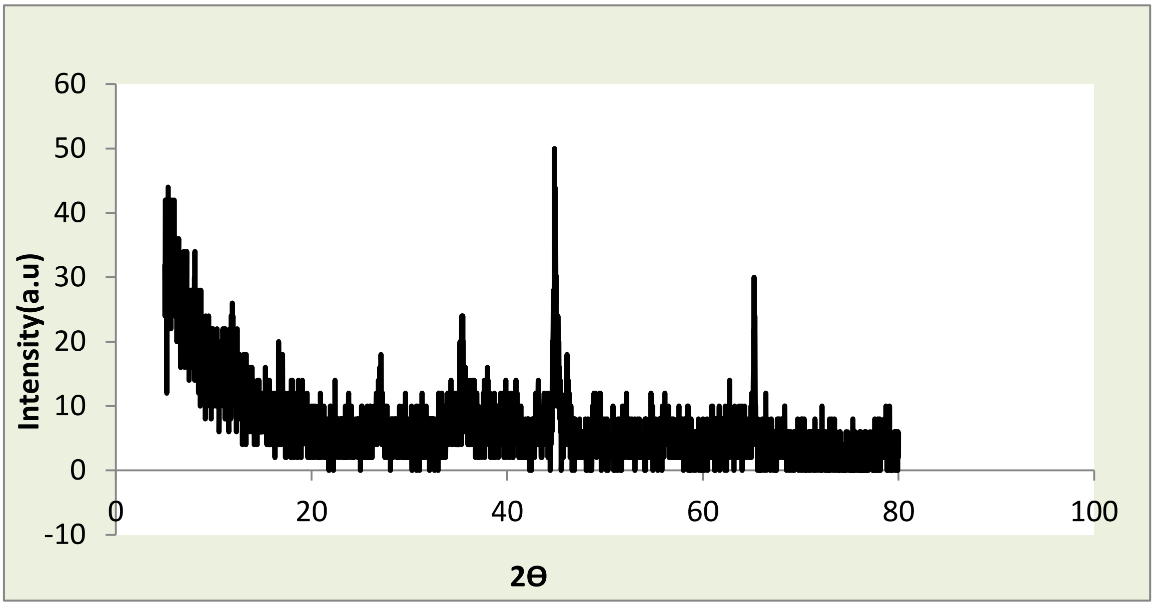


Figure (3.19) X-ray diffraction pattern of steel sample (Blank)

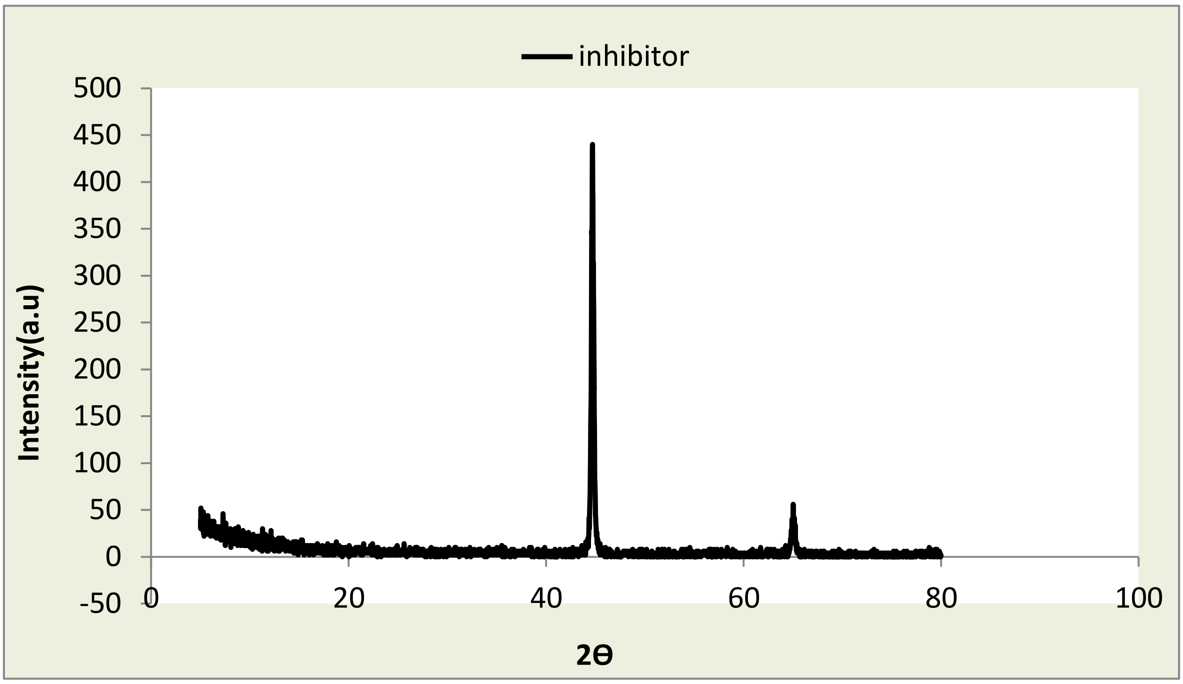


Figure (3.20) X-ray diffraction pattern of steel sample (Inhibitor)

3.8. Atomic Force Microscopy

Atomic Force Microscopy Characterization (AFM) is a powerful technique used to investigate the surface morphology at nano –to micro–scale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal solution interface [90,93]. The three dimensional (3D) AFM morphology and the AFM cross–sectional profile for polished carbon steel surface (a) thase immersed in 1M HCl (b) and immersed in 2.5mL/L NaI.

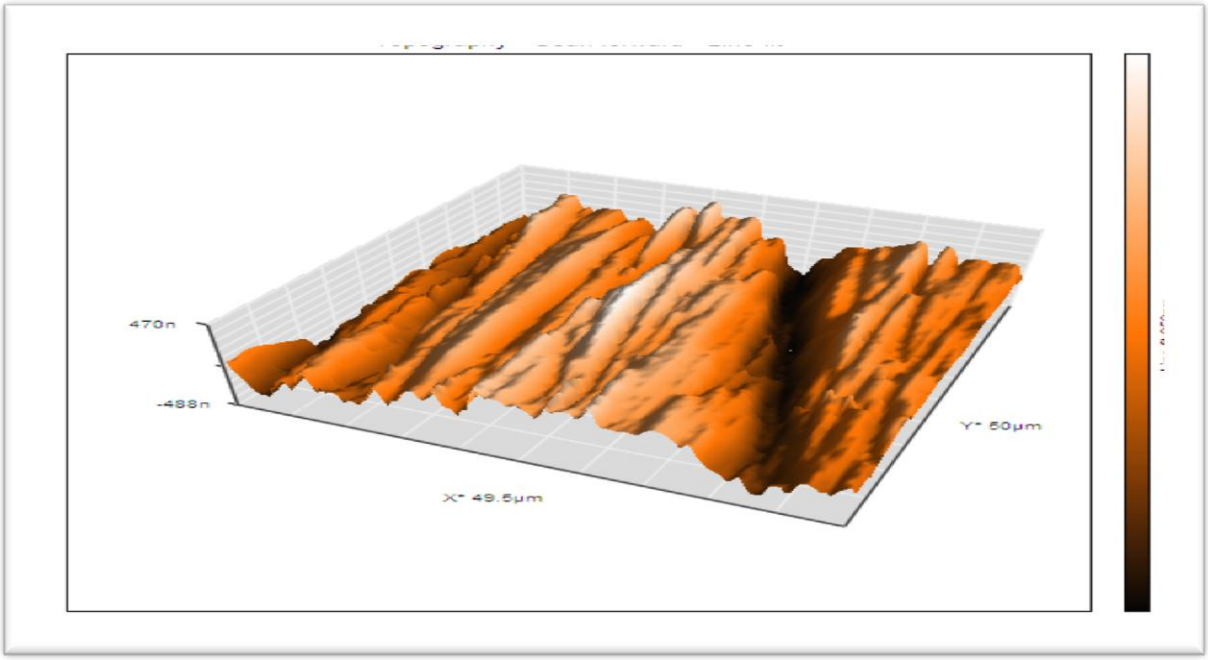
Root – mean – square roughness, average roughness, and peak–to–valley value

AFM image analysis was performed to obtain the average roughness Ra (the average deviation of all points roughness profile from a mean line over the evaluation length), root–mean–square roughness Rq (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak–to–valley (P – V) height values (largest single peak–to–valley height in five adjoining sampling heights) [90]. Table (3.11) is a summary of (Rq) , (Ra) and (P–V) values for carbon steel surface immersed in inhibited and uninhibited environment.

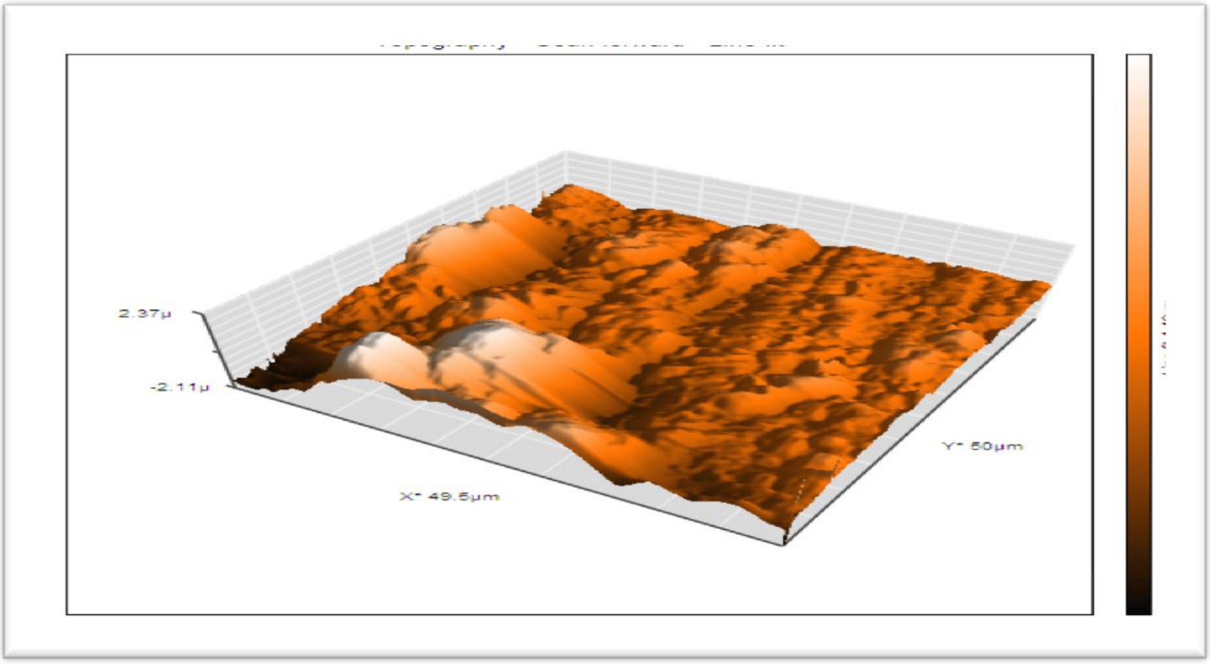
Table (3.11) AFM Data for Carbon Steel Surface Immersed in Inhibited and Uninhibited HCl solution.

Sample	Average Roughness (Ra) / (nm)	RMS (Rq) Roughness / (nm)	Maximum Peak – to valley Height (R_y) /(nm)
1.Polished carbon steel	131.35 nm	168.97 nm	991.87 nm
2.Carbon steel immersed in 1M HCl (blank)	1343.4 nm	1660.7 nm	12421 nm
3.Carbon steel immersed in 1M HCl Presence 2.5 ml /L NaI	219.65 nm	280.93 nm	4483.6 nm

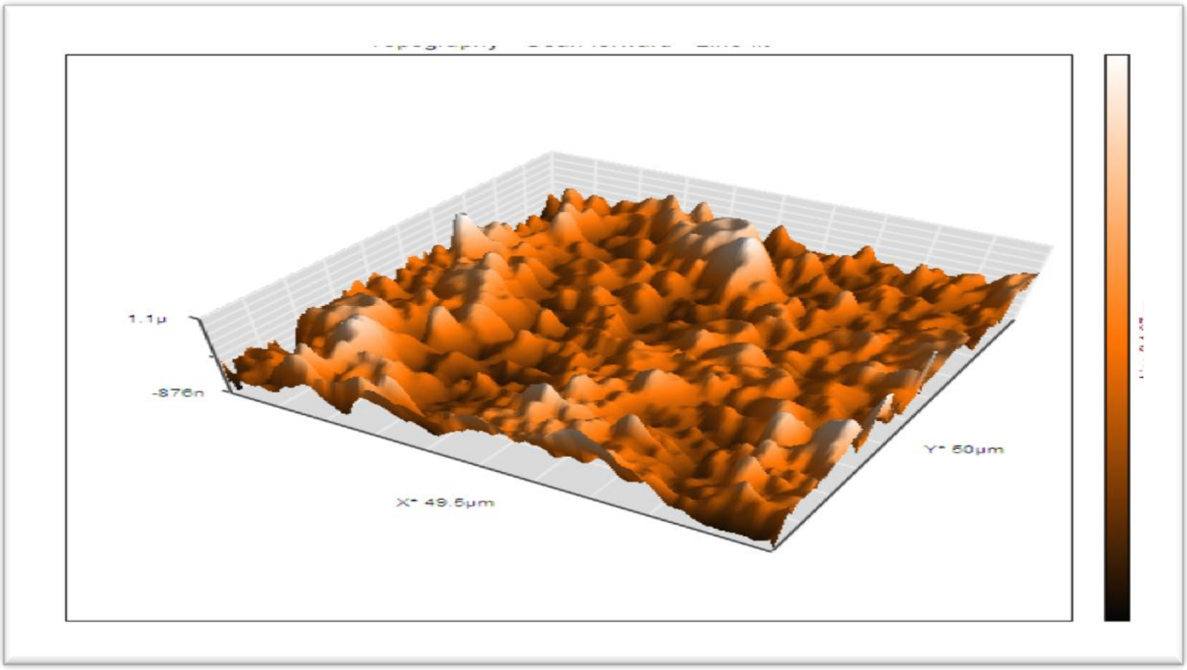
In image (a) of Fig (3.21) the surface topography of uncorroded metal surface is shown. The values of Rq , Ra and P – V height for the polished carbon steel surface (pure sample) were measured . The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. Image (b) of Fig (3.21) shows the pitted corroded metal surface in the absence of the inhibitor immersed in 1M HCl . These data suggest that carbon steel surface immersed in 1M HCl has a greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher due to the corrosion of the steel in 1M HCl environment. Image (c) of Fig (3.21) show the steel , surface after immersion in 1M HCl containing NaI. The (Rq), (Ra),(P–V) height values are considerably less in the inhibited environment compared to the uninhibited environment. These parameters confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of NaI complex on the metal surface thereby inhibiting the corrosion of steel [90].



(a)



(b)



(c)

Figure (3.21) Three dimensional (AFM) images of the surface of :

a. Polished carbon steel .

b. Steel immersed 1M HCl (blank).

c. Steel immersed in 1M HCl Presence 2.5 mL/L NaI .

3.9. Conclusion

The following conclusions can be drawn from the present study:

1. By increasing the temperature, the corrosion rate of mild steels in solution (1M HCl) is also increasing .

2. Sodium iodide inhibitor proved to be an effective inhibitor of mild steel corrosion in 1M hydrochloric acid solution. Maximum inhibition efficiency obtained is 96.07 % at 60℃ and inhibitor concentration of 2.5mL/L.
3. Adsorption isotherms test as a means to understand the model of adsorption agreed to Langmuir adsorption isotherm.

4. The negative sign of the free energy of adsorption (ΔG^0_{ads}) indicates that the adsorption of the inhibitors on the low carbon steel surface was a spontaneous process .

5. Activation energy is in general less in the presence of the inhibitor than in absence which refers to the mechanism of chemical adsorption .

6. AFM and XRD confirm the corrosion of mild steel in 1 M HCl and its inhibition by NaI in weight loss technique .

7. Thermodynamic coefficients (enthalpy of activation, entropy of activation) were in good agreement in weight loss technique .

8. Polarization Technique was used to find the anodic and cathodic polarization curves at different temperatures (303.15,313.15, 323.15, and 333.15) K in 1M hydrochloric acid with concentrations ranging (0-2.5) mL/L of NaI . The polarization curves in the presence and absence of inhibitory materials at different temperatures indicate that the corrosion rate increases by increasing the temperature at the concentration of the inhibitory material and that the erosion voltage generally shifts to the positive direction with increasing concentration, and shifts to negative direction with increasing temperature as well.

3.10. Suggestions for Further Research

Several suggestions may be forwarded for further research on carbon steel which may be summarized as:

1. Other metals can be used such as, copper, aluminum, chromium , zinc etc.

2. Similar work can be repeated in other acidic solutions, such as H_3PO_4, H_2SO_4 ,HNO_3 and seawater .

3. A study of the efficiency of inhibitors under other temperature levels can be conducted .

4. The corrosion medium can also be subjected to chemical analysis after corrosion tests to estimate the amounts of various metallic ions that can be formed through anodic dissolution of the working electrode.

5. An attempt may be made to protect the metal surface by coating with nano materials or paints prior to the electrochemical investigation.

6. Methods of hydrogen evolution can be used as alternative method .

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الخلاصة

في هذا العمل تمت دراسة تأثير تثبيط يوديد الصوديوم كمثبط للتاكل غير العضوي على تآكل الحديد المطاوع في محلول حامض الهيدروكلوريك عند درجات حرارة مختلفة (303.15,313.15.323.15 and 333.15)K باستخدام طريقة فقدان الوزن كما تم استخدام طريقة الاستقطاب الكهروكيميائي . وقد وجد ان كفاءة تثبيط التآكل تزداد مع زيادة التركيز والوقت، كانت القيمة القصوى لكفاءة المثبط (96.07%) ، عند درجة حرارة 333.15 K وتركيز المادة المانعة(2.5 mL/L) والزمن 4 ساعات. واظهرت النتائج ان معدل التاكل بوجود وعدم وجود المادة المانعة (يوديد الصوديوم) يزداد مع زيادة درجة الحرارة عند اي تركيز لمانع التاكل , معدل التآكل يقل مع زيادة تركيز المادة المانعة عند اي درجة حرارة . تم استخدام ميكانيكيات اثنين لتفسير عملية امتزاز مثبطات التاكل على سطح المعدن(*Freundlich Adsorption* , *Langmuir Adsorption Isotherm*, لوحظ ان المواد المثبطة تتبع تفسير لنكماير *Langmuir Adsorption Isotherm* في ميكانيكية عملها اكثر من تفسير فريندلش *Freundlich Adsorption Isotherm* اي ان المواد المثبطة للتاكل تعمل وفق الامتزاز على سطح المعدن وتكوين طبقة احادية . تم استخدام قيم ثابت الاتزان لتقييم الطاقة الحرة القياسية للامتزاز (*Heat of adsorption* , ΔG^0_{ads}) لتحديد نوع الامتزاز (فيزيائي أو كيميائي أو مختلط). في هذه الدراسة ، يشتمل الإمتزاز على الامتزاز الكيميائي هو السائد وان الامتزاز يحدث بشكل تلقائي على سطح المعدن وذلك لان قيم الطاقة الحرة للامتزاز سالبة . تم استخدام معادلة ارينيوس *Arrhenius Equation*) ومعادلة الحالة الانتقالية (*Transition state Equation*) لايجاد قيم طاقة التنشيط E_a *وانثالبي التنشيط* ΔH^* *وانتروبي التنشيط* ΔS^*. ايضا تم إجراء تحليل *XRD* وتحليل *AFM* لدراسة خاصية تثبيط يوديد الصوديوم في محلول HCl أظهرت تحاليل *XRD* و *AFM* أن وجود سطح يوديد الصوديوم يصبح سلسًا بسبب تشكيل طبقة المثبط على السطح المعدني. تمت دراسة معدلات التآكل بطريقة الاستقطاب الكهربائي في ظل ظروف الدرجات الحرارية K (,15. (303313.15, 323.15 and 333.15 وتركيز المادة المثبطة (0, 0.5,1 ,1.5, 2 and 2.5 mL/L) تشير منحنيات الاستقطاب في وجود وغياب المواد المثبطة في درجات حرارة مختلفة إلى أن قيم كثافات تيار التآكل تزداد بزيادة درجة الحرارة عند أي تركيز للمثبط وكذلك أن كثافة كثافة التآكل تقل مع زيادة تركيزات المانع عند أي درجة حرارة أن قيمة E_{Corr} لا تتغير بشكل كبير في وجود NaI مما يشير إلى أنه مثبط نوع مختلط . قيم المنحدرات الكاثودية (βc) أكبر مقارنةً بقيم الميل الأنودي (βa)

وزارة التعليم العالي والبحث العلمي
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تقييم معدلات تآكل الحديد المطاوع في الوسط الحامضي باستخدام تقنيات مختلفة

رسالة مقدمة الى
مجلس كلية العلوم / جامعة ديالى
وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء
من قبل الطالبة

ورود نجدت احميد

بكالوريوس في علوم الكيمياء 2016
كلية العلوم – جامعة ديالى
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