

An Electrochemical Study for Corrosion Inhibition of Iron by Some Organic Compounds in Acidic Media

Thesis Submitted

By

Nashwa Saad Abd El-Shafy Mohamed

M.Sc., Education (

For

The Degree of

Ph. D. for Teacher's Preparation in Science (Physical Chemistry)

To

Chemistry Department Faculty of Education Ain Shams University Cairo, Egypt



Approval Sheet

Name of candidate: Nashwa Saad Abd El-Shafy Mohamed

<u>Degree:</u> Ph. D. for Teacher's Preparation in Science (Physical Chemistry)

<u>Thesis Title:</u> An Electrochemical Study for Corrosion Inhibition of Iron by Some Organic Compounds in Acidic Media

Inis Thesis has been approved by:
Approved
Prof. Dr. Sayed Sabet Abdel-Rehim(D.Sc.)
Prof. of Physical Chemistry, Faculty of Science, Chemistry Department,
Ain Shams University.
Prof. Dr. Reda Mohamadi Abdel Rahman(D.Sc.)
Prof. of Organic Chemistry, Faculty of Education, Chemistry Department
Ain Shams University.
Dr. Khaled Fouad Khaled Mahmoud
Ass. Prof. of Physical Chemistry, Faculty of Education, Chemistry
Department, Ain Shams University.
Dr. Fawzya Fouad Abdullah
Lecturer of Physical Chemistry, Faculty of Education, Chemistry
Department, Ain Shams University.

Prof. Dr. E. A. Mohamed Head of the Chemistry Department Faculty of Education Ain Shams University



An Electrochemical Study for Corrosion Inhibition of Iron by Some Organic Compounds in Acidic Media

By Nashwa Saad Abd El-Shafy Mohamed

M.Sc., Education ()

Under the Supervision of

Prof.Dr. Sayed Sabet Abdel-Rehim

Prof. of Physical Chemistry, Faculty of Science, Chemistry Department. Ain Shams University (D.Sc.)

Prof. Dr. Reda Mohamadi Abdel Rahman

Prof. of Organic Chemistry, Faculty of Education, Chemistry Department. Ain Shams University (D.Sc.)

Dr. Khaled Fouad Khaled Mahmoud

Ass. Prof. of Physical Chemistry, Faculty of Education, Chemistry Department. Ain Shams University.

Dr. Fawzya Fouad Abdullah

Lecturer of Physical Chemistry, Faculty of Education, Chemistry Department. Ain Shams University.



Title Sheet

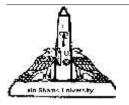
Name of researcher : Nashwa Saad Abd El-Shafy Mohamed

Date of Birth : //

Place of Birth : Elmansora

First University Degree: B.Sc. & Ed., May

Name of University : Ain Shams



Faculty of Education Chemistry Department

ABSTRACT

An Electrochemical Study for Corrosion Inhibition of Iron by Some Organic Compounds in Acidic Media.

$\mathbf{B}\mathbf{y}$

Nashwa Saad Abd El-Shafy Mohamed

Department of Chemistry, Faculty of Education Ain-Shams University, Roxy, Cairo, Egypt

Electrochemical frequency modulation (EFM) can be used as a rapid and non-destructive technique for corrosion rate measurements without prior knowledge of Tafel constants. Corrosion rates obtained with this technique were in good agreement with other traditional techniques as Tafel extrapolation and EIS. Causality factors used by EFM are good internal check for verifying the validity of data obtained by this technique.

The corrosion inhibition of iron in \ M hydrochloric acid solution by some new thiourea derivatives, \(\frac{9}{2}\)-(\(\frac{2}{2}\)-fluorophenxyl aminothioxo)carbazole (\(\begin{align*} FPAC\), \(\frac{1}{2}\)-octayl-\(\frac{1}{2}\)-phenyl- thiourea (\(\begin{align*} OPT\), \(\frac{1}{2}\)-(\(\frac{1}{2}\)-hydroxyphenyl)-\(\frac{1}{2}\)-phenylthiourea (\(\begin{align*} HPP\), and \(\frac{1}{2}\)-(anthraquinon) thiosemicarbazone

(ATC) was studied using the following techniques: Tafel extrapolation method, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM). These measurements show that the inhibition efficiency increased by increasing the inhibitor concentration. The inhibition efficiency follows the order: FPAC > OPT > HPP > DAT > ATC.

Polarization studies show that these compounds act as mixed type inhibitors in \ M HCl solution. The effect of temperature on corrosion inhibition was studied using polarization technique. The fundamental thermodynamic parameters for dissolution and adsorption were determined and discussed. These inhibitors function through adsorption following Flory-Huggins and kinetic-thermodynamic model isotherm. Equivalent circuits of the investigated system are suggested.

The electronic properties of these inhibitors, obtained using MNDO semi-empirical self-consistence field method, have been correlated with their experimental efficiencies using non-linear regression method.

Keywords: iron; corrosion; EFM; EIS; Tafel; MNDO; acid inhibition

List of Figures

a

h

List of Tables

Chapter I

Introduction
\. General Mechanism of corrosion inhibition
\.\. Adsorption isotherms
۱٫۳. Electrochemical methods in corrosion studies
. DC techniques
. The Butler-Volmer equation
. The Tafel equation
. The Stern-Geary equation
. AC techniques
. Electrochemical Impedance Spectroscopy
. Fundamental aspects of EIS
. The interpretation of EIS
. Electrochemical Frequancy Modulation
. Calculating the corrosion current and the corrosion
rate
. Causality Factors
۱٫٤. Quantum chemical calculations
<u>Chapter II</u>
EXPERIMENTAL PROCEDURE
Y, V. Electrochemical cell.
. Working electrode

List of Contents	Page
Summary	• • • • • • • • • •
References	• • • • • • • • • • • • • • • • • • • •
Published Paper	
Arabic Summary	• • • • • • • • • •
Arabic Abstract	

- (a). The impedance Nyquist plot of an electrode undergoing a simple corrosion reaction.
- (b). Equivalent circuit simulating the simple electrode impedance. R_{Ohm} is the solution resistance. Rp is the polarisation resistance. Cdl is the double layer capacitance.

A typical Nyquist plot.

- (a). The impedance Nyquist plot of an electrode filmed with a non-conducting surface film.
- (b). Equivalent circuit for the electrode. R_{Ohm} is the solution resistance. R_{pore} is the resistance of the surface film in pore area. C_{fim} is the capacitance of the surface film. R_t is the charge transfer resistance. C_{dl} is the double layer capacitance.

Intermodulation spectrum for iron in \M HCl.

Intermodulation spectrum for iron in ^{1}M HCl in presence of $10^{-4}M$ ATC.

Intermodulation spectrum for iron in ^{1}M HCl in presence of $3 \times 10^{-4} M$ ATC.

Intermodulation spectrum for iron in $^{\text{M}}$ HCl in presence of $5 \times 10^{-4} M$ ATC.

Intermodulation spectrum for iron in 1 M HCl in presence of $7 \times 10^{-4} M$ ATC

Intermodulation spectrum for iron in $^{\ }M$ HCl in presence of $9 \times 10^{-4} M$ ATC

Intermodulation spectrum for iron in ${}^{1}M$ HCl in presence of $10^{-4}M$ DAT

Intermodulation spectrum for iron in ^{1}M HCl in presence of $3 \times 10^{-4} M$ DAT

Intermodulation spectrum for iron in ${}^{1}M$ HCl in presence of $5 \times 10^{-4} M$ DAT

Intermodulation spectrum for iron in ^{1}M HCl in presence of $7 \times 10^{-4} M$ DAT

Intermodulation spectrum for iron in $^{\ }M$ HCl in presence of $9 \times 10^{-4} M$ DAT

Intermodulation spectrum for iron in ${}^{\ }M$ HCl in presence of $10^{-4}M$ HPP

Intermodulation spectrum for iron in ^{1}M HCl in presence of $3 \times 10^{-4} M$ HPP

Intermodulation spectrum for iron in ${}^{1}M$ HCl in presence of $5 \times 10^{-4} M$ HPP

Intermodulation spectrum for iron in ^{1}M HCl in presence of $7 \times 10^{-4} M$ HPP

Intermodulation spectrum for iron in $^{\ }M$ HCl in presence of $3\times10^{-4}M$ OPT

Intermodulation spectrum for iron in ${}^{\backprime}M$ HCl in presence of $5 \times 10^{-4} M$ OPT

Intermodulation spectrum for iron in ${}^{1}M$ HCl in presence of $10^{-4}M$ FPAC

Intermodulation spectrum for iron in \M HCl in presence of $\mbox{$^{\tau}$}$ x $\mbox{$^{-\epsilon}$}$ M FPAC

Intermodulation spectrum for iron in ^{1}M HCl in presence of $9 \times 10^{-4} M$ FPAC

Tafel plots for iron in ${}^{\backprime}M$ HCl in absence and presence $10^{-4}M$ of various thiourea derivatives at ${}^{\backprime}\circ{}^{\circ}C$.

Tafel plots for iron in ${}^{1}M$ HCl in absence and presence $3 \times 10^{-4} M$ of various thiourea derivatives at 1 °C.

Tafel plots for iron in ${}^{1}M$ HCl in absence and presence $5 \times 10^{-4} M$ of various thiourea derivatives at ${}^{1}\text{C}^{\circ}\text{C}$.

Tafel plots for iron in ${}^{1}M$ HCl in absence and presence $7 \times 10^{-4} M$ of various thiourea derivatives at ${}^{1}\circ {}^{0}C$.

Tafel plots for iron in ${}^{1}M$ HCl in absence and presence $9 \times 10^{-4} M$ of various thiourea derivatives at 1 °C.

Nyquist plots for iron in ${}^{\backprime}M$ HCl without and with $10^{-4}M$ of various thiourea derivatives at ${}^{\backprime}\circ{}^{\circ}C$.

Nyquist plots for iron in ${}^{1}M$ HCl without and with $3 \times 10^{-4} M$ of various thiourea derivatives at 1 °C.

Nyquist plots for iron in ${}^{\backprime}M$ HCl without and with $5 \times 10^{-4} M$ of various thiourea derivatives at ${}^{\backprime}$ °C.

Nyquist plots for iron in ${}^{1}M$ HCl without and with $7 \times 10^{-4} M$ of various thiourea derivatives at 1 °C.

Nyquist plots for iron in ${}^{1}M$ HCl without and with $9 \times 10^{-4} M$ of various thiourea derivatives at 1 °C.

Bode plots for iron in ${}^{\backprime}M$ HCl without and with $10^{-4}M$ of various thiourea derivatives at ${}^{\backprime}\circ{}^{\circ}C$.

Bode plots for iron in ${}^{\backprime}M$ HCl without and with $3 \times 10^{-4} M$ of various thioureal derivatives at ${}^{\backprime}\circ{}^{\circ}C$.

Bode plots for iron in ${}^{\backprime}M$ HCl without and with $5 \times 10^{-4} M$ of various thiourea derivatives at ${}^{\backprime}o{}^{\circ}C$.

Bode plots for iron in 'M HCl without and with 'X ' · · · M of various thiourea derivatives at 'Co°C.

Bode plots for iron in ${}^{1}M$ HCl without and with $9 \times 10^{-4} M$ of various thiourea derivatives at ${}^{1}\circ{}^{0}C$.

Electrical equivalent circuit representing iron/HCl/Inhibitor.

- (a) Nyquist plot of iron in \M HCl solution
- (b) Bode-phase plots of iron corrosion in 'M HCl solution at

 $E_{\it corr}$.

- (a) Nyquist plot of iron in ${}^{1}M$ HCl solution with $5 \times 10^{-4} M$ ATC
- (b) Bode-phase plots of iron corrosion in $^{\}M$ HCl solution with $5\times10^{-4}M$ ATC at E_{corr} .
- a) Nyquist plot of iron in 'M HCl solution with $5\times10^{-4}M$ DAT (b) Bode-phase plots of iron corrosion in 'M HCl solution with $5\times10^{-4}M$ DAT at E_{corr} .
- (a) Nyquist plot of iron in 'M HCl solution with $5\times10^{-4}M$ HPP (b) Bode-phase plots of iron corrosion in 'M HCl solution with $5\times10^{-4}M$ HPP at E_{corr} .
- (a) Nyquist plot of iron in 'M HCl solution with $5\times10^{-4}M$ OPT (b) Bode-phase plots of iron corrosion in 'M HCl solution with $5\times10^{-4}M$ OPT at E_{corr} .
- (a) Nyquist plot of iron in ^{1}M HCl solution with $5 \times 10^{-4} M$ FPAC
- (b) Bode-phase plots of iron corrosion in $^{\}M$ HCl solution with $5\times10^{-4}M$ FPAC at E_{corr} .

Tafel plots for iron in M HCl in absence and presence $10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $10^{-4}M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $10^{-4}M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $10^{-4}M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $3 \times 10^{-4} M$ of thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $3 \times 10^{-4} M$ of various thiourea derivatives at ${}^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $3\times10^{-4}M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $3\times10^{-4}M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $5 \times 10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $5 \times 10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $5 \times 10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $5 \times 10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $7 \times 10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $7 \times 10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $7 \times 10^{-4} M$ of various thiourea derivatives at °C.

Tafel plots for iron in M HCl in absence and presence $7 \times 10^{-4} M$ of various thiourea derivatives at °C.

Tafel plots for iron in M HCl in absence and presence $9 \times 10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $9 \times 10^{-4} M$ of various thiourea derivatives at ${}^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $9 \times 10^{-4} M$ of various thiourea derivatives at $^{\circ}$ C.

Tafel plots for iron in M HCl in absence and presence $9 \times 10^{-4} M$ of various thiourea derivatives at ${}^{\circ}$ C.

Arrhenius plot of iron in \M HCl in the presence and absence of different concentrations of FPAC.

Arrhenius plot of iron in \M HCl in the presence and absence of different concentrations of OPT.

Arrhenius plot of iron in 'M HCl in the presence and absence of different concentrations of HPP.

Arrhenius plot of iron in 'M HCl in the presence and absence of different concentrations of DAT.

Arrhenius plot of iron in 'M HCl in the presence and absence of different concentrations of ATC.

Transition-State plot of iron in \M HCl in the presence and absence of different concentrations of FPAC.

Transition-State plot of iron in \M HCl in the presence and absence of different concentrations of OPT.

Transition-State plot of iron in \M HCl in the presence and absence of different concentrations of HPP.

Transition-State plot of iron in \M HCl in the presence and absence of different concentrations of DAT.

Transition-State plot of iron in 'M HCl in the presence and absence of different concentrations of ATC.