An-Najah National University
Faculty of Graduate Studies

KINETICS AND MECHANISMS OF AQUATION REACTIONS OF TRIS (FERENE) IRON(II) COMPLEX . ANALYTICAL APPLICATIONS IN KINETIC DETERMINATIONS.

BY

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SUPERVISED BY

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Submitted in the partial fulfillment of the requirements for the degree of master of science in chemistry at .

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Dedication

To my father , mother , sisters , brothers and friends .

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Acknowledgments

First of all I thank "ALLAH" for all the knowledge and science "HE" has given to the humankind .

I would like to express my profound thanks and indebtedness to prof. Dr. Bassem Shraydeh , my supervisor, for his supervision , encouragement , guidance and inspiration throughout this study .

I wish to express my gratitude to my family and friends for their encouragement and endless support .

DAOUD MAHFOUZ

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Abstract :

In the present work the tris (Ferene) iron(II) complex has been applied for kinetic determinations of N-acetylcysteine ,phenol , 1,4-phenylendiamine , 2,4-diaminotoluene and 8-aminochinolin . Kinetic determinations of NAC , phenol and these amines were undertaken using fixed time method whereby absorbance of the tris (Ferene) iron(II) complex was measured after 5 minutes of addition of Fe(III).

The stability of the tris (Ferene) iron(II) complex in mixed aqueous organic cosolvent was studied and the kinetics determined . The order with respect to the complex is found to be unity and zero order with respect to acid . A suitable mechanism was postulated for the aquation of the above complex . The activation parameters were also determined .

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CHAPTER ONE

INTRODUCTION

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1.1: Introduction:

Several methods for N-acetylcysteine determination in drugs have been reported in literature, including spectrophotometry [1-3], ion - pair liquid chromatography[4], high pressure liquid chromatography[5], Titrimetry [6-7] and catalytic colorimetry[8]. However some of these methods are slow and not sufficiently sensitive and selective. . Several methods have been reported for the determinations of different amines . Among these methods are chromatographic [9-11], and voltametric methods[12,13]. Literature survey showed that there exists many spectrophotometric methods for the determination of different amines[14,15] . However virtually no work has been conducted for the spectrophotometric determination of 1,4-Phenylenediamine , 1,4-Diaminotoluene , 8-Aminochinolin and Phenol , in the presence of the ligand Ferene hence this work was made .

In this research, it was found that phenol , N-acetyl cysteine and some amines can reduce Fe(III) to Fe(II). The Fe(II) produced from this oxidation – reduction process reacts with Ferene (FS) forming a stable violet coloured complex .

The FS-Fe(II) complex exhibits one absorbance maximum at 593 nm[16] , while FS-Fe(III) complex does not show any absorption at this wavelength . Aquation kinetics in mixed aqueous organic cosolvent was followed for this Ferene. complex of iron(II) .

This complex can be utilized in analytical determination of N-acetylcysteine, 1,4-phenylenediamine , 2,4-Diaminotoluene and 8-Aminochinoline and Phenol .

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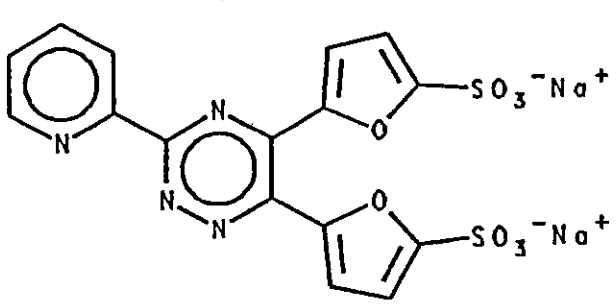
1.2: Ferene :

Ferene is a ferroin type of compound with enhanced iron chelating ability [16-19]. Ferene forms a tris complex with ferrous ion and is characterized by improved water solubility and stability over a pH range of 4.0 to 7.0 [17,20].

The compound has a molar absorptivity of 35,500 L / mol cm and 27 % higher sensitivity than Ferrozine [17,18]. It is commonly used in diagnostic reagent kits for the quantitative determination of serum iron at **593** nm[16]. Ferene is also effective for use in detection of trace metals, including cyanide at 382 nm[21], palladium at 432 nm [22] and ruthenium at 520 nm [23].

This new reagent (**whose structure is shown below**), constitutes an alternative for the commonly used ferrozine for determination of serum iron [9,12,13].



Structure of Ferene

[3-(2-pyridyl)-5,6-bis(2-(5-furyl sulfonic acid))-1,2,4-triazine,disodium]

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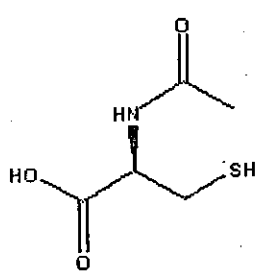
1.3: N-acetyl cysteine (N A C) :

N-acetyl cysteine (NAC) is an altered form of amino acid cysteine , which is commonly found in food and synthesized by the body. NAC is considered to be quite important for its established use in hospitals and pharmaceutial preparations for treating bronchitis and decomposing mucus [24-28] .

No consistent adverse effects of NAC (**whose structure is shown below**) have been reported in humans . One study found that daily amounts of 1.2 grams or more could lead to oxidative damage of human cells[29] . For it could be toxic to nerve cells and may increase urinary zinc excretion [30] .



Structure of N-acetylcysteine (NAC)

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1.4: Phenol :

Phenol is primarily a man-made chemical , although it is found naturally in animal wastes and decomposing organic material. It is a colorless to white solid when pure , the commercial product is in liquid form . It has a sweet and acrid odor. The largest single use of phenol is in plastic industry. It is used as a slimicide , a chemical that kills bacteria and fungi found in water slimes , as a disinfectant and in medical products [31] , including ointment , ear and nose drops , cold sore lotions and throat lozenges .

Health effects :

Very high concentrations of phenol can cause death if ingested , inhaled or absorbed through skin . Systemic absorption causes convulsion , as well as liver and kidney damage . Laboratory animals that have drunk very large amounts of phenol in water had muscle tremors and loss of coordination .We do not know whether phenol causes cancer in humans , but cancer occurs in mice when phenol is put on the skin. When phenol is combined with other chemicals that cause cancer and put on the skin, more cancer may occur than when the other chemicals are put on alone. Phenol can have positive effects when used for medical reasons. It is an antiseptic (kills germs) when put on the skin and may also have antiseptic properties when gargled as a mouth wash [32] .

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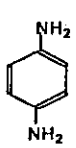
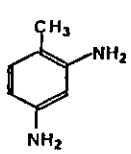
1.5: Importance of amines :

Amines are used as raw materials for synthesis of valuable pharmaceuticals, fibres and pesticides [33,34], and to prepare dyes for hairs and leather [35]. For example dimethylamine is used in the synthesis of the antihistamine (trade name Benadryl). The synthesis of the insect repellent N,N-diethyl-m-toluamid incorporates diethylamine, while that of the synthetic fibre kevlar requires aromatic amines [34]. Because amines are considered of utmost importance as shown above, therefore it is valuable and noteworthy to devise a cheap method for their determination. In our work the spectrophotometric determination of **1,4-phenylenediamine**, **2,4-Diaminotoluene** and **8-Aminochinolin** gave excellent results.

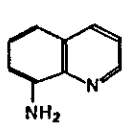
Structures of amines under investigation



1,4-phenylenediamine



2,4-Diaminotoluene



8-Aminochinolin

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1.6: Kinetic methods of analysis :

Kinetic methods of analysis are definitely useful for the determination of trace quantities of an element. They are extremely high sensitive compared to conventional methods.

They have been used successfully in determination of micro – quantities elements in biological samples [36].

Kinetic determination could be performed in various ways depending on the reproducibility .

Upon using kinetic methods of analysis, two sets of methods for determining concentration can be used.

1.6.1: The fixed time method :

In this method the reaction is allowed to proceed for a strictly determined time interval and after this time interval the concentration of one of the reactants in the solution is determined. This can be done by measuring the absorbance at a specified moment.

1.6.2: The fixed concentration method :

In using this method the time required for the concentration of one of the reactant to reach a specified value is measured.

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In this work the fixed time method is used in the analysis of data since this method proved to be reproducible and giving accurate results .

1.7: Transition State Theory :

The main assumption of this theory is that all chemical reaction proceed via a transition state (T.S) , for which an equilibrium exist between the reactants and the activated complex (X*) for the reaction . This could be written as :

$$A+B \rightleftharpoons X^* \longrightarrow \text{product}$$

The rate of reaction is assumed to be proportional to the concentration of the activated molecule and this concentration is governed by the laws of chemical equilibria [37,38] .

The thermodynamic parameters ΔH^*, ΔS^* and ΔG^* are determined by using the transition state theory equations.

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8: Effect of temperature

Chemical reactions are generally very sensitive to temperature. rrhenius (1889) found the variation of a rate constant (k) with mperature could be expressed by the equation :

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$$k = A\, e^{\frac{-Ea}{RT}}$$

The pre-exponential factor **A** is known as the frequency factor nd Ea as the activation energy . A plot of ln k vs 1/T (where T s the absolute temperature) well give a srtaight line of slope - ***Ea /R***. vhere **R** is the gas constant .The other thermodynamic parameter **ΔS^*, ΔH^*, ΔG^*)** can be then calculated using the appropriate ransition state theory equations[37] .

$\ln A = \ln k_b T / h + 1 + \Delta S^* / R$, where $k_b = R/N$ (Boltzman constant).

Then simple rearrangement gives :

$\Delta S^* = R (\ln A - \ln k_b T / h - 1)$

The Enthalpy : $\Delta H^* = Ea - R T$

The Gibbs free energy : $\Delta G^* = \Delta H^* - T \Delta S^*$

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1.9: Aquation :

The term aquation means dissociation of a complex using an acid[39-43] .

In this work sulphuric acid was used to dissociate tris (Ferene) iron (II) complex.

Aquation kinetics have been undertaken also in mixed aqueous organic cosolvent .

1.10: Spectrophotometric method :

A colored species in solution is one which absorbs electromagnatic radiation with certain wavelength (visible radiation) . For a given wavelenght , the absorption is given by Beer's law [44] which states :

$$A = \epsilon b c$$

Where A is a measured absorbance , c is a molar concentration of the colored species , b is an optical path length or thickness of the absorbing solution in centimeters , and ϵ is a molar absorptivity with units of L /mol cm whose magnitude depends on the nature of the absorbing solute and the wavelength . If the thickness of the vessel holding the solution is fixed , the absorbance at a particular wavelength is clearly proportional to the concentration of the colored species .

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1.11: The purpose of this work :

Phenol , NAC and **amines** are present in pharmaceutical and industrial products . Therefore the purpose of this work is to develop a sensitive kinetic method for detemination of these reducing agents in trace amounts . To achieve that , the fixed time method was used by measuring the absorbance of the tris (Ferene) iron(II) complex containing trace amounts of phenol, NAC or amine after 5 minutes of addition of Fe(III) . The kinetics of aquation of the tris (Ferene) iron(II) complex have not been studied in aqueous organic cosolvent. Hence the purpose of this work to:

1. Develop a new spectrophotometric method for determination of phenol, NAC and amines.
2. Study the aquation kinetics of the tris (Ferene)iron(II) complex in various aqueous organic solvent mixtures .

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CHAPTER TWO

EXPERIMENTAL

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2.1: Chemicals :

1] Ferene S solution:

Stock solution (0.01M) of Ferene (FS), which is [3-(2-pyridyl-5,6-bis(2-(5-furyl sulfonic acid)) 1,2,4-triazine,disodium] , (Sigma), ($C_{16}H_8N_4O_8S_2Na_2$, M.Wt =494.4 g/mole) was prepared by dissolving 0.4944g in water and the volume is completed to 100 ml.The solution was stored in a cold place .

2] Phenol solution:

Stock solution (0.01M) of phenol (C_6H_6O) , (Riedel) , (M.Wt = 94.11 g/mole) was prepared by dissolving 0.0941 g in water and the volume is completed to 100 ml.

3] N-acetylcysteine solution:

Stock solution (0.01M) of N-acetylcysteine,($C_5H_9NO_3S$) , (M.Wt=163.2 g/mole) , (Sigma), was prepared by dissolving 0.1632 g in water and the volume is completed to 100 ml .

4] Iron(III) perchlorate hydrate solution:

Stock solution (0.01M) of iron (III) perchlorate hydrate ($Fe(ClO_4)_3.H_2O$)(M.Wt =354.20g/mole),(Aldrich chemical company), was prepared daily by dissolving 0.3542 g in water and the volume completed to 100 ml .

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5] 1,4-phenylendiamine solution :

Stock solution (0.01M) of 1,4-phenylendiamine (1,4-PDA) , (M.Wt = 108.14 g /mole) was prepared from ($C_6H_4(NH_2)_2$) ,(Aldrich chemical company), by dissolving 0.0541 g in 50 ml methanol .

6] 2,4-Diaminotoluene solution :

Stock solution (0.01M) of 2,4-Diaminotoluene (2,4-DAT) (M.Wt=122.2 g/mole) ,($CH_3C_6H_3(NH_2)_2$) (Aldrich chemical company) was prepared by dissolving 0.0611 g in 50 ml methanol .

7] 8-Aminochionolin solution :

Stock solution (0.01M) of 8- Aminochionolin (8-AC) ,($C_9H_8N_2$), (M.Wt= 144.18 g/mole),(Merck Sehuchardt) was prepared by dissolving 0.0721 g in 50 ml methanol .

In each case , working solution were prepared by appropriate dilution.

8] Sodium sulfate solution:

Stock solution (1M) of sodium sulfate (Na_2SO_4),(to keep ionic strength constant) was prepared by dissolving 7.102 g in 50 ml deionized water .

9] Buffer solution :

An array of buffer solutions were prepared in **pH** range of 2-9 using acetic acid – sodium acetate and Hydrochloric acid , Sodium hydroxide mixtures [45]

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2.2: INSTRUMENTATION :

UV/Visible spectrophotometer :

All spectrophotometric measurments were carried out using UV/visible spectrophotometer of the type (CPS-240A-visible), (SHIMADZU) with thermostatic attachment and two 1-cm glass cells.

pH meter :

The pH measurments were carried out using a pH meter of type JENWAY 3310.

2.3: Kinetic procedure :

The tris (Ferene) iron(II) complex was prepared by mixing 10 ml of $4.0x10^{-3}$ M Ferene with 10 ml $1.0x10^{-3}$ *M* Ferrous ammonium sulfate. The acid used was 1M sulphuric acid . 0.5 ml of the complex was mixed with 1 ml solvent . The reaction was initiated by injecting rapidly 1 ml sulphuric acid . The kinetics was followed spectrophotometrically by following the decrease in absorbance at 593 nm . When the acid was varied , constant ionic strength was maintained by adding sodium sulfate . The total volume of acid and sodium sulfate is 2.5 ml .

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2.4: General Analytical Procedure :

All kinetic runs were performed on a Shimadzu 1601 UV/Visible spectrophotometer equipped with kinetic facilities . All solutions were placed separately in a thermostatic cell-chamber of the spectrophotometer , then 1 ml of each of the following were quickly added in the sequence : reducing agent , buffer solution , Ferene, Fe(III) . The zero time was taken at the moment of addition of Fe(III). The solution was shaken and immediately transferred into 1-cm cell in a temperature controlled cell compartment . Care was also excercised so that there is no air bubbles along the inside walls . The absorbance was measured at 593 nm against reagent blank after a fixed time of 5 minutes .The total volume of reaction mixture was 4 ml .

2.5: Determination :

The afforementioned proposed method has been applied for the spectrophotometric determination of NAC, phenol and amines in synthetic solutions . Also the determination of NAC was undertaken in a medical sample (Siran) .

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CHAPTER THREE

RESULTS AND DISCUSSION

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Part (A)

Analytical application of *Fe-FS* complex in kinetic determinations of phenol , NAC and some amines.

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3.1: Absorption spectra of the tris (Ferene) iron(II) complex :

The tris (Ferene) iron(II) complex absorbs at a maximum wavelength of **593** nm as shown graphically in **Figure 3.1**.

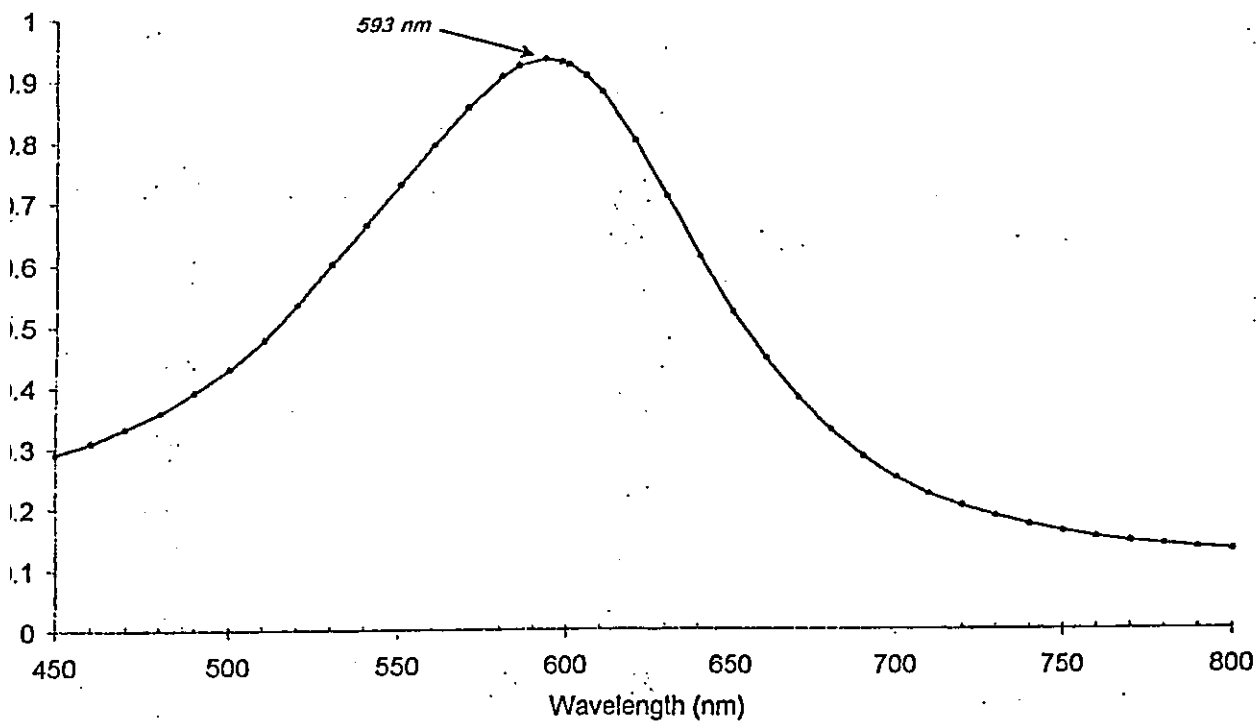

Figure 3.1 : Absorption spectra of the tris (Ferene) iron(II) complex .

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3.2: Effect of pH on the absorbance :

The effect of ***pH*** on the absorbance at 593 nm was studied in the pH range 2.0-9.0 using acetate buffers for N-acetylcysteine , phenol, 1,4-phenylendiamine , 2,4-diaminotoluene and 8-aminochinolin. The effect of pH was carried out by changing the pH of the solution while keeping other variables fixed . The results obtained showed that the absorbance is nearly the same over a pH range of 3-7 in acetate buffers[16] .This is virtually the same range as reported for the formation of the Ferrozine-iron(II) complex in acetate buffer[46]. Thus it would seem that a pH range 3-6 could be relied on to give the best test results . The lower stability of the complex at high pH values is probably due to the unavailability of the Fe(II) due to the formation of iron(III) hyroxide . In this work the pH 5 was selected for further work . **Table 3.1** and **Figure 3.2** shows the results obtained for N-acetylcysteine system . Similar results are obtained using the other reducing agent .

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Table (3.1) :

Effect of pH on the absorbance of the tris (Ferene) iron(II) complex for determination of (NAC)

pH	Absorbance *
2	0.4668
3	0.5712
4	0.5852
5	0.5854
6	0.5824
7	0.5413
8	0.1850
9	0.0840

• Absorbance after 5 minutes after additon of Fe(III) .

Conditions :

[NAC]= 5.0×10^{-6} *M*

[Ferene]= 4.0×10^{-3} *M*

Temp. = 25°C

pH= varied

[Fe(III)]= (0.001*M*)

$\lambda = 593$ nm

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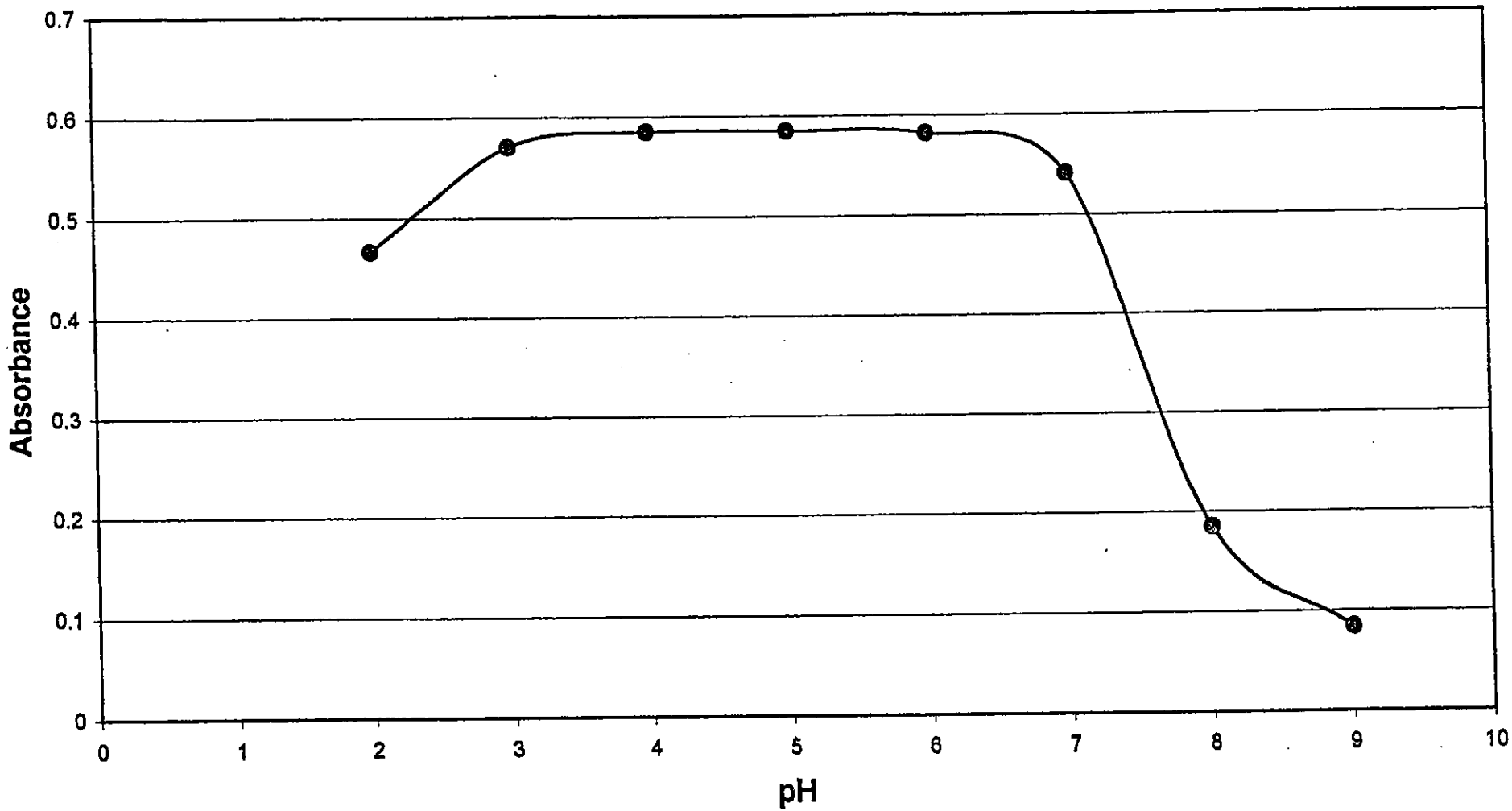
Figure(3.2): Effect of pH on absorbance



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3.3: Effect of Ferene concentration on the absorbance :

The effect of increasing the Ferene concentration on the absorbance for the reducing agent systems under investigation is studied at *593* nm . The results obtained are similar for the phenol , NAC and amines system . It was found that keeping the reducing agent concentration fixed and increasing the concentration of Ferene concentration , produced an increase in the absorbance up to Ferene to Fe(III) mole ratio of 3:1. Any further increase in the Ferene concentration did not effect the absorbance .

Typical results for the effect of Ferene concentration on the absorbance using NAC is presented in **Table 3.2** and shown graphically in **Figure 3.3 .**

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Table (3.2) : Molar ratio data for complexation of Fe(II) with Ferene

Ferene concentration x 10^{-3}(*M*).	Ferene / Fe(III) Mole ratio	Absorbance*.
0.5	0.5:1	0.1145
1	1:1	0.1873
1.5	1.5:1	0.3124
2	2:1	0.3833
2.5	2.5:1	0.4684
3	3:1	0.5854
3.5	3.5:1	0.5864
4	4:1	0.5871
5	5:1	0.5877
6	6:1	0.5821
7	7:1	0.5831
8	8:1	0.5816
9	9:1	0.5883

*Absorbance after 5 minutes of addition of Fe(III).

Conditions

[Fe(III)] = 0.001 *M* [NAC] = 5.0×10^{-6} *M*

Temp . = 25 ^{0}C pH = 5 λ = 593 nm

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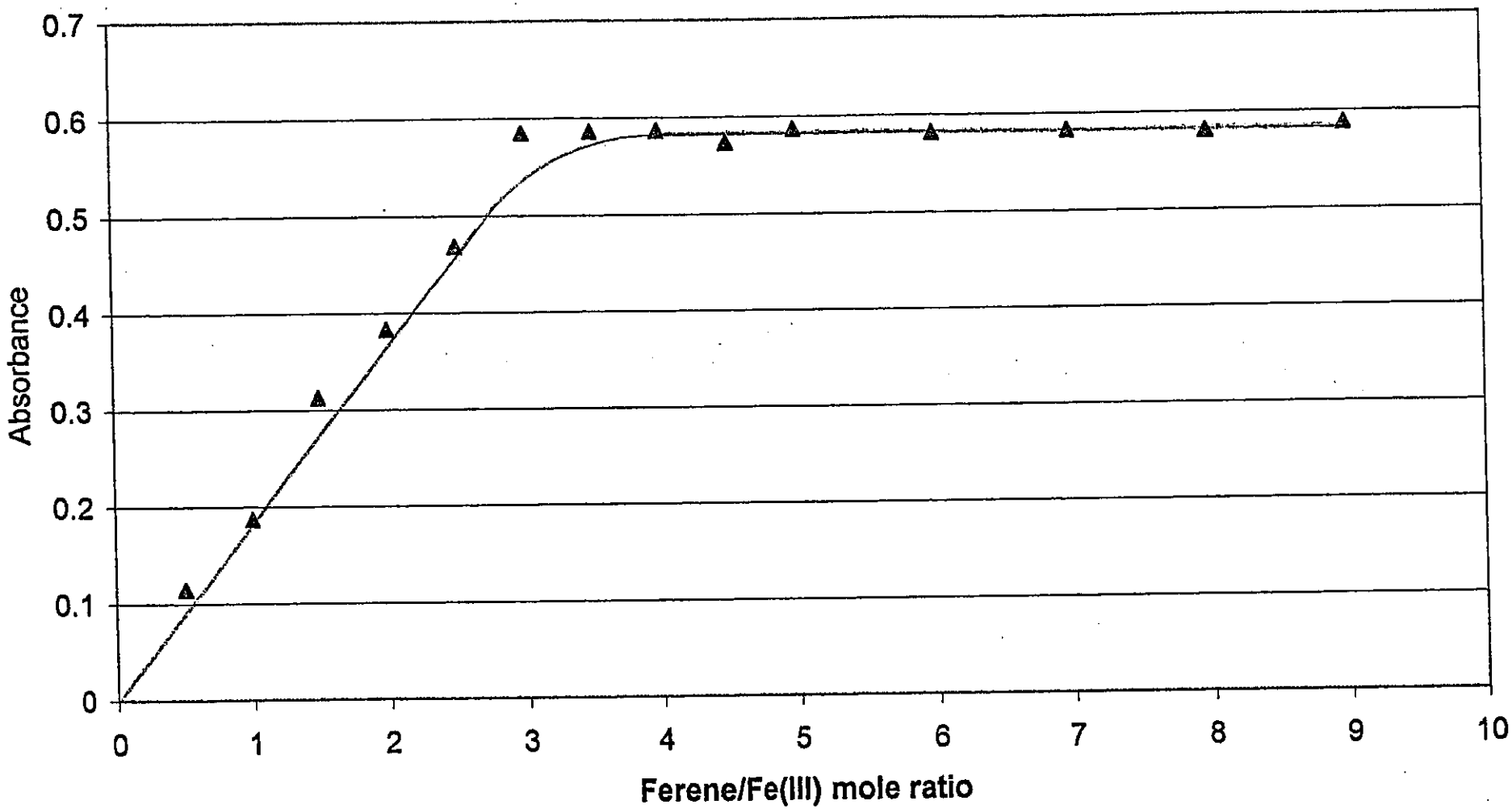
Figure (3.3) : The molar ratio absorbance plot for complexation of Fe(III) with Ferene



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3.4: Effect of Fe(III) concentration on the absorbance :

The effect of Fe(III) concentration on the absorbance of the blue complex was studied at 593 nm . A straight line with slope ~1 was obtained when log initial rate was plotted against log Fe(III) , indicating that the effect of Fe(III) follows first order plot .The results using NAC are represented in **Table 3.3** and shown graphically in **Figure 3.4** . Similar results are obtained using the other reducing agent .

Table (3.3) : The effect of the Fe(III) concentration on the initial rate of the reaction .

[Fe(III)] x$10^{-4}M$	Initial rate	- log [Fe(III)]	- log Initial rate
0.4	0.087	4.398	1.060
0.8	0.168	4.097	0.775
1.00	0.205	4.000	0.688
1.20	0.254	3.921	0.595

Conditions :

[Ferene] = 4.0 x10^{-4} M [NAC] = 5.0 x 10^{-5} M pH = 5

λ = 593 nm Temp. = 25°C

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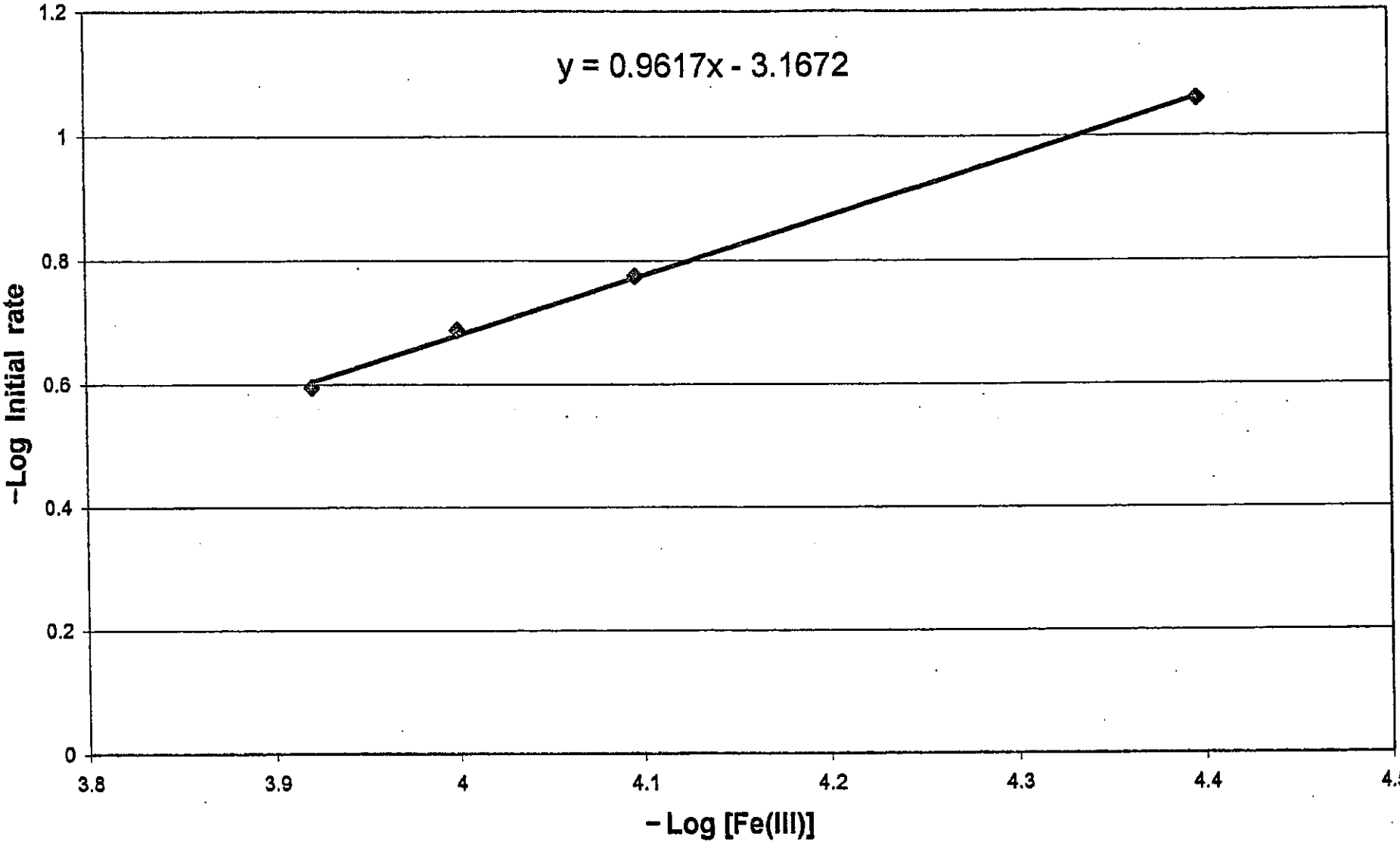
Figure (3.4) : The effect of iron(III) concentration on the absorbance



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3.5: Beer's laws and sensitivities :

From the investigation of the variables that effect the absorbance , the conditions for the color development and the absorbance measurements were selected . Following the recommended procedure , linear plots were obtained between phenol , NAC , amine concentrations and the corresponding absorbances . It can be seen that the phenol and NAC systems are the most sensitive, while the least sensitive is 8- Aminochinolin . The results are presented in **Table 3.4** .

The difference in the molar absorptivity and the sensitivity of the reducing agent systems might be due to the difference in their molecular structure and the ability of the reducing agent to reduce Fe(III)-Ferene complex to Fe(II)-Ferene complex .

Table (3.4) : Molar asborptivity and detection limits for Fe(II)-Ferene complex using different reducing agents .

Reducing agent	**Detection limit**	**Molar absorptivity**
Phenol	0.094 ppm	1.12805×10^5
NAC	0.16 ppm	1.127×10^5
2,4-Diaminotoluene	0.19 ppm	9.7646×10^4
1,4- Phenylenediamine	0.108 ppm	7.1184×10^4
8- Aminochinolin	0.114 ppm	5.4296×10^4

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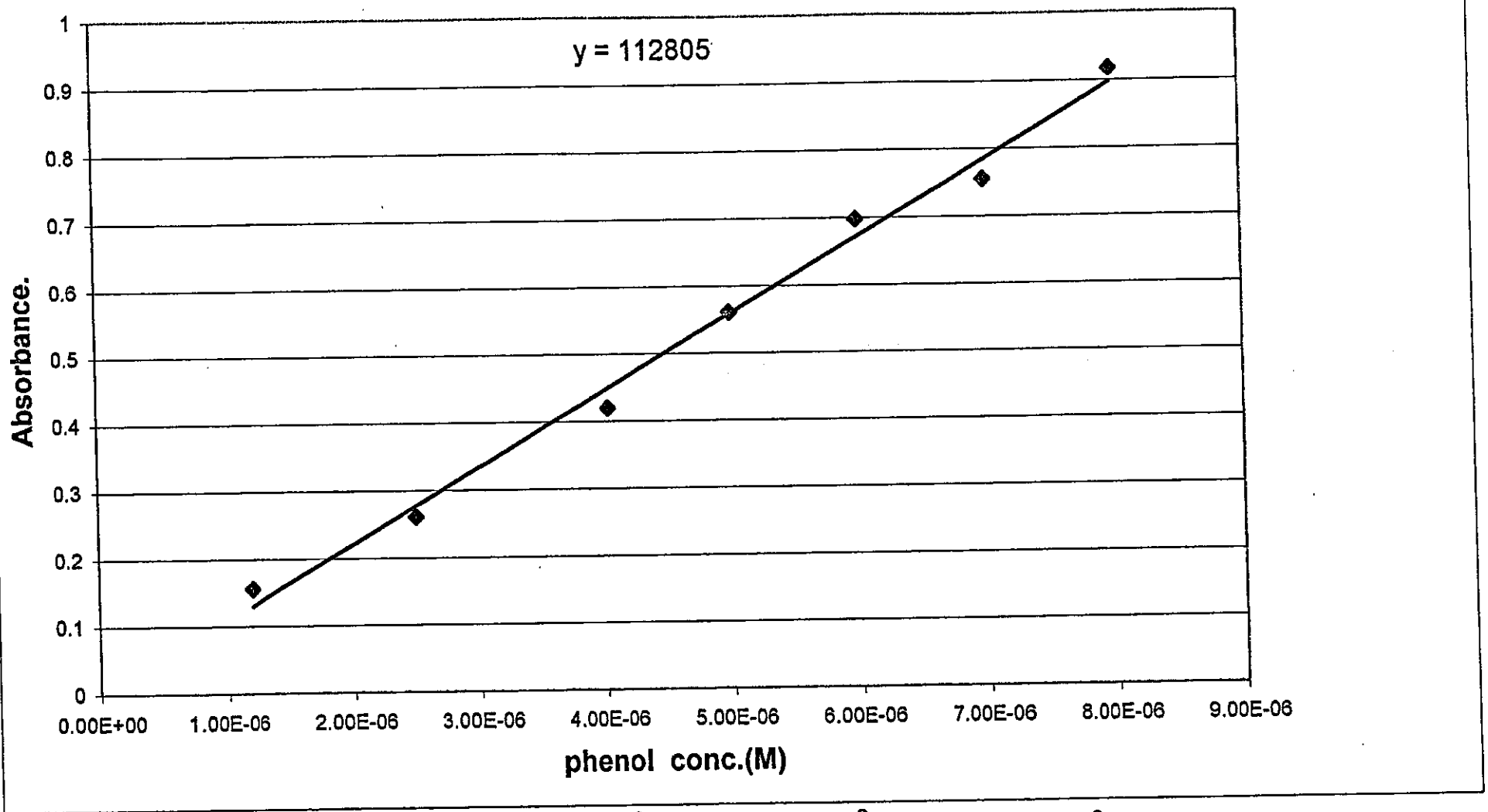
Figure 3.5 : The calibration graph for ***Phenol*** by Fe/Ferene method at 593 nm .



Conditions: [Ferene]= 4.0×10^{-3} *M*, [Fe(III)]=1.0×10^{-3} *M* , pH= 5 ,Temp.=25^{o}C

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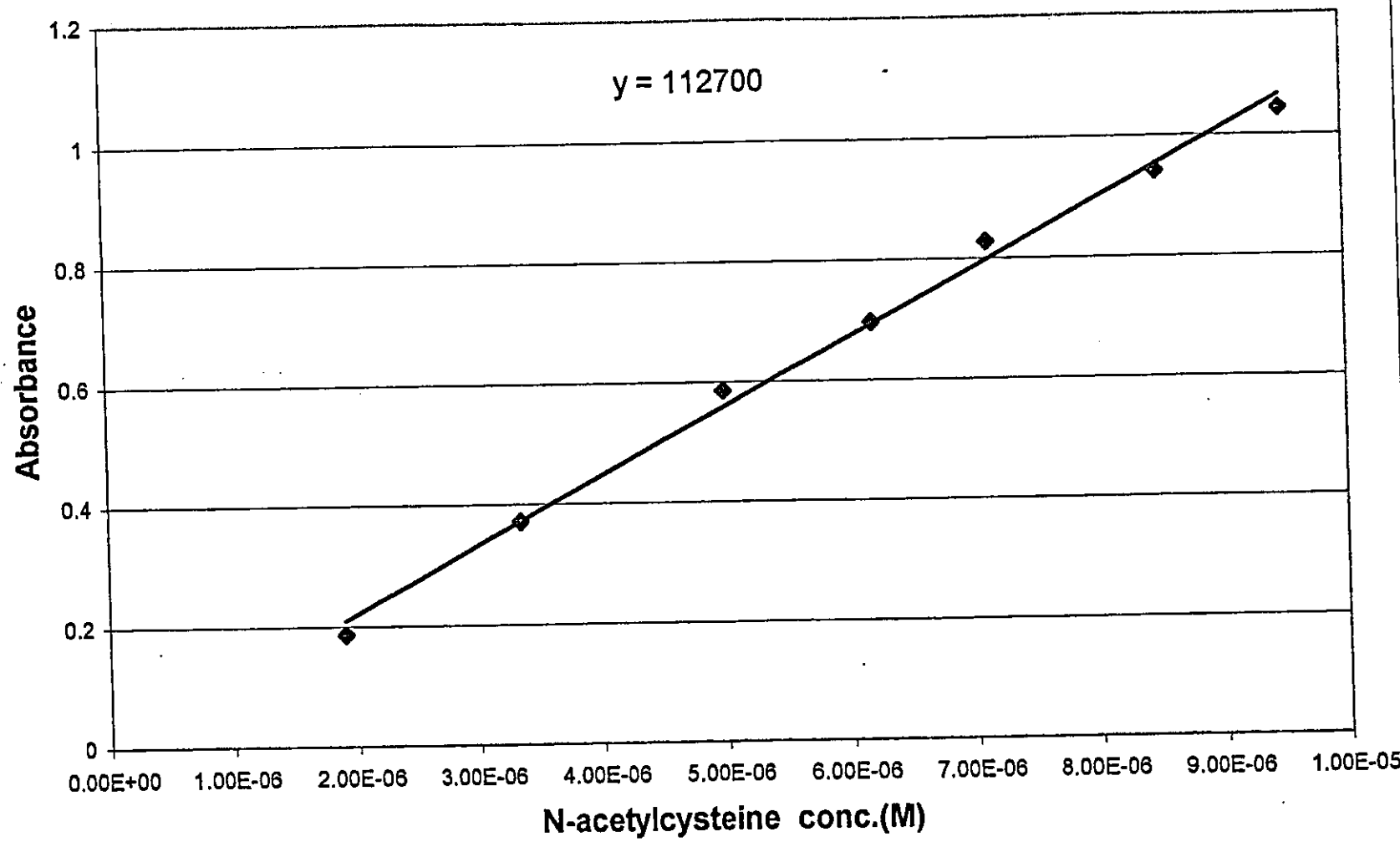
Figure 3.6 : The calibration graph for *NAC* by Fe/Ferene method at 593 nm .



Conditions: [Ferene]= 4.0×10^{-3} *M*, [Fe(III)]=1.0×10^{-3} *M*, pH= 5 ,Temp.=25^{o}C

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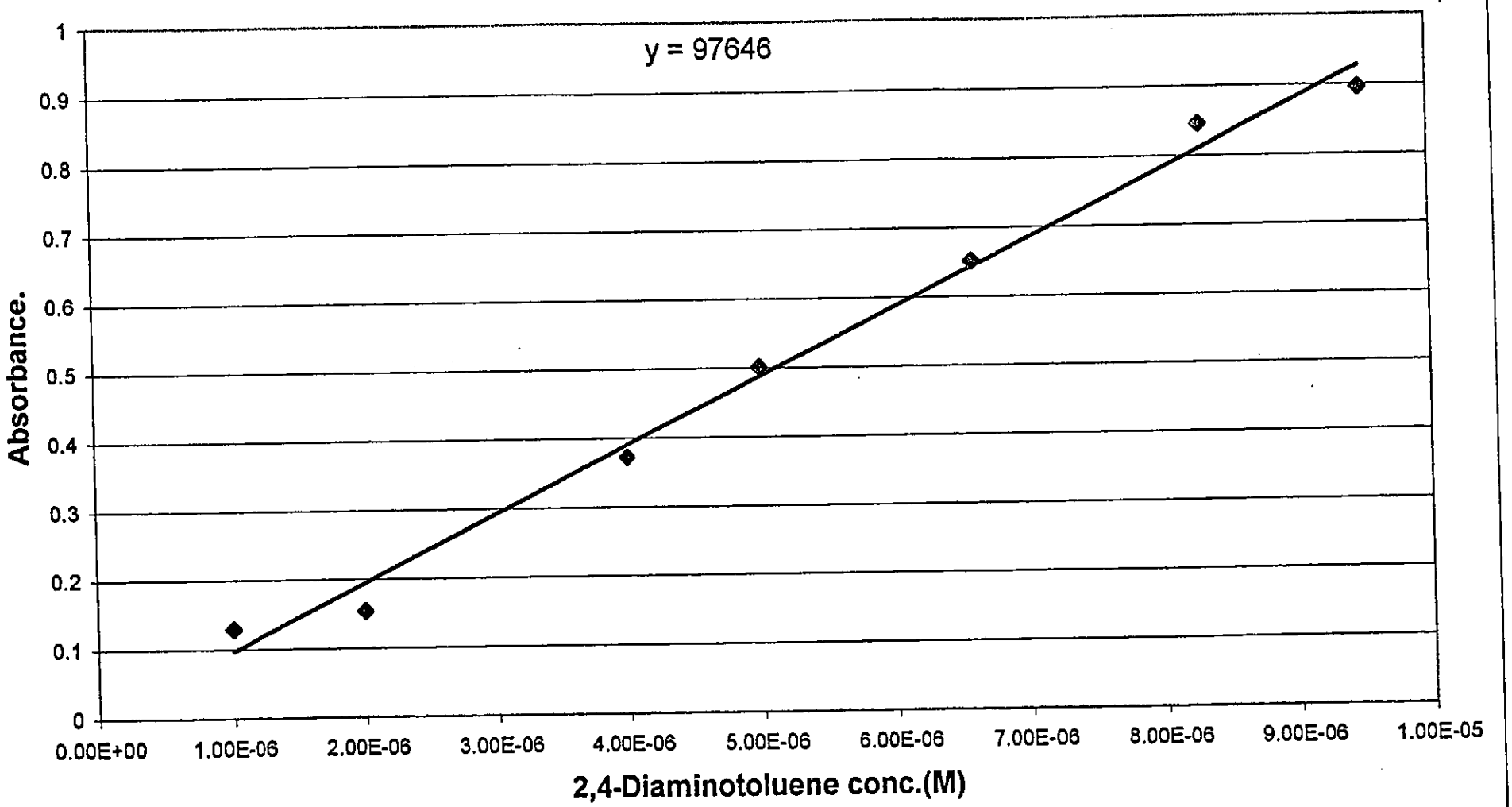
Figure 3.7 : The calibration graph for **2,4-DAT** by Fe/Ferene method at 593 nm .



Conditions: [Ferene]= 4.0×10^{-3} *M*, [Fe(III)]=1.0×10^{-3} *M* , pH= 5 ,Temp.=25 ^{o}C

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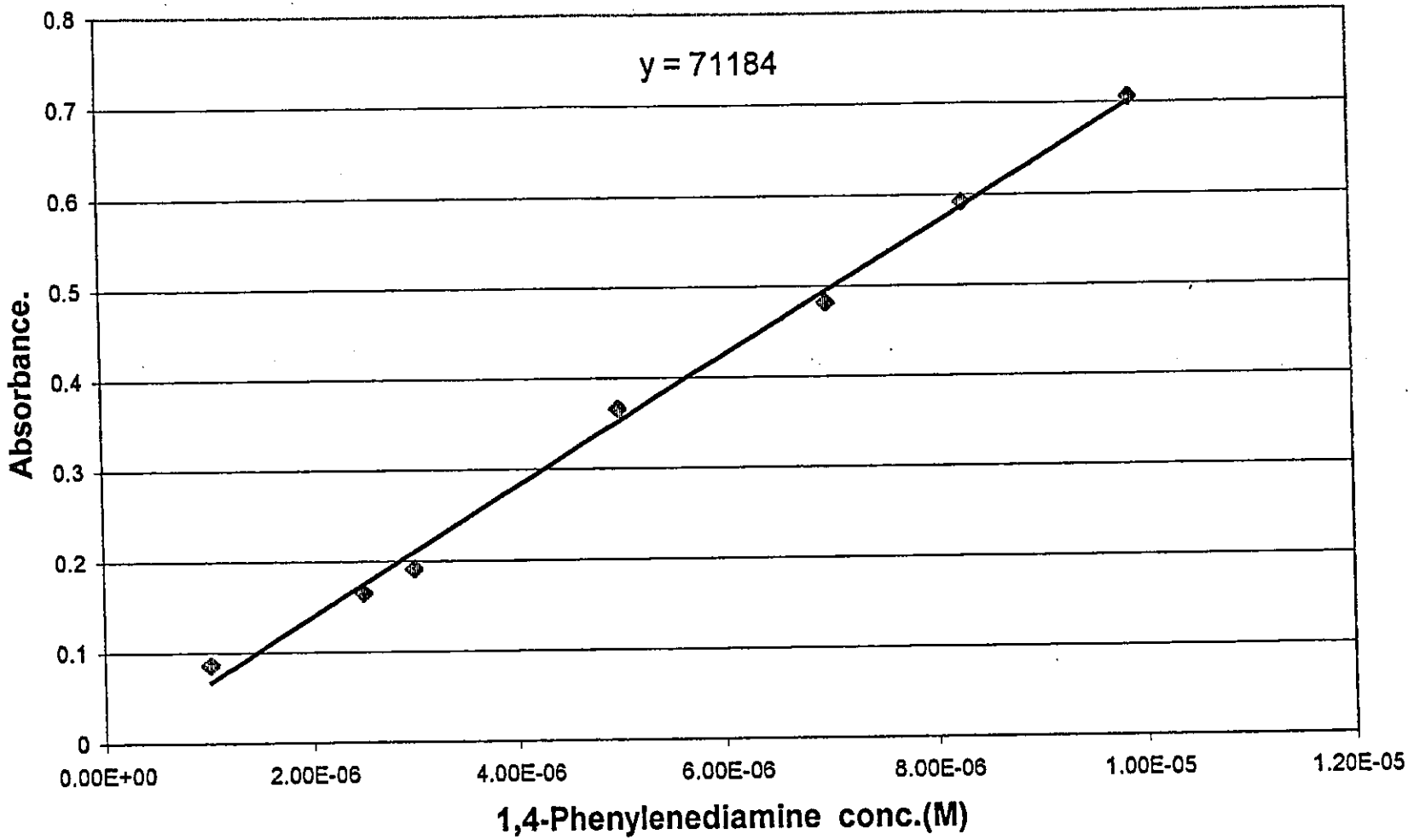
Figure 3.8 : The calibration graph for *1,4-PDA* by Fe/Ferene method at 593 nm .



Conditions: [Ferene]= 4.0×10^{-3} *M*, [Fe(III)]=1.0×10^{-3} *M* , pH= 5 ,Temp.=25 ^{o}C

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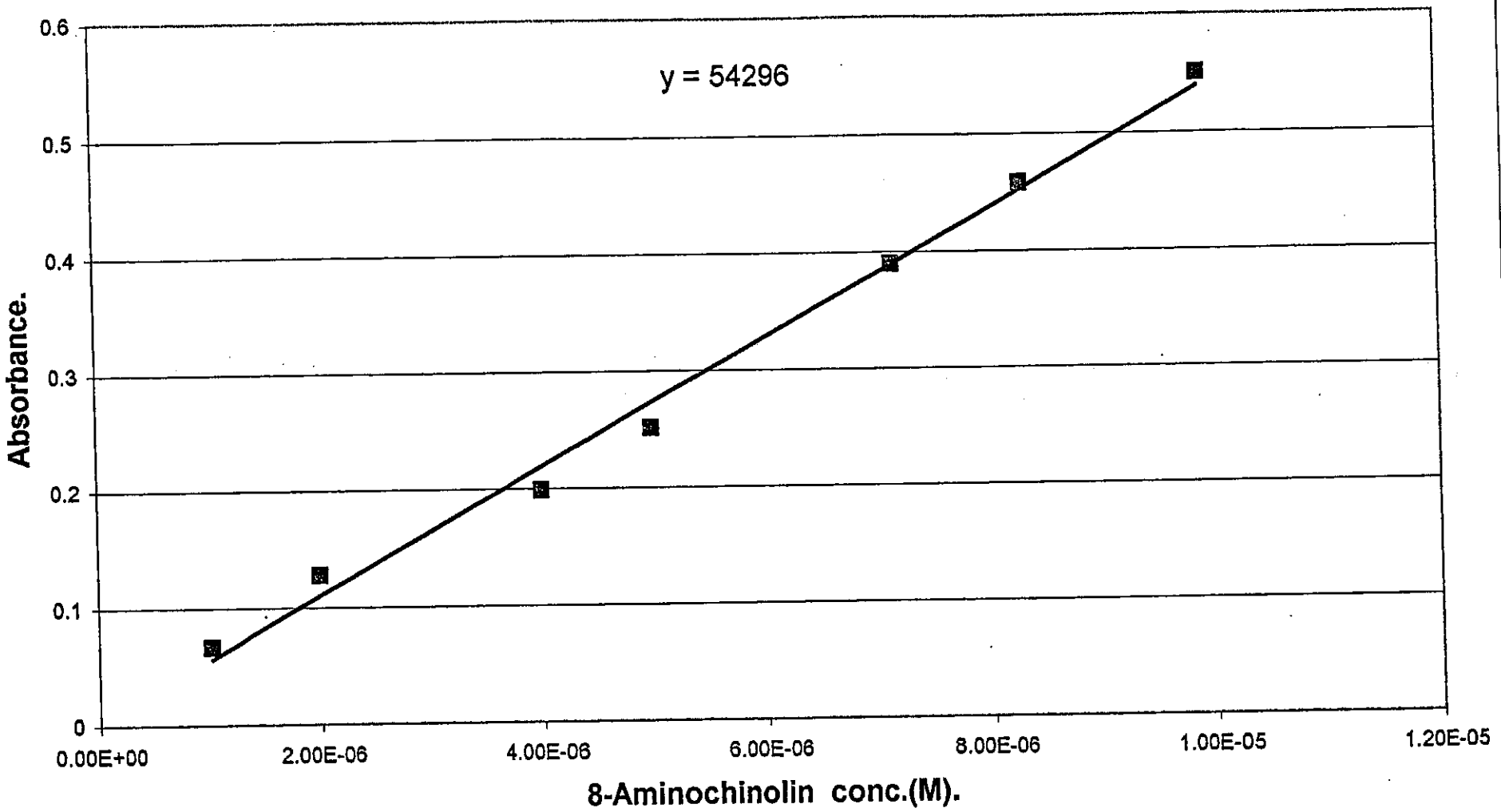
Figure 3.9 : The calibration graph for *8-AC* by Fe/Ferene method at 593 nm .



Conditions: [Ferene]= 4.0×10^{-3} *M*, [Fe(III)]=1.0×10^{-3} *M* , pH= 5 ,Temp.=25^{o}C

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3.6: Determination of *NAC* in a medical sample :

The medical sample used is the mucolytic agent Siran [commercially avialable as sachets from Temmler Pharma-Germany] . Siran which contain 0.2 g NAC and 2.8 g sugar was dissolved in 250 ml of water , then one ml of this solution was taken and diluted to 1 liter with water . The method suggested in the procedure was applied for determination of NAC in Siran and corrected for sugar to eliminate its interference in Siran . The sugar absorbance was found by using the recommended procedure on a solution that contains the same amounts of sugar present in Siran .

The results are shown below for 3 runs and corrected for sugar absorbance .

Table (3.5) : Determination of *NAC* in Siran

Run number	**Siran absorbance**	**Sugar absorbance**	**Difference**
1	0.8221	0.2364	0.5857
2	0.8262	0.2398	0.5864
3	0.8216	0.2371	0.5845
The	**Average**	**Absorbance**	0.5855

*Absorbance was measured after 5 minutes of addition of Fe(III).

Conditions:

[Ferene]=4.0×10^{-3} *M* [Fe(III)]=1.0×10^{-3}*M* pH=5

Temp.= 25°C λ = 593 nm

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The average absorbance corresponds to $5.0 \times 10^{-6} M$ of NAC from the calibration graph . This is equivalent to 0.20 gm of NAC exactly as written on the sachet .

Therefore this method is found to be sensitive , effective and cheap for determination of NAC in medical samples .

The ease of applicability , sensitivity , short analysis time , low cost and reliability are the main advantages of the proposed method.

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Part (B)

Aquation kinetics of the tris (Ferene) iron(II) complex in various aqueous organic mixtures.

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3.7: Introduction to aquation :

Virtually no detailed kinetics of the dissociation of the tris Ferene complex of iron(II) has been found in the literature, especially the dissociation in various aqueous organic cosolvents. Therefore the purpose of this part is to study the aquation kinetics in various aqueous organic solvents in the prospects of discovering new information on the effects of solvents upon the rate of the complex dissociation reaction.

In the presence of acid, the Ferene complex of iron(II) dissociates to give Fe(II) and the ligand Ferene.

The kinetics of this dissociation or aquation was studied under pseudo first order conditions by following the decrease in the absorbance of the complex at 593nm. When the acid was varied, constant ionic strength was maintained by adding sodium sulfate .

3.8: Order of decomposition with respect to complex.

The plot of *ln A* vs. **time** were linear indicating that the decomposition reaction in both water and organic midia solvent is a first order process with respect to the tris (Ferene) iron (II) complex. The rate constants have been found from the slopes of these linear plots.

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3.9: Order with respect to the acid for aquation of tris (Ferene) iron(II) complex .

The plots of *ln A* vs. *time* for the aquation of tris (Ferene) iron(II) complex in water at various concentration of acid (M) are shown in **Figures 3.10-3.14** . The slope of each linear plot is equal to the first order rate constant . These rate constants are tabulated in **Table 3.6** .This Table proves exclusively that the rate constant was not affected by various concentrations of acid, indicating that the order with respect to the acid is zero .

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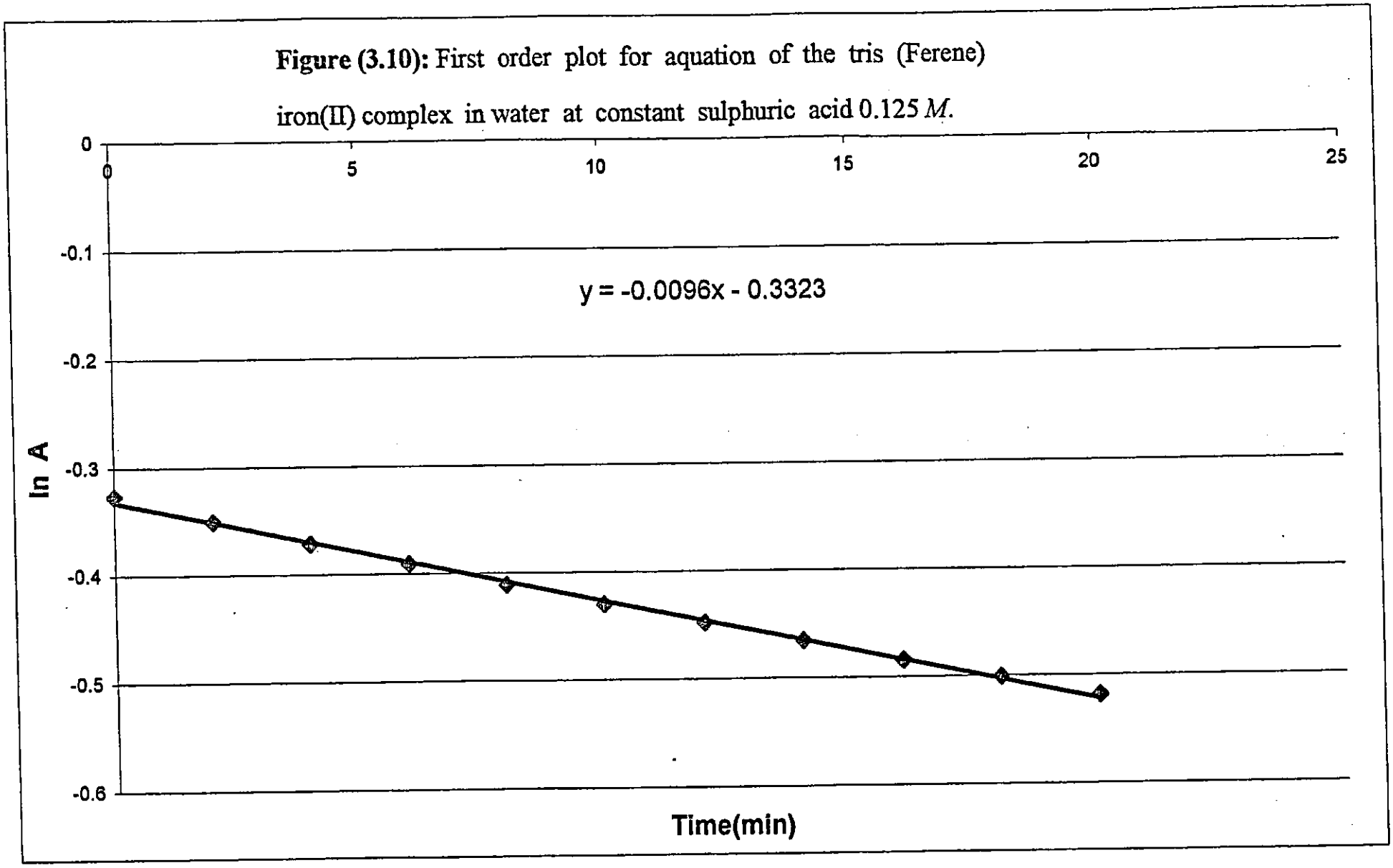
Figure (3.10): First order plot for aquation of the tris (Ferene) iron(II) complex in water at constant sulphuric acid 0.125 *M*.



Temp. = 25^{0}C I = 1.875 *M* λ = 593 nm

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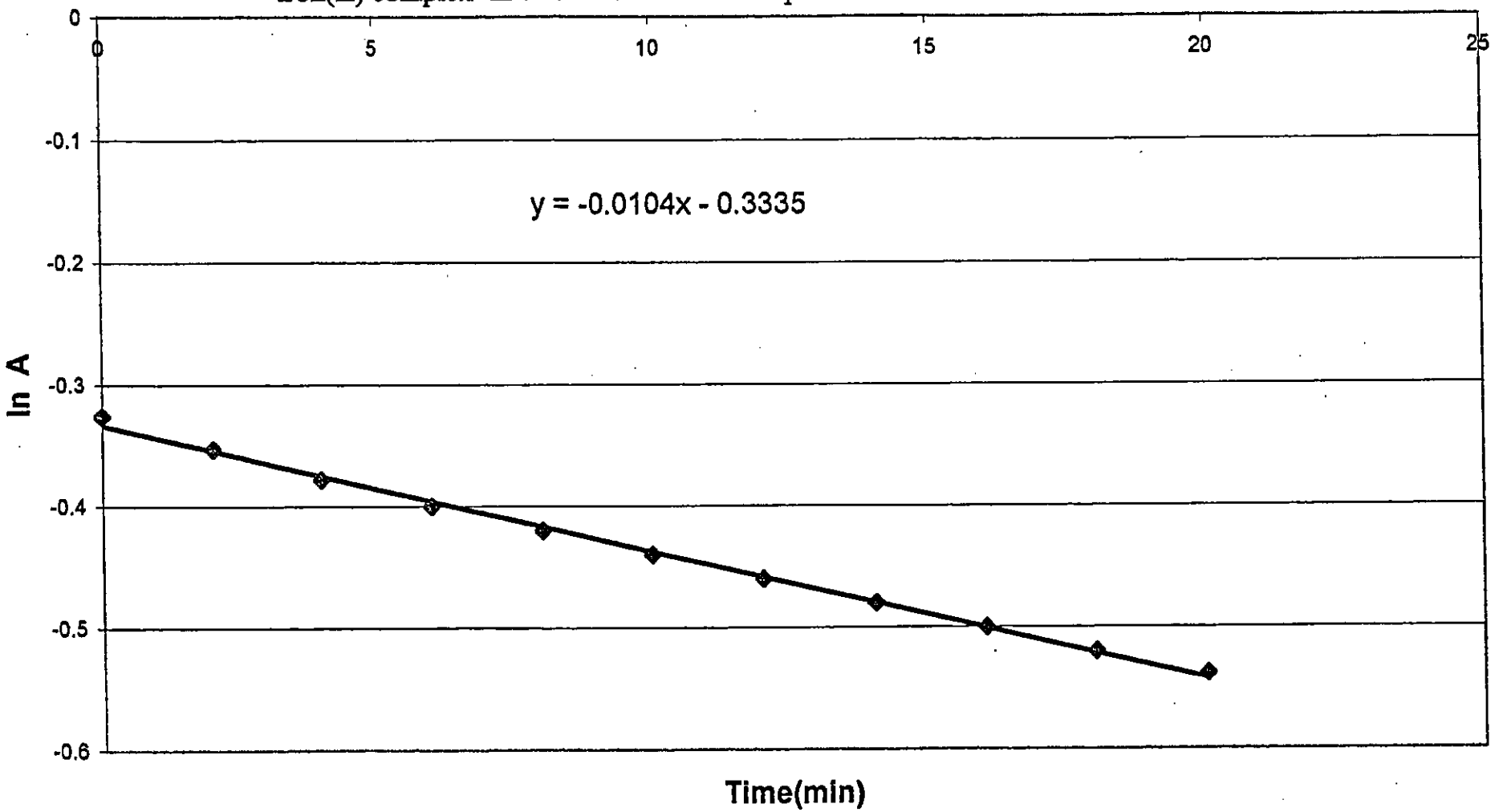
Figure (3.11): First order plot for aquation of the tris (Ferene) iron(II) complex in water at constant sulphuric acid 0.25 M.



Temp. = 25^{0}C I = 1.875 M λ = 593 nm

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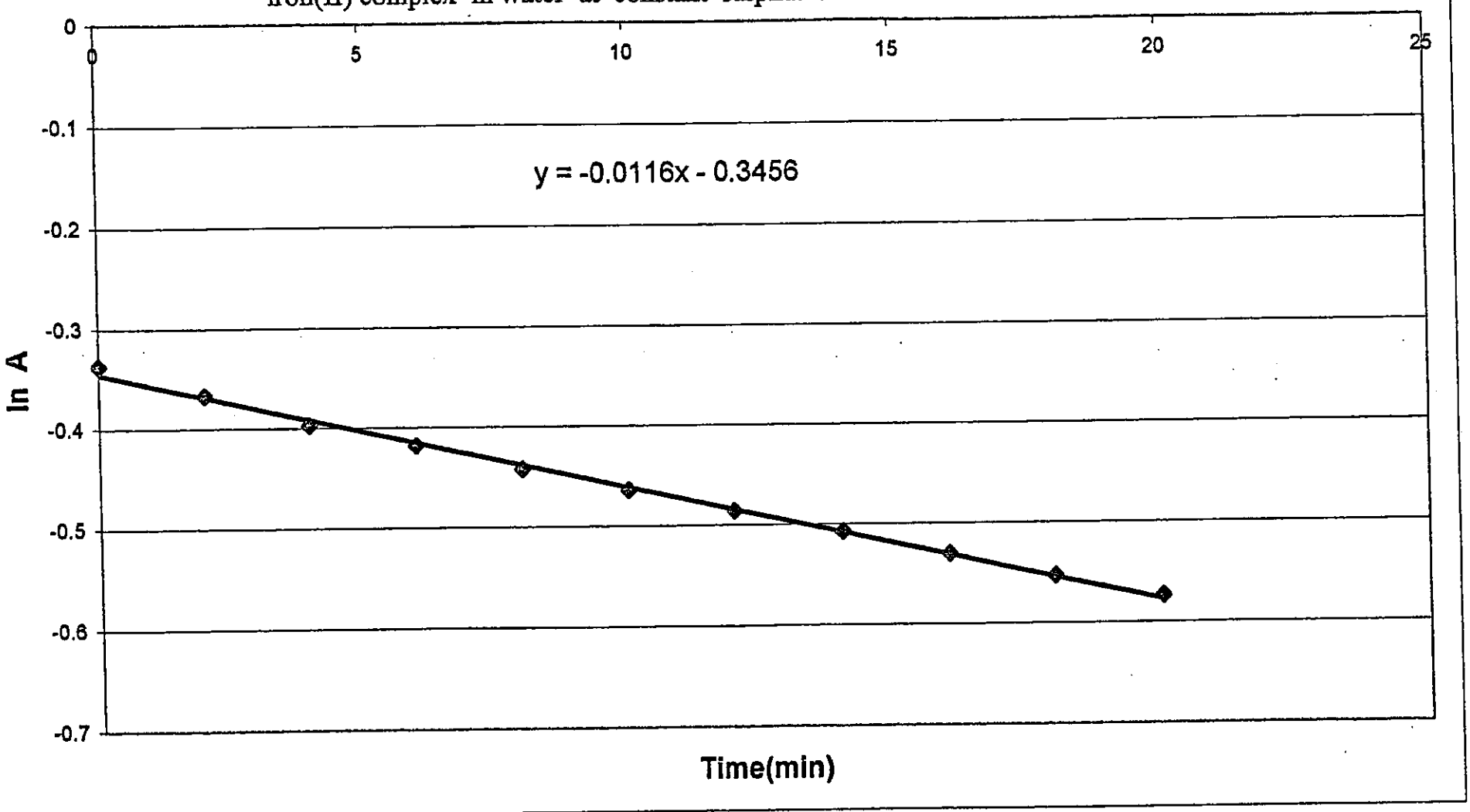
Figure (3.12): First order plot for aquation of the tris (Ferene) iron(II) complex in water at constant sulphuric acid 0.375 *M*.



Temp. = 25^{0}C I = 1.875 *M* λ = 593 nm

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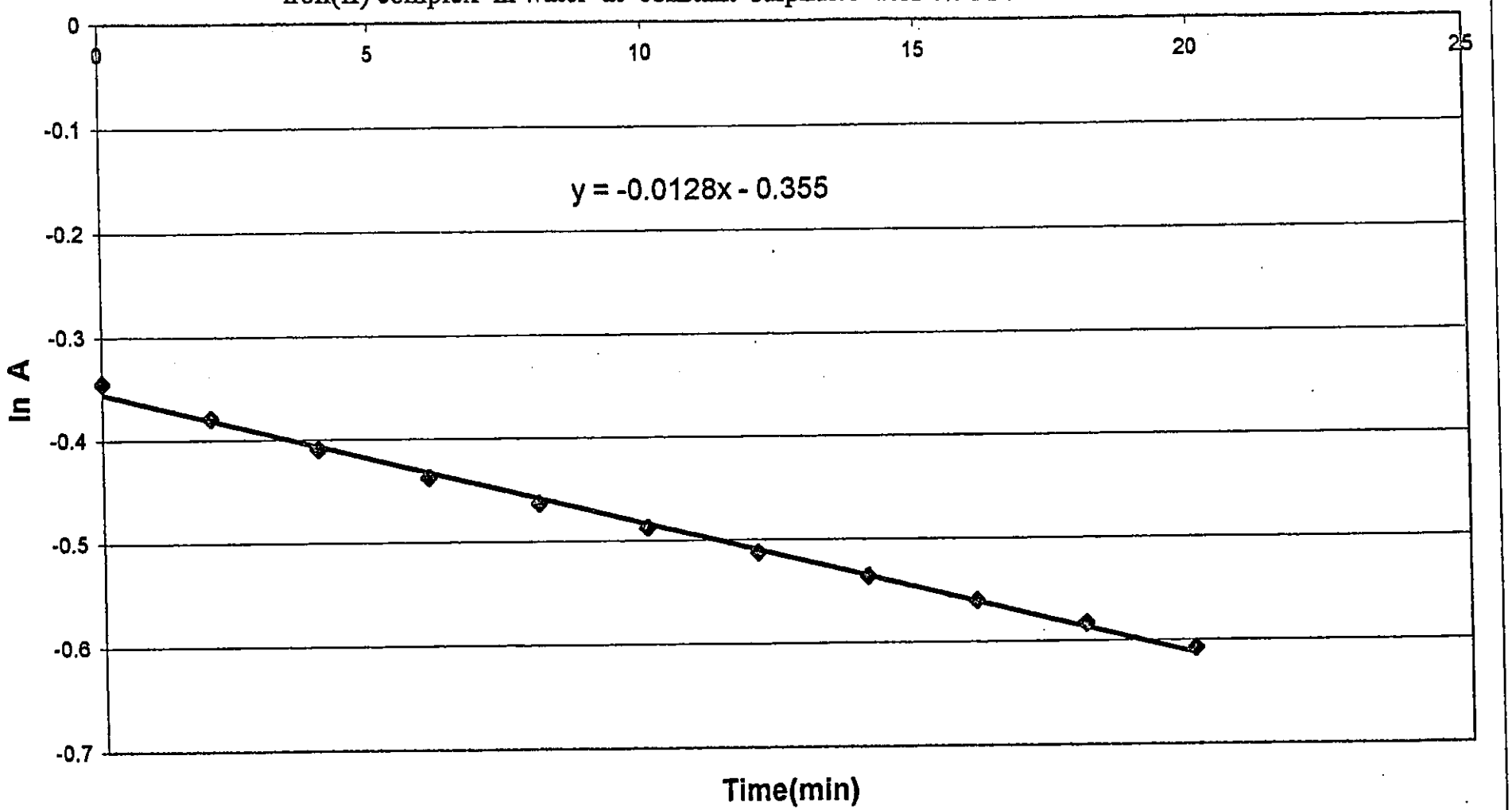
Figure (3.13): First order plot for aquation of the tris (Ferene) iron(II) complex in water at constant sulphuric acid 0.5 M.



Temp. = 25^0C I = 1.875 M λ = 593 nm

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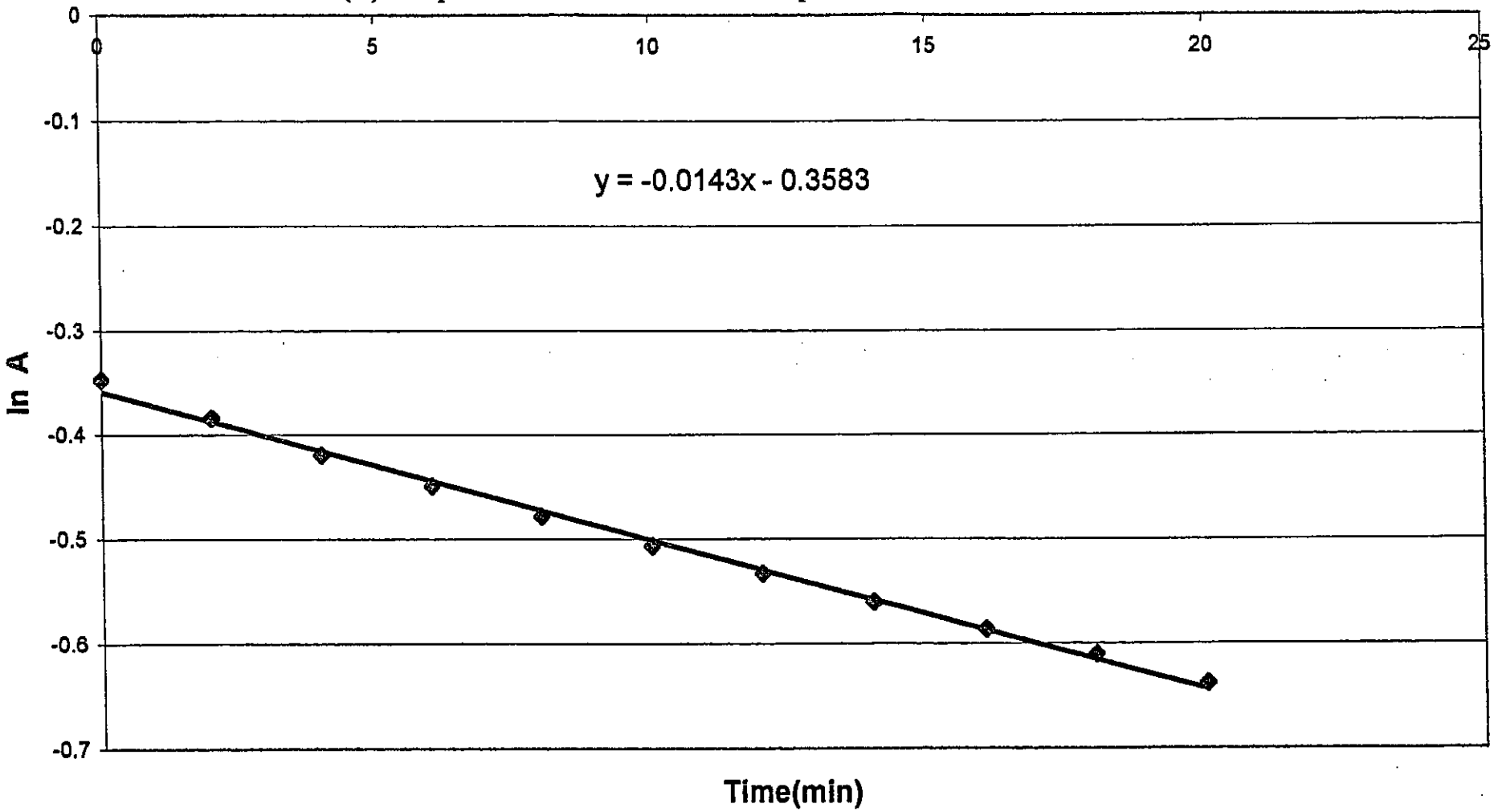
Figure (3.14): First order plot for aquation of the tris (Ferene) iron(II) complex in water at constant sulphuric acid 0.625 M.



Temp. = 25^{0}C I = 1.875 M λ = 593 nm

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Table (3.6) : Average observed firsr-order rate constants(k) for aquation of tris (Ferene) iron(II) complex in water at varing sulphuric acid concentrations at 25.0 ^{0}C and at constant ionic strength of (1.875*M*) maintained with sodium sulfate .

Concentration of acid(*M*)	Rate constants(k) (min^{-1})
0.125	0.0096
0.250	0.0104
0.375	0.0116
0.500	0.0128
0.625	0.0143

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3.10]Effect of temperature on rate of aquation of tris (Ferene) iron(II) complex in aqueous media :

The effect of temperature on the rate of aquation reaction of tris (Ferene)iron(II) complex has been studied in the temperature range (10^0C-60^0C). Increase in temperature increases the rate of the reaction as shown in **Table 3.7** . The importance of studying the effect of temperature was to determine the activation energy of reaction by plotting $ln\, k_{obs}$ vs. 1/T as shown in Figure **3.15** and Table **3.8.**

Table (3.7): The effect of temperature on the rate of aquation reaction of tris (Ferene)iron(II) complex in aqueous media at 593 nm.

Temp. / C^0	T/ K	k_{obs} 1/Min	- ln k_{obs}	1/Temp K^{-1} x10^{-3}
10	283	0.0012	6.7254	3.53
20	293	0.0061	5.0994	3.40
30	303	0.0219	3.8210	3.30
37	310	0.0543	2.9130	3.22
45	318	0.1293	2.0456	3.15
60	333	0.4068	0.8994	3.00

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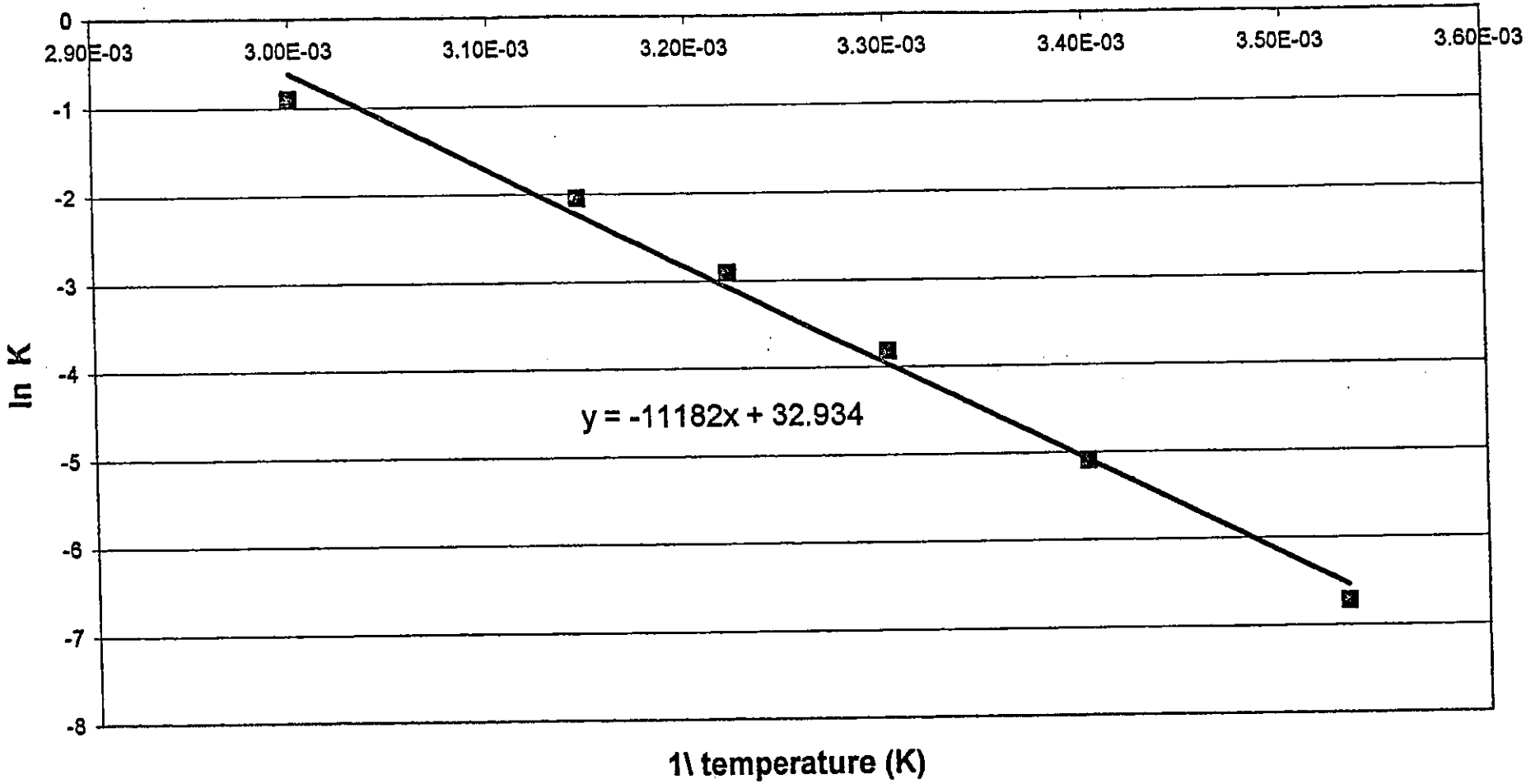
Figure (3.15) : Arrhenius plot for aquation of the tris (Ferene) iron(II) complex in aqueous media



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3.11] Determination of activation parameters :

From Arrhenius equation and using the transition-state theory, the activation parameters were determind as shown in **Table 3.8**.

Table (3.8) : The activation parameters of the aquation of (Ferene) iron(II) complex in aqueous at $T = 25^0C$.

The activation parameters	The value
Activation Energy (Ea*)	92.97 kJ mol-1
Entropy (ΔS^*)	20.59 J K-1mol-1
Enthalpy (ΔH^*)	90.49 kJ mol-1
Gibbs Energy (ΔG^*)	83.86 kJ mol-1

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3.12: Effect of organic solvent on the aquation reaction of tris (Ferene) iron(II) complex:

The first order plots of *ln A* vs. *time* were linear for all the solvents used namely 2-ethoxy ethanol ,DMSO and polyethylene Glycol (300) . Figures **3.16-3.18** . The order with respect to the acid in 25% organic solvent was found again to be zero as depicted for the constancy of the rate constants with varing acidity at constant ionic strength(I=1.875M). **Table 3.9.**

Table (3.9) : rates constants data for aquation of the tris (Ferene) iron (II) complex in organic solvent .

Solvent	*Acid /M*	*k (min.$^{-1}$)x10^{-3}*
25% 2- Ethoxy Ethanol	**0.125**	**3.4**
	0.250	**3.6**
	0.375	**3.9**
	0.500	**3.8**
25% Dimethylsulphoxide	**0.125**	**3.5**
	0.250	**4.0**
	0.375	**4.4**
	0.500	**4.2**
25 % Polyethylene Glycol	**0.125**	**4.9**
	0.250	**5.5**
	0.375	**5.6**
	0.500	**5.7**

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It could be seen from this table that the rate constants decrease with increase in the mole fraction of organic solvent. This is probably due to the better solvation of the hydrophilic portion in pure water, so as the portion of water decreases when the mole fraction of organic solvent increases then the water become less availiable to solvate the leaving molecules and the rate constants decreases.

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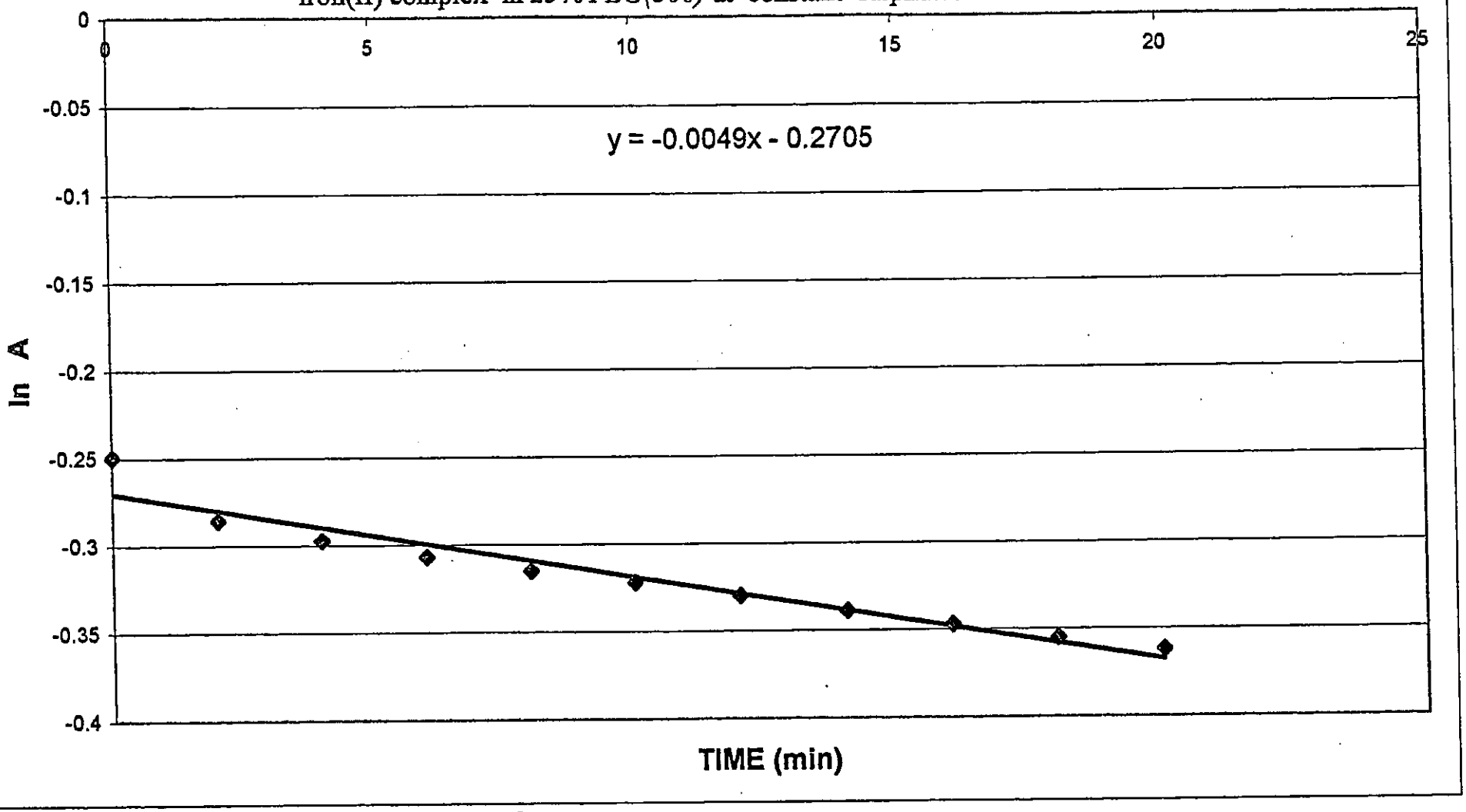
Figure (3.16): First order plot for aquation of the tris (Ferene) iron(II) complex in 25% *PEG(300)* at constant sulphuric acid 0.125 *M*



Temp. = 25^{0}C I = 1.875 *M* λ = 593 nm

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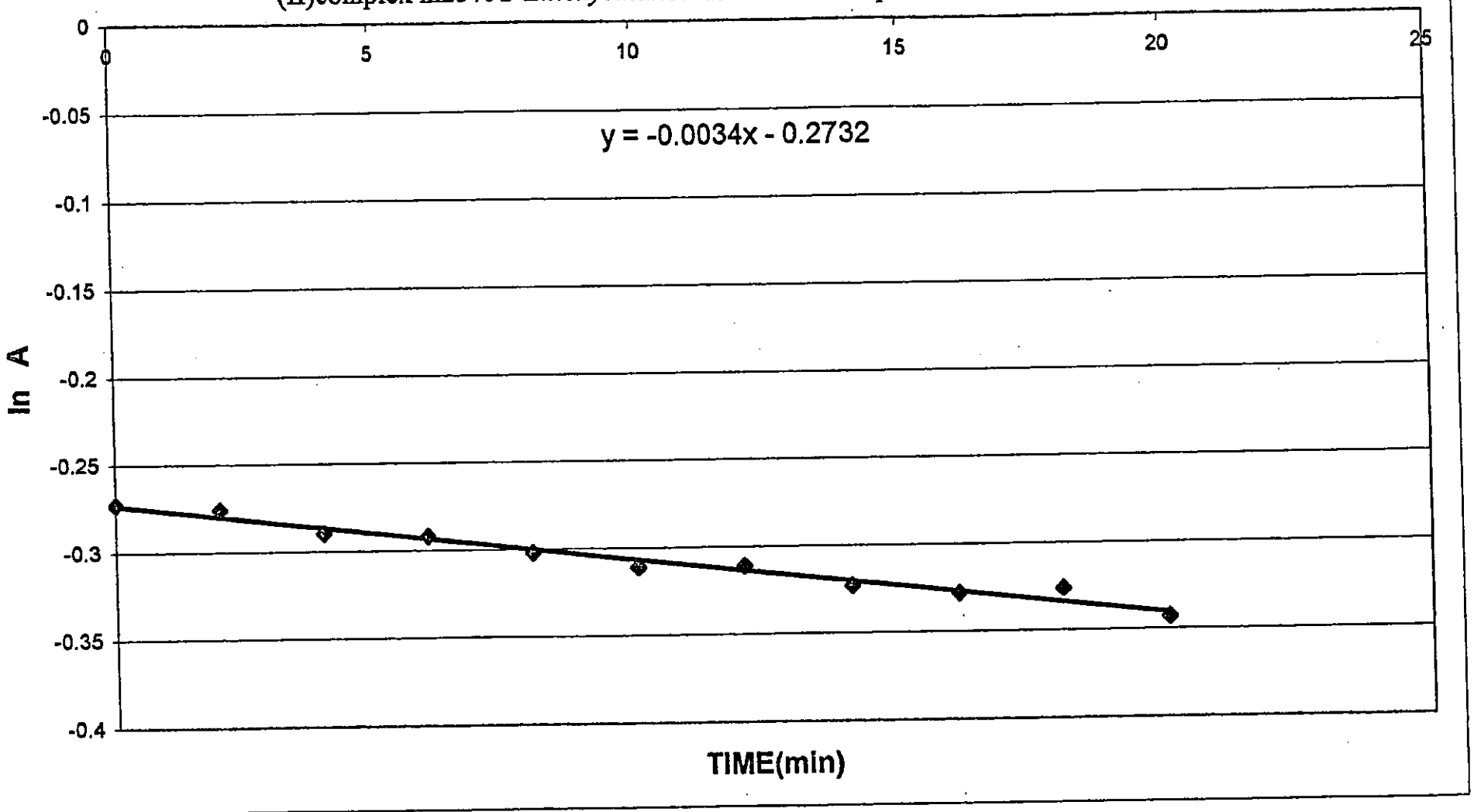
Figure (3.17): First order plot for aquation of the tris (Ferene)iron (II)complex in25% *2-Ethoxyethanol* at constant sulphuric acid 0.125 *M*



Temp. = 25^{0}C I = 1.875 *M* λ = 593 nm

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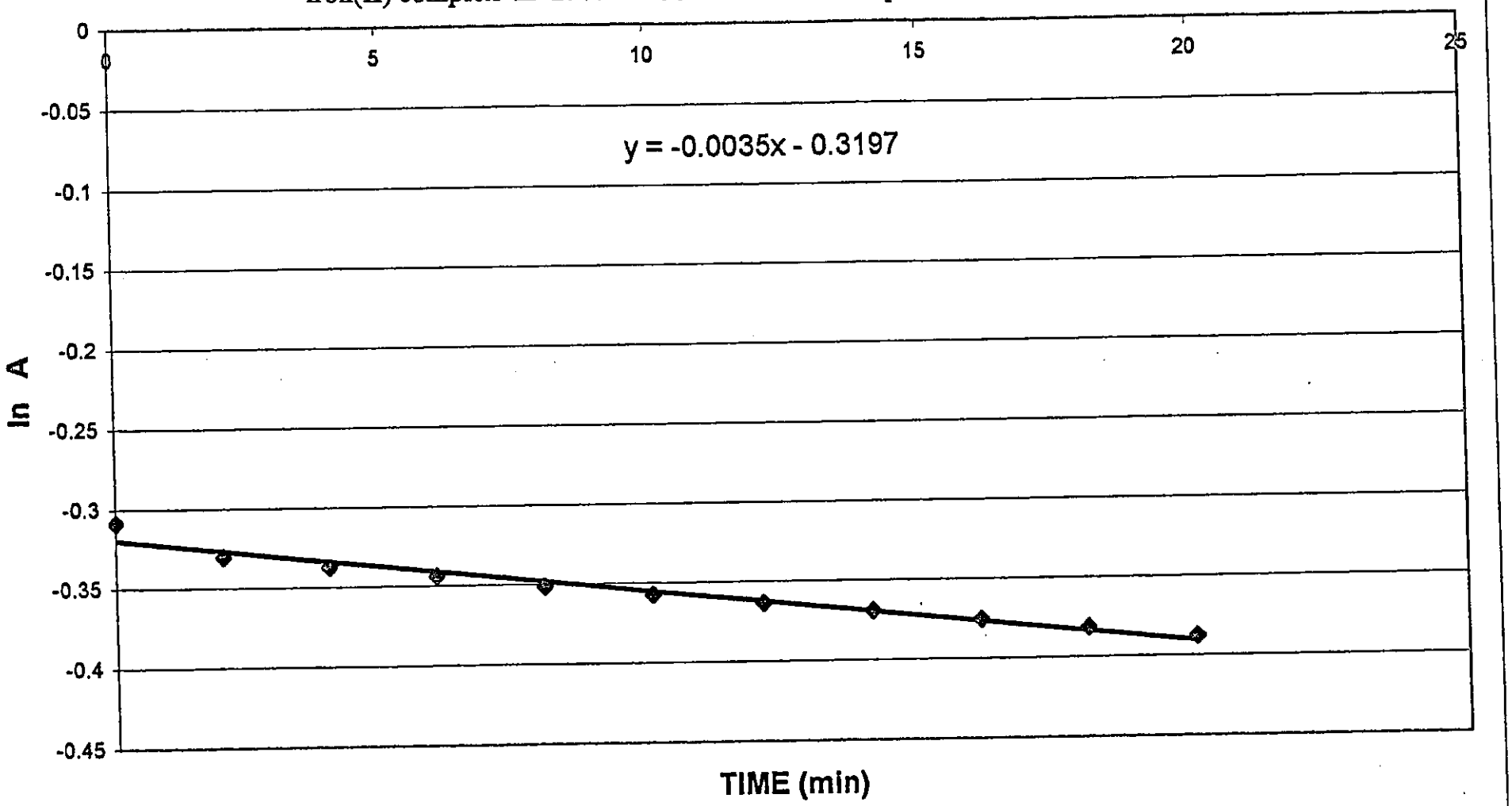
Figure (3.18): First order plot for aquation of the tris (Ferene) iron(II) complex in 25% *DMSO* at constant sulphuric acid 0.125 *M*



Temp. = 25^{0}C I = 1.875 *M* λ = 593 nm

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3.13: Mechanism :

The complexation of iron(II) with Ferene was found to be first order with respect to Fe(II) and third order with respect to the ligand . Thus the formation of the complex was of the fourth order overall and a mechanism was suggested that involves three equilibria [47] . The mechanism for dissociation is believed to occur via the reversal of the same three steps and the following mechanism is postulated :

$$FeL_3^{+2} \underset{}{\overset{k}{\rightleftharpoons}} FeL_2^{+2} + L \qquad \text{slow}$$

$$FeL_2^{+2} \rightleftharpoons FeL^{+2} + L$$

$$FeL^{+2} \rightleftharpoons Fe^{+2} + L$$

Where **L** symbolizes the ligand Ferene .The reaction is forced to proceed in the direction of aquation by addition of acid so that the liberated ligand is protonated and thereby prevented from recombining with the iron .

The rate - determining is the forward reaction in the first of the

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above steps . Since the reaction is of zero order with respect to the acid in both aqueous and in aqueous organic mixtures , then the role of acid is the same in both and participate in the reaction in a fast step after the rate - determining step . Therefore it is reasonable to assume that Ferene exists in the protonated form LH^+ as the case for 1,10-phenanthroline [48] and 2,2-bipyridine [49] .

$$L + H^+ \rightleftharpoons LH^+$$

The above mechanism yields the following rate law :

$$\frac{-d\,[FeL_3^{+2}]}{dt} = k\,[FeL_3^{+2}]$$

Consistent with the results obtained , then the overall reaction proceeds according to the following net equation :

$$FeL_3^{+2} + 3H^+ \rightleftharpoons Fe^{+2} + 3LH^+$$

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3.14: The effect of temperature on the aquation of tris(Ferene)iron(II) in 16.66% 2-Ethoxy Ethanol

The Arrhenius plot for the aquation of tris (Ferene)iron(II) complex in 16.66 % by volume of 2-Ethoxyethanol is shown in **Figure 3.19** . From the Arrhenius plots the activation parameters are found and tabulated below.

Table (3.10) :

The activation parameters for the aquation of tris (Ferene) iron(II) complex in 16.66 % *2-Ethoxy Ethanol* .

The activation parameters	The value
Activatin Energy (Ea)	109.84 kJ /mole
Entropy (ΔS^*)	72.56 J/K mole
Enthalpy (ΔH^*)	107.36 kJ/ mole
Gibbs Energy (ΔG^*)	85.74 kJ/ mole

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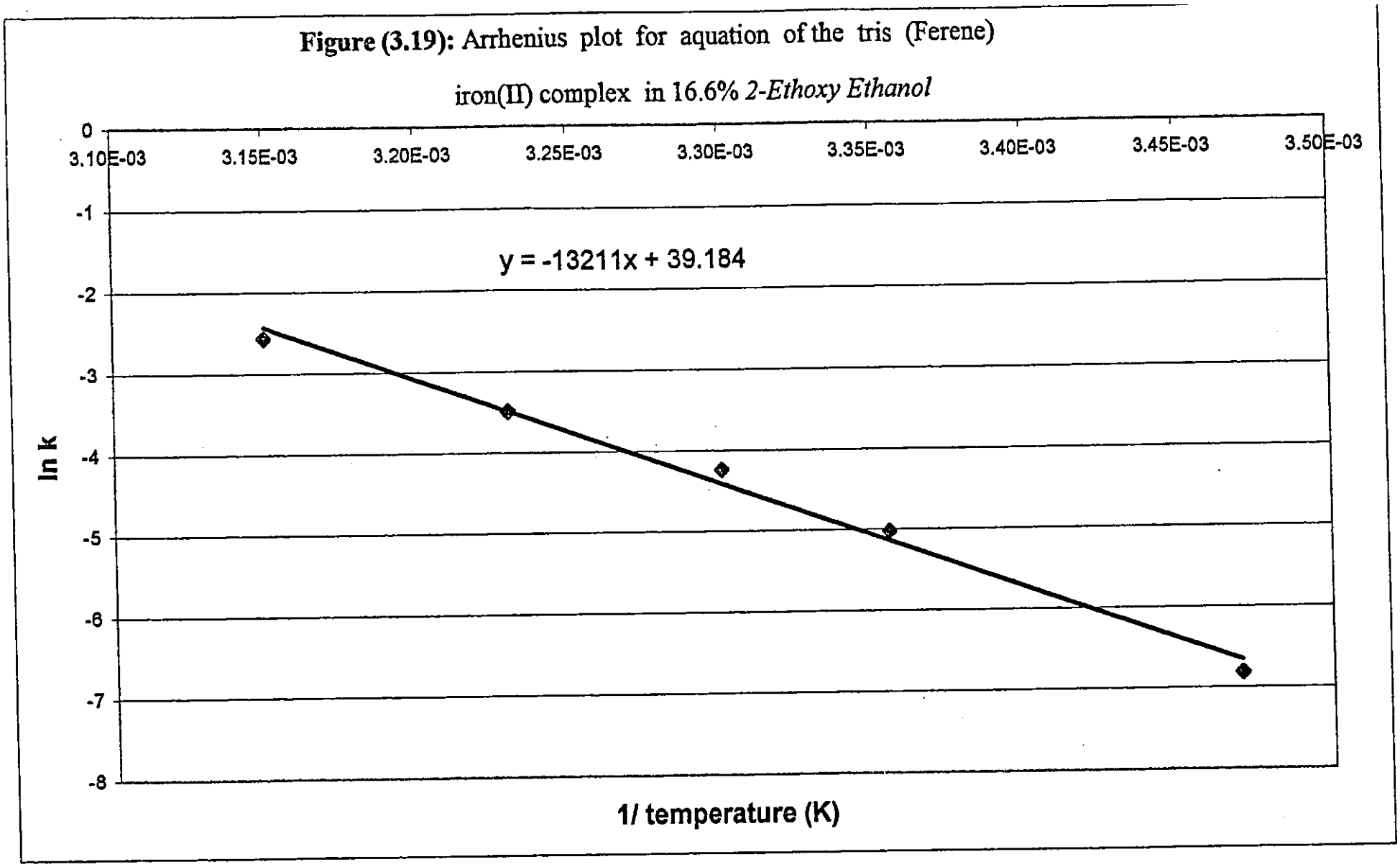
Figure (3.19): Arrhenius plot for aquation of the tris (Ferene) iron(II) complex in 16.6% *2-Ethoxy Ethanol*



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ملخص بالعربية

تتناول هذه الدراسة كيفية تحديد تركيز كل من الأسيتيل سستين والفينول وبعض الأمينات باستخدام جهاز المطياف الضوئي ، وتعتمد هذه الطريقة الحركية على اختزال أيونات الحديديك بواسطة هذه العوامل المختزلة الى الحديد الثنائي الذي يلتحم مع متصلة الفرين ليكون متراكب ذو لون بنفسجي يمتص عند طول موجه 593 نانوميتر.

لقد طبقت الطريقة المبينة اعلاه في تعيين تركيز الاسيتيل سستين في عينة دوائية(سيران). وأستخدمت كذلك في تحديد تركيز الفينول والأمينات المذكورة في عينات حضرت مخبريا ، ولقد وجد أن الطريقة فعالة وتعطي نتائج دقيقة .

لقد تم ايضا تطبيق قانون بير لتعيين الأمتصاصية المولارية لهذه العوامل المختزلة وكانت :

1.128×10^{5} , 1.127×10^{5} , 9.764×10^{4} , 7.118×10^{4} , 5.429×10^{4} $L.mol^{-1}.cm^{-1}$

لكل من الفينول والأسيتيل سستين و4,2- داي امينوتولوين و4,1-فينيلين داي أمين و 8-أمينو كينولين على الترتيب .

لقد تم ايضا دراسة ميكانيكية سرعة تكسير المركب المعقد $Fe(II)-(FS)_3$ في محاليل مائية عضوية وعند تراكيز مختلفة من أيونات الهيدروجين وكانت رتبة التفاعل بالنسبة للحمض صفرا. واخيرا درسنا تكسير المركب المعقد عند درجات حرارة مختلفة وتم حساب طاقة التنشيط ومتغيرات ارهينيوس .

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