KINETICS AND MECHANISMS OF REDOX REACTIONS OF TETRAKIS(2,2'-BIPYRIDINE)-μ-OXODIIRON(III) COMPLEX AND SOME REDUCTANTS IN AQUEOUS HYDROCHLORIC ACID

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRDUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A DOCTOR OF PHILOSOPHY DEGREE IN INORGANIC CHEMISTRY

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ZARIA, NIGERIA

DECEMBER, 2016

Declaration

I declare that the work in this thesis entitled "Kinetics and Mechanisms of Redox Reactions of Tetrakis (2,2□-Bipyridine)-μ-Oxodiiron(III) Complex and Some Reductants in Aqueous Hydrochloric Acid"has been carried out by me in the Department of Chemistry. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other Institution.

Idongesit Bassey ANWETING ---------- ----------

Name of Student **Signature** **Date**

Certification

This thesis entitled "KINETICS AND MECHANISMS OFREDOX REACTIONS OF TETRAKIS (2,2'-BIPYRIDINE)-μ-OXODIIRON(III) COMPLEX AND SOME REDUCTANTS IN AQUEOUS HYDROCHLORIC ACID" by Idongesit Bassey ANWETING meets the regulations governing the award of the Degree of Doctor of Philosophy in Inorganic Chemistry of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Dean, School of Postgraduate Studies	Signature	Date

Dedication

This work is dedicated to the blessed memory of my late parents Mr and Mrs A. I. Anweting, may their souls rest in peace.

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Abstract

The electron transfer reactions of tetrakis (2, 2'- bipyridine)-μ-oxodiiron(III) complex ion (Fe_2O^{4+}) with thiourea (TU), *N*-methylthiourea (MTU), *N*–allylthiourea (ATU), *N,N'*–dimethylthiourea (DMTU), *N,N'*-dimethylthiourea (DETU), dithionite ion($S_2O_4^{2-}$), dithionate ion ($S_2O_6^{2-}$), semicarbazide (EH_2), diphenylcarbazide (DH_2) and glutathione (GSH) were studied spectrophotometrically, in aqueous hydrochloric acid medium at T = 27.0 ± 3.0^oC, I = 0.3 mol dm^{-3} (NaCl), $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} (HCl) and λ_{max} = 520 nm. The stoichiometry was found to be 1:1(Fe_2O^{4+}/reductant) in all other systems but 1:2 in theFe_2O^{4+}- GSH system. The reactions of Fe_2O^{4+}- thioureas follow identical kinetics, being first order each with respect to [oxidant] and [thiourea] and second order overall. The reaction of Fe_2O^{4+} with dithionite($S_2O_4^{2-}$)ion, dithionate($S_2O_6^{2-}$) ion, semicarbazide (EH_2), diphenylcarbazide (DH_2) and glutathione(GSH) follow first order and zero order with respect to oxidant and reductants respectively and first order overall. Changes in hydrogen ion concentration, the dielectric constant and ionic strength of the medium have no considerable influences on the rate in all the systems. The reactions involving thioureas were not affected by addition of cations but there was inhibition of the rate of reaction when anions were added. However, for all other systems the rate of reaction was independent of added cations and anions. Under comparable experimental conditions, the rate of oxidation of the thioureas followed the order k_2(TU) < k_2(DETU) < k_2(ATU) < k_2(MTU) < k_2(DMTU), sulphur oxyanions $k_{obs}(S_2O_6^{2-}) < k_{obs}(S_2O_4^{2-})$ and that for the carbazides is $k_{obs}(EH_2) < k_{obs}(DH_2)$. The observed kinetics in the reactions involving thioureas is in agreement with the rate law;

$$\frac{d}{dt}[Fe_2O^{4+}] = k_2[Fe_2O^{4+}][\text{thioureas}]$$

While that for other reductants can be given as:

$$\frac{d}{dt}[Fe_2O^{4+}] = k_{obs}[Fe_2O^{4+}]$$

In all the reactions, Fe^{2+} was found to be the product of Fe_2O^{4+} reduction. The oxidation products of the reactions of thioureas were urea/urea derivatives and sulphur using both spectroscopic and qualitative methods. Whereas sulphate ion was qualitatively identified in $S_2O_4^{2-}$ and $S_2O_6^{2-}$ reactions, disulphide was identified as the product of the reaction of GSH with Fe_2O^{4+}. Spectroscopic evidence and Michaelis-Menten plots did not indicate the formation of intermediate complex prior to electron transfer, there was also absence of free radicals formation in all the systems. Based on the Michaelis- Menten plots, interactions with added ions, all the reactions are proposed to have proceeded through the outer-sphere electron transfer mechanism. Plausible mechanisms have been proposed for all the systems.

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Abbreviations

A_t	absorbance at time (t)
A_∞	absorbance at infinity
I	ionic strength
Aq	aqueous
ATU	*N*- allylthiourea
ATP	adenosine triphospate
B.D.H	British drug house
Bipy, bpy	2,2□- bipyridine
D	dielectric constant
DH_2	diphenylcarbazide
DETU	*N, N*□-diethylthiourea
DMTU	*N, N*□-dimethylthiourea
DMSO	dimethylsulphoxide
DNA	deoxyribonucleic acid
EDTA	ethylenediammine tetraacetic acid
EH_2	semicarbazide
EPR	electron pair repulsion
ESR	electron spin resonance
ET	electron transfer
FTIR	fourier transformed infrared
HEDTA	N-2-(hydroxyethyl) ethylenediamminetriacetic acid
GSH	glutathione
GPX	glutathione peroxidase

GST	glutathione S-transferases
GSSG	oxidised glutathione
k_{cal}	calculated rate constant
k_{obs}	observed rate constant
k_2	second order rate constant
k_{redox}	rate of oxidation- reduction process (electron transfer)
k_{subs}	rate constant for substitution
MTU	*N*- methylthiourea
NADH	nicotinamide adenine dinucleotide reduced form
NMR	nuclear magnetic resonance
phen	1,10-phenanthroline
PCET	proton couple electron transfer
redox	reduction – oxidation
TU	thiourea
RNA	ribonucleic acid
terpy	terpyridine
UV/Vis	ultraviolet/visible
λ_{max}	wavelength of maximum absorption
ν	vibrational quantum number

CHAPTER ONE

1.0 INTRODUCTION

Electron transfer (ET) is one of the unique chemical processes which have received considerable attention due to its role in physical and biochemicalsystems (Marcus and Sutin, 1985).It occurs when an electron moves from an atom or a chemical species (e.g. a molecule) to another atom or chemical species. Since the late 1940s, the field of ET processes has grown enormously. The development of the field, experimentally and theoretically, aswell asits relation to the studyof other kinds of chemical reactions, presents an intriguing history, one inwhich many threads have been brought together(Marcus, 1997). The process is a mechanistic description of the thermodynamic concept of redox, wherein the oxidation states of both reaction partners change. Numerous biological processes involve ET reactions. These processes include oxygen binding,photosynthesis, respiration, and detoxification. Additionally, the process of energy transfer can be formalised as a two-electron exchange (two concurrent ET events in opposite directions) incase of small distances between the transferring molecules. ET reactions commonly involve transition metal complexes, but there are now many examples of ET in organic chemistry and other areas as depicted in Figure 1.1(Marcus and Siddarth, 1992; Greenwood and Earnshaw, 1997; Holleman and Wiberg, 2001). Moreover, many reactions in bioinorganic systems involve the electron transfer at one stage or the other and proper understanding of these electron transfer processes would help in the understanding development and eventual effective control of a wide area of science and technology (Iyun, 1982).

Nonradiative and radiative ET are found to be a key elementary step in many important processes involving isolated molecules, ions and excess electrons in solution, condensed phase, surfaces and

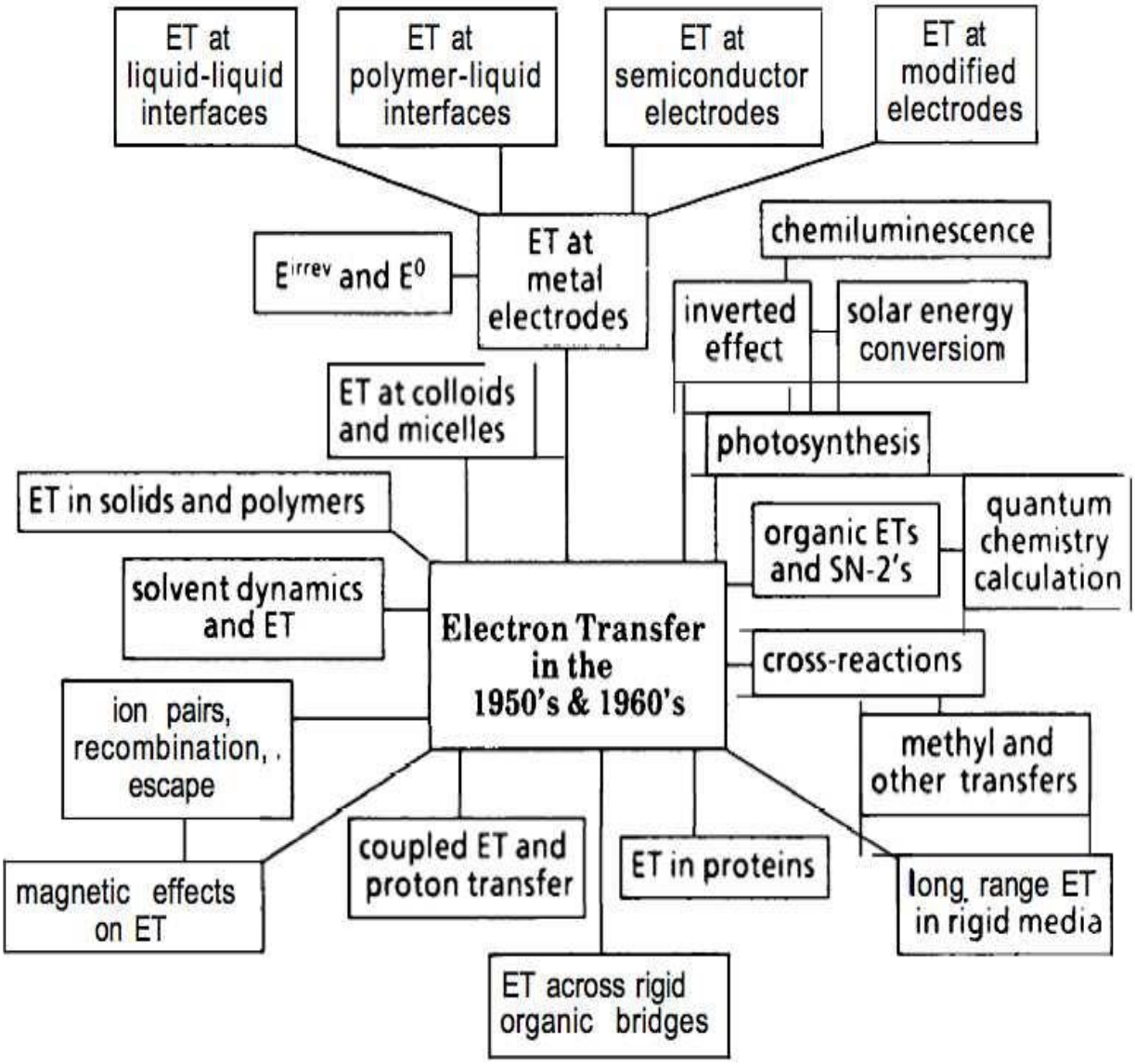


Figure 1.1: Examples of topics in the electron transfer field (Marcus and Siddarth, 1992)

interfaces, bioelectrochemical systems and in solar cells, in particular. Marcus (1964) observed that one of the active areas in reaction kinetics during the post-war years has been that of ET reactions. These reactions constitute one type of oxidation-reduction process and include both chemical and electrochemical systems. Many rate constants have now been measured and they have stimulated a variety of theoretical studies. The field has been characterised by a strong interplay of theory and experiment, which now includes the testing of theoretically predicted quantitative correlations.

Chemical kinetics is concerned with the study of rates of chemical reactions and the effect ofphysical conditions such as temperature, light, pressure, ionic strength, and solvent concentration etc. on the reacton rate. The measurement of these rates under different conditions give information about the mechanismof the reaction.Chemical kinetics tries to answer the question of what happens as the reactants are converted to products. Does the reaction occur in one step, or in multiple steps via intermediates? The rates of chemical reactions are of great importance in industrial and biological processesespecially in determining optimum reaction as in organic synthesis and chemical manufacturing (Chigwada, 2005). Scientists use kinetic studies to postulates theories to mimic natural occurrences, calculate how fast the products will be formed and use thermodynamics topredict the equilibrium composition of the reaction mixtures.

The economic viability of many industrial processes is largely affected by the rate at which the reactions occur. Also, every chemical reaction taking place in living organisms occur at a rate carefully controlled by the complex catalysts called enzymes. Life would have been impossible without the rates of countless, complicated chemical processes being controlled with exceptional precision by exquisitely formed enzymes. The above processes in living and chemical industries are essentially redox reactions involving one or more electron transfer between any two chemicalentities (Muhammad, 2003).

A reaction mechanism is a detailed stepwise or step by step sequence of elementary reactions involving molecules, atoms, radicals or ions that occur simultaneously or consecutively andculminate in the overall reaction (Cooke, 1979). It is the theoretical framework accounting forthe fate of bonding electrons and illustrates which bonds are broken and which are formed. Forproper understanding of mechanisms, the experimentally determined rate equation, the exactnature of both reactants and products, the presence of any equilibrium and stoichiometry of the reaction are indispensable (Basolo and Johnson, 1964).

1.2 Electron Transfer Theories

In many instances, theory plays a role in unifying the structural and spectroscopic information, assisting the understanding of the many chemical reactions, including the frequent transfer of electrons between different sites, proton and proton coupled-electron transfers, and various bonds breaking and bondforming reaction steps (Marcus, 2009, 2012).Many theories have been postulated for electron transfer in chemical reactions and each are interrelated to give a

wholesomeand vivid explanationof what happened, how it happened and why it happened. Those relevant to the electron transfer are hereby described.

1.2.1 Franck – Condon principle

The Franck-Condon principle originated in molecular spectroscopy in 1925 when James Franck proposed (and later Edward Condon provided a theoretical basis for) the idea that, when molecules absorb photons to undergo an electronic transition from the ground state E_0 Figure 1.2) to an excited state (E_1), the electronic transition occurs so rapidly that heavy nuclei do not have time to rearrange to their new equilibrium positions q_{01} (Figure 1.2). The electron and nuclear motions being $10^{-15}s^{-1}$ and 10^{-12} s^{-1} respectively. In effect, this means that the photon-induced electronic transitions are most likely to occur from the ground vibrational level (i.e., ν'' = 0) of the ground electronic state to an excited vibrational level (i.e., ν' = 2) of the upper electronic statevertical arrow as illustrated in Figure 1.2.

1.2.2 Marcus theory

Marcus theory is a theory originally developed by Rudolph A. Marcus, starting in 1956, to explain the rates of electron transfer reactions – the rate at which an electron can move or jump from one chemical species (called the electron donor) to another (called the electron acceptor).Marcus' inspiration to develop his theory for what is now referred to as Marcus theory, was a paper of Bill Libbyin which Franck-Condon principle was used to explain some experimental results, namely, why some isotopic exchange reactions which involve electron transfer between pairs of small cations in aqueous solution, such as reaction in equation 1.1, are relatively slow, whereas electron transfers involving larger ions, such as $Fe(CN)_6^{3-}$ - $Fe(CN)_6^{4-}$

and MnO_4^- - MnO_4^{2-}, are relatively fast (Marcus, 1997).In contrast with the classical chemical reaction (equation 1.1) in simple electron transfer reactions no chemical bonds are broken or formed, so different picture is needed for the reaction-rate for electron transfer.

$$AB+C \rightarrow A+ BC \qquad (1.1)$$

An example of reaction 1.1is the transfer of an H, such as in

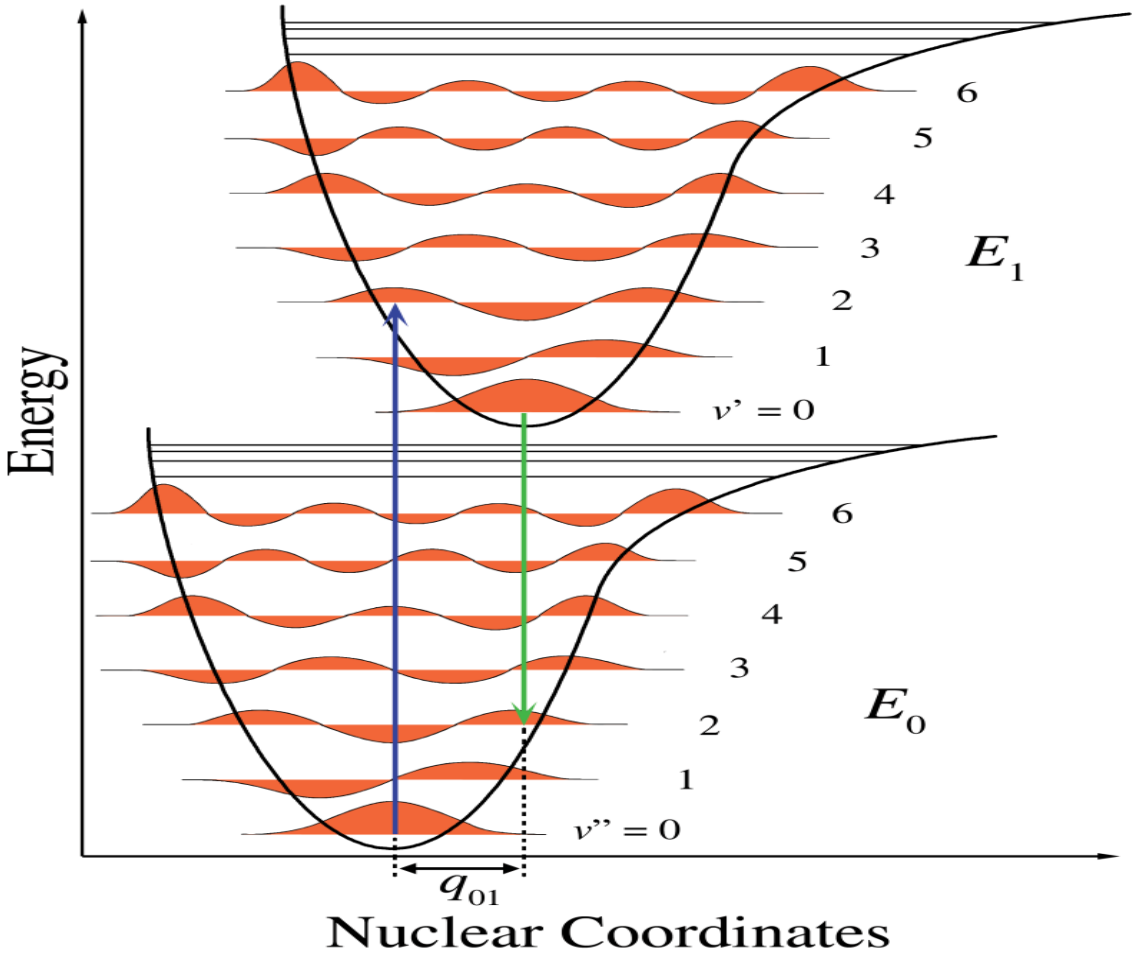


Figure 1.2: A schematic representation of the Franck-Condon principle. The upward arrow indicates the most favored vibronic (i.e., both vibrational and electronic) transition predicted by the Franck - Condon principle

$HI + Br^{-} \rightarrow I^{-} + HBr$(1.2)

or the transfer of a CH, group from one aromatic sulphonate to another.Libby (1952) noted that when an electron transfers from one reacting ion or molecule to another, the two new ions or molecules formed are in the wrong environment of the solvent molecules since the nuclei do not have time to move during the fast electron jump. Looking at the electron transfer reaction in equation(1.1), after the electron jump, the Fe^{2+} ion would be formed in some configuration of the many nearby dipolar solvent molecules that was appropriate to the original Fe^{3+} ion. This introduces a "solvatation energy barrier" for the process. The "solvatation energy barrier" is not the only mechanism playing an important role in the electron transfer reaction rate: the self-exchange reaction 1.3 involves big ions but the experimental rate for the reaction is really slow, in contrast to the picture of an electron transfer governed by the "solvatation energy barrier".

$[Co^{*}(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+} \rightarrow [Co^{*}(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$(1.3)

According to Marcus, the missing ingredient to explain the slow rate of the reaction 1.6 is the factthat there is a dramatic difference in the equilibrium Co-N bond length inthe +3 and +2 ions so that each ions would be formed in a very "foreign "configuration of the vibrational coordinates. It is clear then that electrontransfer implies changing in the chemical structure of the

reactants. To understand how the Franck-Condon principle is used, reference is made to its classical definition in spectroscopy: “an electronic transition is most likelyto occur without changes in thepositions of the nuclei in the molecular entityand its environment”. The resulting state is called a Franck-Condon state,and the transition involved a vertical transition. As electronic transitions,electron transfers are instantaneous compared to the motion of the nuclei ofthe molecules or ions involved in the process and of the orientation of themolecules in the medium (e.g. solvent molecules). The foreign environmentfor the new electronic state after the electronic jump can be seen as anenergetic barrier for the ET process (Marcus, 1997).

1.3Statement of the Research Problem

The kinetic data of electron transfer reaction oftetrakis (2,2'-bipyridine)-μ-oxodiiron(III) complex are scanty, besides there is no kinetic data of reactions between the oxidant and the biochemical species (thioureas, dithionite ion, dithionate ion, semicarbazide, diphenyl carbazide and glutathione) used as reductants in this research. Moreover, there is no established mechanism of reactions between the oxidant and the biomolecules used as reductants. This has constituted a great impediment with respect to proper understanding of some important kinetic information about the oxidant.

In fact, iron deficiency leads to the deficiency of neurotransmitters such as dopamine and serotonin in brain, inducing several mental diseases such as Parkinson’s disease, depression and schizophrenia(Nishida, 2005). Thus, the ancient Greeks concocted portions of iron filings dissolved in vinegar, hoping that drinking this liquor would empower them with the properties of the element(McCord, 1996).Large amounts of ingested iron can cause excessive levels of iron in the blood. High blood levels of free ferrous iron react with peroxides to produce free radicals,

which are highly reactive and can damage DNA, proteins, lipids, and other cellular components. Thus, iron toxicity occurs when there is free iron in the cell, which generally occurs when iron levels exceed the capacity of transferrin to bind the iron. Damage to the cells of the gastrointestinal tract can also prevent them from regulating iron absorption leading to further increases in blood levels. Iron typically damages cells in the heart, liver and elsewhere, which can cause significant adverse effects, including coma, metabolic acidosis, shock, liver failure, coagulopathy, adult respiratory distress syndrome, long-term organ damage, and even death (Cheney *et al.*, 1995).

As thiourea is toxic and cancer supporting agent, the environmental concerns have promoted studies on the destruction of thiourea.The presence of thiourea in urine was reported to be a non-specific indicator of cancer (Sandhyamayee, 2011). However, it has been tagged as carcinogenic by U.S Department of Health and Human Services (Sandhyamayee, 2011), and so all work with this compound should be performed with greatest care to prevent direct exposure to human.

1.4 Justification of the Study

It is generally recognised that iron, the most abundant transition metal ion in mammalian systems, is a necessary trace element and is required for normal metabolic processes spanning molecular oxygen transport, respiratory electron transfer, DNA synthesis, drug metabolism and numerous biological processes (McCord, 1996;Que and Ho, 1996; Wallar and Lipscomb, 1996; Beutler*et al.,* 2003;Costas *et al.,* 2004;Dlouhy and Outten, 2013;Yee and Talman, 2015*).*Iron metalloproteins serve as agents for oxygen transport and storage while haemoglobin and myoglobin are essential for electron transfer in the cytochromes. The group of enzymes called nitrogenases are iron complexes containing either iron and molybdenum, iron and vanadium or

only iron. Each of these enzymes contain two metalloproteins and serve as agents for transfering electrons to larger proteins or reservoirs for electrons before they are transferred. They have the ability to transform many substances*in vitro* including nitrous oxide, cyanide, isocyanides, unsaturatedhydrocarbon, and so on. Iron enzymes, the hydrogenases also abound and play important physiological role. They convert dihydrogen to protons *in vivo* and delivered electrons from dihydrogen to the membrane-bound electron transport chain and also trap dihydrogen involvedin the enzyme reactions (Voordouw, 1992; Andrews, 2000).However, the study of the electron transfer reactions of binuclear complex of iron(III) would possibly go a long way to throw more light on some of the observed biological processes involving iron. Oxo-bridged iron complex has beensynthesised and characterised (Khedekar *et al.,* 1967;Schugar *et al.,* 1967, 1969, 1972; Stephen *et al.,* 1967; Reiff *et al.,* 1968; Cohen, 1969;Ménage *et al.,* 1998).

The use of thiourea and its derivatives, dithionite ion, dithionate ion, semicarbazide, diphenyl carbazide and glutathione as choice of reductants in this work is due to their rolesin biochemical andchemical systems.Thiourea is an organosulphur compound, which is of high industrial potential. It is used to tone silver-gelatin photographic prints, as a plant growth stimulator to break bud dormancy and increase crop yield and more recently as a therapeutic agent in the treatment of thyroid dysfunction (Salem, 2010). As a chaotropic agent, it has been used to solubilise membrane and organelle specific proteins for analysis by two-dimentional gel electrophoresis (Rabilloud, 1998). Reactionof thiourea with hydrogen peroxide under certain conditions produces a powerful reductive bleaching agent, which is routinely used in the textile industry (Arifoglu *et al.,* 1992; Cagarra *et al.,* 1988). It is used as corrosion inhibitors (Ayres, 1970;Atwoodand Hale,1971;Klern*et al.,* 1971;Santanu *et al.,* 1997). Solution of thiourea in

dilute hydrochloric acid has found use as acomplexing agent for removing scales from such boilers (Frost, 1993).Thiourea is also used as a spectrophotometric reagent for the determination ofseveralmetals(Snell, 1978). Thiourea has also found use as a vulcanisation accelerator, additive for slurry explosives, viscosity stabiliser for polymer solutions and molality buffer in petroleum and gold extractions (Groenewald, 1977). It is used as reactant in the production of pharmaceuticals (sulfathiazole, thiobarbituric acid, thiouracil, tetramicol and cephalosporin) (Hilsona and Mouhemius, 2006), a class of drugs used in the treatment of hyperthyroidism (Mertschenk and Beck, 1995; Ardiwlaga, 1999). Several thioureaderivatives have various agricultural, biological, pharmaceutical and analytical applications which include applications in rubber industries as accelerators, in photography fixing agents and to remove stains from negatives, and in agriculture as fungicides, herbicides, and rodenticides (Ren, 2000;Yuan *et al.*,2001; Zhang, *et al.*, 2004; Zhou, *et al.*, 2004; Eweis *et al.*, 2006). Furthermore, in this research it is hopeful that, the carcinogenic substances (thiourea and its derivatives) would be converted to non carcinogenic products that will be of immense benefits to mankind.

Dithionites and dithionates are oxyanions of sulphur which are good reducing agents.The reducing property of the dithionate ion has made it gain wide application in photographic processing as a fixer and also used in gold extraction. Sodium dithionite is used as a reducing agent in dyeing application. It undergoes reduction reaction with water insoluble vat dye and sulphur dye to form water-soluble alkali metal salt of the dye (leuco form) so that they have affinity for the textile fibre. The reductive decomposition of the excessive dye by sodium dithioniteimprove the colour fastness. It is used in bleaching mechanical paper pulp, cotton, wool and kaolin clay. Additional applications include water treatment, leather processing, food

processing, gas purification, cleaning, printing and stripping. In biological sciences sodium dithionite is often used in physiology experiments as a means of lowering solutions' pH 7 (Mayhew, 1978).Carbazides (semicarbazide and diphenyl carbazide) are used in preparing pharmaceuticals including nitrofuran antibacterials (furazolidone, nitrofurazone,and nitrofurantoin) and related compounds.Semicarbazide products (semicarbazones and thiosemicarbazones) are known to have an activity of antiviral, antiinfective, and antineoplastic through binding to copper or iron in cells.

Glutathione (GSH) is awater soluble tripeptide thiol compound of the amino acids glutamine, cysteine, and glycine. The thiol group is a potent reducing agent, rendering GSH the most abundant intracellular small molecule thiol, reaching millimolar concentrations in some tissues. As an important antioxidant, GSH plays a role in the detoxification of a variety of electrophilic compounds and peroxides via catalysis by glutathione S-transferases and glutathione peroxidases. The importance of GSH is evident by the widespread utility in plants, mammals, fungi and some prokaryotic organisms (Anderson, 1998). In addition to detoxification, GSH plays a role in other cellular reactions, including, the glyoxalase system,reduction of ribonucleotides to deoxyribonucleotides, regulation of protein and gene expression via thiol:disulphide exchange reactions (Pastore *et al.*, 2003).

In view of the roles played by these reductants, as enumerated above, there is need for kinetic data of the electron transfer of these importants reductants with tetrakis(2,2□- bipyridine)-µ-oxodiiron(III) complex.The kinetic data generated from the electron transfer reaction between these biochemical compounds and Fe_2O^{4+} will complement the much needed kinetic information

and will bring to the limelighttheir electron transfer properties with the aim of explaining and subsequently improving their physico-chemical properties. Also, the reactions will biomimic some biochemical processes *in vitro*.

1.5 Aim and Objectives of the Study

The aim of this research is to carry out kinetic studies and propose mechanismsof electron transfer reactions of tetrakis (2, 2'- bipyridine) - μ - oxodiiron(III) ions and some reductants. The objectives to this study are to:

i. synthesise and characterise the tetrakis(2,2'-bipyridine)-μ-oxodiiron(III) complex ions,
ii. determine the stoichiometries of the reactions.
iii. determine the pseudo-first order and second order rate constants of the reactions,
iv. determine the order of reactions with respect to each of the reductants,
v. determine the effects of changing the hydrogen ion concentration on the rates of the reactions that took place in acid medium,
vi. determine the effects of changes of ionic strength and dielectric constant of reaction medium on the rates of the reactions,
vii. determine the effect of added ions to the reaction medium on the rates of reactions,
viii. determine the participation of free radicals in the various reactions and
ix. determine the formation of intermediate complexes in the course of the reactions.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Binuclear Coordination Compounds of Iron(III)

The chemistry of diiron complexes for the past decades have continued to be of great interest because of the presence of such diiron centres in a variety of non-haem iron proteins. Participation of the μ-oxo diiron cores of the metalloproteins, hemerythrin, ribonucleotide reductase, and purple acid phosphatase in their biological oxygen-transport and oxygenation processes is well known (Stenkamp *et al.,* 1981; Anatanaitis and Aisen, 1983; Reichard and Ehrenberg, 1983; Sjoberg and Graslund 1983;Wilkins and Harrington, 1983; Sheriff *et al*., 1987).Though the diiron complexes have been known for long, to a large extent, greater focus was on their synthesis and characterisation. Numerous diiron(III) complexes have been prepared and characterised using several spectroscopic techniques such as infrared, UV-visibe and nuclear magnetic resonance (Gaines *et al.,* 1936; Evans 1959;Gustafson and Martel 1963; Khedekar *et al.,* 1967;Stephen *et al.,* 1967; Schugar *et al.,* 1967, 1969; Reiff *et al.,* 1968; David *et al.,* 1972; Reiff, 1977; Nozaki *et al.,* 1999).

Studies on their stability in aqueous and acid media have been carried out (Cohen, 1969; David and de Mello, 1973; Ukoha 1999; Ukoha and Iyun, 2001; Idris, 2005). Electronic, infrared and

Massabauer spectra measurement have depicted that compounds of the form $enH_2[(FeHEDTA)_2O].6H_2O$, $Na_4[(FeHEDTA)_2O].12H_2O$, $[Fe(terpy)_2O][NO_3]_4.H_2O$ and $[Fe_2(bpy)_4O]Cl_4$,were actually µ-oxo-bridged dimeric iron(III) species, containing structural unit of Fe-O-Fe. However, the electronic data of the compounds such as$enH_2[(FeHEDTA)_2O].6H_2OandNa_4[(FeHEDTA)_2O].12H_2O$ displayed two visible absorption bands at 530 and 475nm. The magnetic susceptibility measurements depicted that Fe(III) dimers with pairs of S = 5/2, Fe(III) ion interact antiferromagnetically with J $\approx -95cm^{-1}$. It therefore implies that simple high spin ligand field model modified spin-spin interaction described the behaviour of such complexes. Similar observation also applies to the Fe-O-Fe systems that contain phen, bipy or bpy and Salen as non-bridging ligands (Schugar *et al.,* 1972). In a nutshell, the electronic spectra and magnetic properties of the Fe-O-Fe dimers are accommodated by a simple spin-spin coupling model. Interactions of these complexes with hydrogen ion resulted in the rupture of the oxo-bridge leading to the formation of mononuclear species. On the ground that the presence of acid weakens the Fe-O-Fe bonds, due to the protonation at the bridged oxygen, thus accelerating its cleavage leading to the formation of $[FeL_2(H_2O)_2]^{3+}$(L= bpy, phen, HEDTA, EDTA). Hence existence of oxo-bridges dimers in fairly concentrated acid medium is doubtful. David and de Mello (1973) have used spectrophotometric method to study changes in absorbance at the charge transfer band during nitric acid dissociation of $[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+}$ (L=bpy and phen). The phen complex displayed a relatively small acid dependence compared to bpy complex. Both of the complexes indicated a limiting rate at high acid concentration and acid independence at low concentrations. These complexes dissociated in acid with loss of colour and the dissociation follow first order kinetics. Also, no intermediate or isobestic point was observed during the process. This is in conformity with the earlier

observation that the cleavage of the bridge is dependent on hydrogen ion concentration (Baesi and Mesner, 1976; Ukoha, 1999; Ukoha and Iyun, 2001; Idris, 2005).

2.2 Electron Transfer Reaction of Iron(III)

The kinetics of the redox reactions of μ- oxo-bridged iron(III) complex ion, $[(FeHEDTA)_2O]^{2-}$ (hereafter represented as Fe_2O^{4+}) with thiols (β-mercaptoacetic acid,β-mercaptoethanol andβ-mercaptoethylamine) and L-ascorbic acid have been investigated in aqueous perchloric acid medium ($HClO_4$), I = 1.0 mol dm^{-3} ($NaClO_4$) at (25.0 - 28.0) ± 0.1ºC (Ukoha, 1999; Ukoha and Iyun, 2001). The stoichiometry was 2:1 (reductant/oxidant) in the thiol systems and 1:1 in L-ascorbic acid system. The result showed that the rate of the reactions was first order each in [oxidant] and [reductant] for all the systems. The thiols were oxidised to their disulphides while L- ascorbic acid oxidised to dehydroascorbic acid (A), the order of reactivity was k_2 (MSH) □ k_2 (H_2A) □ k_2 (GSH) □ k_2 (LSH). The rates of reactions were inversely dependent on acid concentration. Spectroscopic evidence indicated the rapid formation of ion-pair complex having the same absorption maxima as the iron(III) complex in the MSH-Fe_2O^{4+} and GSH-Fe_2O^{4+}. The ion-pairs were gradually reduced to Fe(II) ions complexes and the organic products in all the reactions. On the basis of Michaelis-Menten plots and interaction with added ions, the reactions were rationalised to follow the outer-sphere mechanistic pathway. The overall rate equation for the reaction was given as:

$$-\frac{d}{dt}[Fe_2O^{4+}] = (a + b[H^+]^{-1})[Fe_2O^{4+}][\text{reductant}]. \quad (2.1)$$

The following reaction schemes were proposed for the reactions.

Scheme 1: Fe_2O^{4+}- Thiols systems

In the above mechanistic scheme, TSH represent thiols(GSH and MSH) only but not LSH. That was because there was negative salt effect in the reaction of Fe_2O^{4+} - LSH, when ionic strength of the reaction medium was varied. The mechanism of Fe_2O^{4+} - LSH system involved all the steps above except equations 2.3 and 2.4 which was reduced to equation 2.10, since the evidence for the formation of ion pair complex was not established.

Consequently, the rate of reaction with respect to Fe_2O^{4+} - LSH system, is given as equation 2.11

Scheme 2: Fe_2O^{4+}- ascorbic acid systems

The kinetics of the redox reactions of μ- oxo-bridged binuclear complex of iron(III) with 1,2-benzenediol, 1,3-benzenediol, mercaptoacetic acid, L-cysteine, thiosulphate ions and metabisulphite ions have also been carried out in aqueous hydrochloric acid medium. Stoichiometric studies showed that one mole of oxidant was reduced per mole of the reductants. All the reactions exhibited first order dependence on [oxidant] and zero order on [reductant] giving first order overall(Idris *et al.,* 2004;Idris, 2005). Spectroscopic studies did not indicate presence of stable intermediate, since there was no change in absorption maximum on scanning eachof the reaction mixture. The rates of reactions were independent of change in ionic strength and dielectric constant of the reaction medium, added ions did not affect the rate of the reactions. The reactions were proposed to occur by the outer-sphere mechanisms through ion-pair intermediates. The reactions conformed to the rate law below:

$$-\frac{1}{2}\frac{d}{dt}[Fe^{3+}] = k_{obs}[Fe_2O^{4+}] \quad (2.19)$$

Aliyu*et al.,* (2012) reported the kinetics of the reduction of the iron(III) complex ion, $[FeSalen(H_2O)_2]^+$, by L-ascorbic acid in aqueous perchloric acid medium at temperature of 28.5 ± 0.3 ^oC. The kinetic data were obtained by monitoring the rate of decay of the complex at λ_{max}

of 515 nm. Under pseudo-first order conditions of concentration of L-ascorbic acid at about 20-fold excess of concentration of the complex, the rate of reaction increased with the concentration of ascorbic acid. Least square fits of observed rate against concentration of ascorbic acid were linear showing first order dependence of rate on concentration of the complex. Also, a plot of log k_{obs} against log [ascorbic acid] gave a slope of 1.05 implying first order dependence on concentration of ascorbic acid. Second order rate constants were within $(31.58 \pm 0.50) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. The rate of reaction increased with increase in the acidity of the medium but was invariant on altering the ionic strength and dielectric constant of the medium. Added anions did not affect the rate of reaction. The reaction was rationalised to follow the inner-sphere mechanistic pathway. The rate law of the reaction was given as:

$$-\frac{1}{2}\frac{d}{dt}[FeSalen(H_2O)_2^{+}] = k_2[Fe_2Salen(H_2O)_2^{+}][H_2A][H^{+}] \quad (2.20)$$

where H_2A represent L- ascorbic acid.

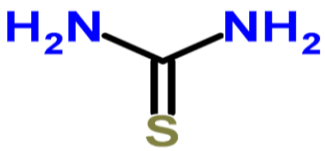
Redox kinetics of the reaction of an adipato bridged iron(III)-salen complex, $[(Fe(salen))_2adi]$ with dithionite ion, $S_2O_4^{2-}$, was investigated in perchloric acid at I = 0.05 mol dm^{-3} ($NaClO_4$) and T = 29 ± 1 °C (Ukoha *et al.,* 2015). Spectrophotometric titrations indicated consumption of one mole of $S_2O_4^{2-}$ per mole of $[(Fe(salen))_2adi]$ reduced. The reaction was carried out under pseudo-first order conditions with $[S_2O_4^{2-}]$ about ten-fold excess of $[(Fe(salen))_2adi]$, observed rates constant increased with increase in $[S_2O_4^{2-}]$ and second order rate constants were fairly constant (0.285 ± 0.01 dm^3 mol^{-1} s^{-1}) indicating first order dependence of the rate on $[(Fe(salen))_2adi]$. A plot of $logk_{obs}$ versus $log\ [S_2O_4^{2-}]$ was linear and gave a slope of 1.0 indicating first order dependence of the rate on $[S_2O_4^{2-}]$. The reaction rate increased with increase in $[H^+]$ within $(3.0 \leq [H^+] \leq 14.0) \times 10^{-3}$ mol dm^{-3}. The reaction was unaffected by variation of ionic strength and

dielectric constant of the medium. Addition of anion and cation did not catalyse the reaction. The reaction has been analysed on the basis of an inner-sphere mechanism mediated by proton transfer. The overall rate equation for the reaction was given as.

$$-\frac{d}{dt}[(Fe(Salen))_2adi] = \{k_d k_p k_1[H^+] + k_4\}[(Fe(Salen))_2adi][H^+][S_2O_4^{2-}] \quad (2.21)$$

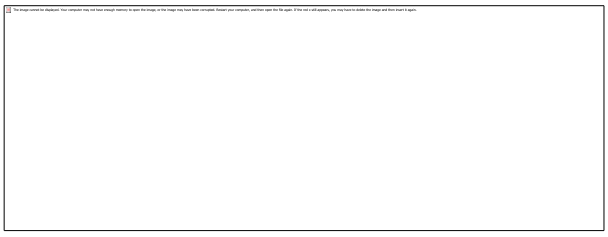
2.3 Thiourea

Thiourea is an organosulphur compoundwith the formula $SC(NH_2)_2$. It is structurally similar to urea, except that the oxygen atom is replaced by a sulfur atom. It is structurally represented as;



Structure of thiourea ($CS(NH_2)_2$)

Thiourea occurs in two tautomeric forms (Eltayeb, 2000), in aqueous solution, the thione shown on the left below predominates.



It behaves like urea as far as the structure is concerned. Previous studies on the simplest thiocarbonyl, thiourea, had shown that the C=S double bond is extremely polar, muchmore than the corresponding C=O double bond due to the mismatch of size between the carbon and sulphur atoms whichresults in an incomplete ð-bond overlap (Jonnalagadda *et al.,* 1996). Thus a

permanent negative dipole resides on the sulphur atom, making it extremely vulnerable to electrophilic attack (Chigwada, 2005).Report has it that changing the substituents on the nitrogen may affect the rate of reaction but not the mechanism since the major reaction is at the sulphur center (Jonnalagadda *et al.,* 1996). Thiourea and its substituents are susceptible to oxidation by a large number of oxidants giving rise to various products including ureas, sulphides, oxides of sulphur, sulphates and nitrogen. In some cases, it undergoes either oxidative cleavage or cyclization (Sandhyamayee *et al.,* 2011).The reaction pathways and the final product of the oxidation reaction depend on the reagents used and condition of the reaction (Prangya *et al*., 2010).

2.3.1 Electron transfer reactions of thiourea and its derivatives

The research on the electron transfer of thiourea and its derivatives has attracted a global interest due to the usefulness of the products obtained from the reactions. Electron transfer reactions of thiourea and iodate (Rabai and Beck, 1985), chlorite (Alamgir and Epstein, 1985), and bromate (Chigwada *et al*, 2007) has been found to give complex kinetic behaviour. With iodate, the reaction displays oligo–oscillation, in which the concentration of iodide goes through several maxima in a single reaction (Rabai and Beck, 1985). Simoyi and Epstein (1987) have used chlorine dioxide at low pH in excess of thiourea to generate sulphur and cyanamide. With excess of chlorine dioxide, formamidine sulphanic acid was obtained. At pH > 3, sulphate was detected as a by-product. In a closed system, the reaction between chlorite and thiourea showed a long induction period followed by a rapid production of ClO_2 (Simoyi, 1986). The long induction period was explained by invoking a two-step process in which the thiourea reduced the chlorite to HOCl, followed by the reaction between HOCl and chlorite to give ClO_2 as shown in equations 2.22 – 2.24.

The reaction between thiourea and excess bromate in acidic medium also proceeded by a long induction period involving a slow evolution of bromine (Simoyi, 1986) as shown in equation 2.25. The long induction period might have resulted from a two-step process, in which thiourea reduced bromate to bromide followed by the reaction of bromide with bromate to give bromine.

The conversions into ureas has been of great interest to chemists long ago(Corsaro and Pistara, 1998). Moreover,the kinetics and mechanism of the oxidation of thiourea to corresponding urea have been studied by various researchers globally using differentreagents such as bromine water (Br_2/H_2O) (Simoyi and Esptein, 1987), bromate (BrO_3^-) (Simoyi *et al.,* 1994), peroxide in alkali(H_2O_2/OH^-) (James *et al.*,1995), chromate(VI) (Maxcy, *et al.,* 1998), peroxide-hypo chloride-bicarbonate ($H_2O_2/NaOCl/HCO_3^-$) (Marshall, 1979), $KHSO_5$ in phosphate buffer (Feil and Meunier, 2000), ferrate(V) (Sharma and O'Connor, 2000),ferrate(VI) (Sharma *et al.,* 1999), and MnO_4^- (Khan *et al.,* 2007).

Simoyi and Epstein (1987) reported the kinetics of oxidation of thiourea in aqueous bromine in the pHrange 1.5 - 4.0. The reaction occurs in two steps: an initial fast step, in which 1 mole of bromine isconsumed per each mole of thiourea, followed by a slower second step, in which the rest of thebromine is consumed. Within the pH range 2 - 4, thiourea is oxidised by bromine water

to urea (equation 2.26). However, at a lower pH, thiourea is converted to ammonium sulphate (equation 2.27).

$4Br_2 + SC(NH_2)_2 + 5H_2O \rightarrow 8Br^- + OC(NH_2)_2 + SO_4^{2-} + 10H^+$ (2.26)

$4Br_2 + SC(NH_2)_2 + 6H_2O \rightarrow 8Br^- + 5(NH_4)SO_4 + CO_2 + 8H^+$ (2.27)

Epstein*et al.,* (1992) studied the kinetics of the reaction between chlorite and thiourea in acidic medium. The stoichiometry of the reaction at pH>3 is indicated in equation 2.28

$2ClO^{2-} + SC(NH_2) + H_2O \rightarrow 2Cl^- + OC(NH_2)_2 + SO_4^{2-} + 2H^+$ (2.28)

At pH<3, $OC(NH_2)_2$ is hydrolysed to NH_4^+ and CO_2. In this reportthiourea is progressively oxidised to sulphonic acid before cleavage of the sulphur-carbon bond and formation of sulphate. A 13-step mechanism was proposed with rate determining step as

$ClO_2^- + SC(NH)_2 + H^+ \longrightarrow HOCl + HOSC(NH)NH_2$ (2.29)

The oxidation of thiourea and two dialkylthioureas to their respective formamidine disulphide cations by hydrogen peroxide in acidic medium has been studied kinetically by Michael and John (1997). The rate law and other data indicate that the reaction proceed via nucleophilic displacement by sulphur on oxygen.

In a recent report, Sahoo *et al.*, (2010) proposed a five steps mechanism for the desulphurizationreaction of thiourea bycetyltrimethylammonium dichromate(CTADC) wherein the initiation of the reaction is due to protonation of CTADC. The proposed mechanism steps are in accord with the conclusion made by Maxcy *et al.,* (1998), who reported the involvement of proton-coupling during the oxidation of thiourea by Cr(VI) to corresponding urea via a

disulphide. From the investigation on the effect of surfactants such ascetyltrimethylammonium bromide(CTAB) and sodium dodecyl sulphate (SDS), it was proposedthat the oxidation occurs at the interface of the CTADC aggregates. With increase in [CTADC], the rate constant decreases. The rate constant is found to be highly sensitive to change in polarity of the solvents. With increasing dielectric constant or dipole moment of the solvent, the rate constant decreases steeply. The order of reaction is one, fractional and two with respect to [CTADC], [TU] and [H^+] respectively.

Also, the oxidation of thiourea has been carried out by Fe(V) in aqueous solution (Sharma and O'Connor, 2000). The rate of oxidation was first order with respect to the reactants and the hydrogen ion concentration. The reaction of Fe(V) with thiourea proceeds via a concerted two-electron oxidation mechanism, which converts Fe(V) to Fe(III). The reactivity of Fe(V) with thiourea is three orders of magnitude faster than with Fe(VI); in addition, Fe(V) reacts preferentially at the sulphur centre of thiourea forming urea as the oxidised product (equation 2.30).

$$8HFeO_4^- + 3H_2NCSNH_2 + 9H_2O \longrightarrow 8Fe(OH)_3 + 3NH_2CONH_2 + 3SO_4^{2-} + 2OH^- \quad (2.30)$$

From the spectral studies of the reaction of Fe(V) with thiourea, no characteristic spectrum of Fe(IV) was detected during the reaction (Melton and Bielki, 1990). And, from the crossover experiments, it was found that the intermediates, Fe(IV) and thiourea radical, were not involved in the reaction of Fe(V) with thiourea. The reaction between Fe(V) and thiourea is, therefore, stoichiometric and may be occurring via a concerted two-electron oxidation, which converts Fe(V) to Fe(III).

The oxyhalogen-sulphur chemistry embarked upon by Simoyi and co-worker was also extended to other thiourea derivatives such as 1,1,3,3-tetramethyl-2-thiourea(TMTU) (Ajibola and Simoyi, 2011), *N*-acethylthiourea (Olagunju *et al.*, 2006) and trimethylthiourea (Chigwada *et al.*,, 2007) using similar oxyanions. The kinetics of oxidation of 1,1,3,3-tetramethyl-2-thiourea by bromine and bromate ion in aqueous acidic media were studied and the mechanisms of the reactions were proposed. Similar chemical dynamics exhibited by the bromate/thiourea and bromate/methyl thiourea reactions were encountered during the course of bromate/1,1,3,3-tetramethyl-2-thiourea reaction. The oxidation pathway went through the formation of sulphenic acid as evidenced by the electrospray ionization mass spectrum of the dynamic reaction solution. This S-oxide was then oxidised to produce tetramethylurea and sulphate as final products of reaction. There was no evidence for the formation of the sulphinic and sulphonic acids in the oxidation pathway. This implicates the sulphoxylate anion as a precursor to formation of sulphate. In aerobic conditions, this anion can unleash a series of genotoxic reactive oxygen species which can explain TMTU's observed toxicity. A bimolecular rate constant of 5.33 ± 0.32 dm^3 mol^{-1} s^{-1} for the direct reaction of TMTU with bromine was obtained. A 15-steps mechanism was proposed to explain the observed kinetic data. However, it was reported that the oxidation mechanism of TMTU by oxybromine species (one of the intermediate reactive species) was remarkably different from that subscribed to by thiourea andother substituted thioureas that have the ability to form stabilizedsulphur oxo-acids.

Kinetics of the redox reactions of methylene blue and CoO_2Co^{5+} with thiourea, 1-methyl-2-thiourea, 1,3-dimethyl-2-thiourea, 1,1,3,3-tetramethyl-2-thiourea and 1-allyl-2-thiourea were investigated spectrophotometrically (Osunlaja, *et al.,* 2013; Osunlaja, 2014). The reactions

ofMB^{+} - thioureas and CoO_2Co^{5+} - thioureas were carried out in HCl and $HClO_4$ medium respectively. The stoichiometries of the reactions were 1:1 (oxidants: reductants) in all the systems studied and the reactions were first order in each of the reactant concentrations making it second order overall for each reaction except MB^{+} - TU system which was second order in [TU] and hence third order overall . All MB^{+} - reductants reactions were acid-dependent while CoO_2Co^{5+} - reductants reactions were acid-independent.The rate of all reactions showed a positive salt effect by changes in ionic strength except. Also, variation of dielectric constant enhanced the rate of reaction involving all CoO_2Co^{5+} systems (except those with TMTU and ATU) but were inhibited with MB^{+} /TU, MTU, DMTU, TMTU systems. All MB^{+} - reductant systems studied yielded reduced methylene blue molecules (that has no conjugation in the phenothiazine ring), sulphate ions, urea/urea derivatives reaction involving. On the other hand, reactions of CoO_2Co^{5+} with the reductants gave Co^{2+} as final inorganic product. Spectroscopic investigations and Michaelis-Menten plots showed that there was no intermediate complex formation for all the systems except reaction involving thiourea and methylene blue. The oxidation of reductants (thiourea, 1-methyl-2-thiourea, 1,3-dimethyl-2-thiourea, 1,1,3,3-tetramethyl-2-thiourea and 1-allyl-2-thiourea) by methylene blue and of CoO_2Co^{5+}followed the order k_2(TU) < k_2(ATU) < k_2(MTU) < k_2(DMTU) < k_2(TMTU). The rate laws of the reactions were

$$-\frac{d[MB^+]}{dt} = (a + b[H^+])[MB^+][\text{thiourea derivatives}] \quad (2.31)$$

$$-\frac{d[MB^+]}{dt} = (a + b\,[H^+])[MB^+][TU]^2 \quad (2.32)$$

$$-\frac{d[CoO_2Co^{5+}]}{dt} = k_2[CoO_2Co^{5+}][\text{thioureas}] \quad (2.33)$$

2.3.2 Oxidative degradation of thiourea and its derivatives

After oral administration to human and animals, thiourea, an antioxidant, is almost completely absorbed and is excreted largely unchanged through the kidneys. However, some metabolic oxidations can take place by biological oxidants. Thyroid gland peroxidase oxidises thiourea in the presence of iodine or iodide and hydrogen peroxide to form formamidine disulphide which, being unstable decomposes at pH > 3.0 to form cyanamide, elemental sulphur and thiourea. It has been reported that, *in vitro* and *in vivo*, both cyanamide and thiourea are inhibitors of thyroid peroxidase (Davidson *et al*., 1979). In liver microsomes, it has been shown that flavin–containing monooxygenase catalyses the S- oxygenation of thiourea to the reactive electrophilic formamidine sulphenic acid and formamidine sulphinic acid. Thiourea is also oxidised in the rat liver (Shubha and Puttaswamy, 2009). In the presence of glutathione, formamidinesulphenic acid is rapidly reduced.

As thiourea is toxic and a cancer-supporting agent, the environmental concerns have promoted studies on the destruction of thiourea.Oxidative degradation of ETU, the mot noxious and carcinogenic metabolite of the widely used ethylene bis-dithiocarbamate fungicides, has been intensively studied. This is usually degraded by using oxidants such as potassium permanganate, sodium hypochlorite(Marshall, 1979), or peroxide (De Zacchini and De Agazio , 2001). However, the oxidants either contain heavy metals or halogens atoms leading to unwanted products.

A fast degradation of thioureas with potassium monopersulphate as oxidant in neutral medium at room temperature, yielding non- carcinogenic ureas as final products. potassium peroxodisulphate is known to degrade diphenylthiourea under strong basic conditions to a

mixture of the corresponding urea, sulphur and phenyl isothiocyanate (Corsaro and Pistara, 1998).

2.4 Electron Transfer Reactions of Dithionite Ion

The kinetics and mechanism of electron transfer reaction of proteins and other compounds of biological interest has been studied (Lambeth and Palmer, 1973), the reaction was investigated under anaerobic conditions by stopped flow spectrophotometry at pH 8.0 and 25^{o}C, under pseudo-first order conditions with dithionite in excess. In the research, the oxidants used were spinach ferredoxin, metmyoglobin, lumiflavin 3-acetate, ferricytochrome, plastocyanin and ferricyanide.

Dependence ofthe observed pseudo-first order rate constant (k_{obs}) on the dithionite concentration was described by the equation:

$$k_{obs} = a[S_2O_4^{2-}]^{1/2} \qquad (2.34)$$

where a = 8.6, 100, and 960 $M^{-1/2}$ s^{-1} for ferredoxin, metmyoglobin, and lumiflavin 3-acetate, respectively. The results supported a mechanism involving SO_2^- as thekinetically important reducing species. With cytochrome c and plastocyanin, the dependence of k_{obs}on dithionite concentration was described by the equation,

$$k_{obs} = a[S_2O_4^{2-}]^{1/2} + b[S_2O_4^{2-}] \qquad (2.35)$$

where a and b are 1450 $M^{-1/2}$ s^{-1} and 1.5 × $l0^4M^{-l}$ s^{-1}, in the case of cytochrome c and 1100 $M^{-1/2}$ s^{-1} and1.35 × $l0^4$ M^{-l} s^{-1} in the case of plastocyanin. These two proteins apparently reacted with both SO_2^- and $S_2O_4^{2-}$.

Davies and Lawther, (1989) studied the kinetics of electron transfer from dithionite to microsomal cytochrome b_5, and forms of the protein associated with charged and neutral vesicles

using Hi-tech SF-2A stopped-flow spectrophotometer. The kinetics of the diithionite reduction of calf hoer microsomal cytochrome b_5, both free in solution and bound to dimyristoyl phosphatidylcholine vesicles were consistent with electron transfer between SO_2^- and the exposed haem edge of the protein, the vesicles membrane did not hinder the approach of SO_2^- to the site of electron transfer on the protein. The cytochrome exhibited an acid dissociation; pka 9.3$\pm$ 0.3 and the rate of electron transfer from dithionite to the high form was about one-third of that to the neutral pH form. The effect of ionic strength on the kinetics was consistent with a reaction between liked charged species and was analysed in terms of a number of theoretical models. In systems comprising cytochrome b_5 and negatively charged vesicles the effects of increasing the charge density of mixed dimyristoyl phosphatidylcholine/dicetyl phosphate vesicles and of increasing the concentration of dicetyl phosphate vesicles was to lower the rate of electron transfer from dithionite to the haemmoiety of the cytochrome. With vesicles of high charge density, however, the kinetics were complicated by vesicles was to lower the rate of electron transfer from dithionite to the haemmoiety of the cytochrome. With vesicles of high charge density, however the kinetics were complicated by vesicle-induced conformation charges of the cytochrome.

Moreover, dithionite is a strong two-electron reducing agent, the property that makes it very suitable for use as a bleaching agent, (Hamza *et al*., 2012) and as a biochemical reductant (Foust*et al.*, 1969; Dixon, 1971;Mayhew, 1978; Davies and Lawther, 1989). It is usedas a general reducing agent in biochemistry for scavenging of oxygen from solutions and maintenance of anaerobiosis and the preparation of the reduced forms of enzymes and electron transfer proteins (Hintz and Peterson, 1980). Reduction-oxidation reactions involving $S_2O_4^{2-}$

with flavodoxin (Mayhew and Massey, 1973), neutrophil cytochrome (Aviram and Sharabani, 1986) and some haemopoetins mainly occurred by a mechanism consistent with the participation of the sulphonyl free radical, $S^*O_2^-$. Dithionite oxidation has been used to measure oxygen transfer parameters (Camacho *et al*., 1997) and is studied only at high pH values because of its rapid hydrolysis below the pH of about 10 (Read *et al*., 2001).

In the study of the oxidation of dithionite by ferrate ions, Read *et al.*, (2001) observed that kinetics for the dithionite oxidation involved two term rate law, one being first order with respect to [hydrogen ion], [dithionite ion] and [ferrate ion] (where acid is used) and the other being first order in only the dithionite and ferrate ion concentrations. The mechanism has a rate determining step involving reaction between the protonated ferrate and the oxysulphur ions, when the reaction is carried out in the presence of acid, and between unprotonated ferrate and dithionite ions (where reaction proceeds in absence of acid). However, in the reduction of hexachloroplatinate(IV) by dithionite examined spectrophotometrically in sodium acetic acid buffer medium, the reaction was reported to be first order in both Pt(IV) species and dithionite (Pal and Gupta, 2012). In the report, H^+ has inhibiting effect on the rate of reaction in the pH range 3.68 – 4.80. The rate of reaction was found to increase with increased in ionic strength and dielectric constant, suggesting a mechanism involving an initial transition state between two like charged ions, which then decomposes to give SO_3^- through the intermediate formation of free radicals, while the study of the kinetics of reactions of cobalamin and cobinamide with dithionite by UV–visible and stopped–flow spectroscopy revealed that the reaction led to the transfer of one electron by dithionite. The reactive species of dithionite oxidation was reported to be $S_2O_4^{2-}$ and SO_2^- (Dereven'kov *et al*., 2013).

Electron transfer reactions of the reduction of monomethyl fushin (mmf) by dithionite was investigated by Onu and Iyun (2000), in aqueous hydrocholoric acid, I = 0.25moldm^{-3}(LiCl), $[H^+] = 3.0 \times 10^{-4}$ moldm^{-3} (HCl), T=30^{o}C the reaction was first order in both [mmf] and $[S_2O_4^{2-}]$. The rate of the reaction showed inverse dependence on $[H^+]$ with empirical rate law.

$$-\frac{d[mmf]}{dt} = a[H^+]^{-1}[mmf][S_2O_4^{2-}] \quad (2.36)$$

The reactions displayed negative salt effect while spectroscopic investigation and Mechaelis-Menten plot showed evidence of intermediate complex formation, inner-sphere mechanistic pathway was implicated in the course of the reaction.

The reduction of Fe(II1) myoglobin derivatives by dithionitewith different ligands attached to the iron atom by rapid-wavelength-scanning stopped-flow spectrophotometryhas been reported(Cox and Hollaway, 1977). The ligands were azide, cyanide, fluoride, imidazole, thiocyanate and water. The reduction of Fe(II1) myoglobin cyanide led to the transient formation of Fe(II) myoglobin cyanide but no intermediate species were observable during the reductions of the other derivatives. The final product of the reaction in all cases was unliganded Fe(II) myoglobin. Investigation of the effect of dithionite concentration on the rate of reduction indicated that the SO_2^- radical ion was the active species in reducing the azide, cyanide, fluoride and thiocyanate derivatives. Comparison of the observed rates of reduction at different ligand concentrations with those predicted for a pathway of reduction involving prior dissociation of the ligand, allowed to estimate the rate of reduction with the ligand in position (outer-sphere reduction). There was a large variation in the relative rates of outer-sphere reduction in the order imidazole □ CN^->SCN^- >N_3^- >F^-.The fluoride derivative was so resistant to outer-sphere reduction that the reaction with

SO_2^-proceeded only by a pathway involving dissociation of F^- before reduction. It was calculated that any direct reduction of this complex was at least 100 times slower than that of the azide derivative.

The results were discussed in terms of the possible role of the axial ligands in haem proteins and it was suggested that the pathway of the electron to the Fe(III) centre may be *via* the p□ orbitals of these ligands.

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Reduction of metmyoglobin derivatives by dithionite ion was carried out by Olivas *et al.*, (1977). The rate constants for reduction by dithionite of a number of metmyoglobin species Mb^+ X (X = H_2O, imidazole, OH^-, F^-, N_3^-, CNO^- SCN^-, HCO_2^-, NO_2^-, and CN^-) were measured at 25 ^oC by stopped flow spectrophotometry. The dependence of the rate was $[S_2O_4^-]^{½}$ and the SO_2^- radical was considered to be the active reductant. Except for X = imidazole and CN^-, reduction occurred through dissociation of Mb^+X. Values for the dissociative rate constant obtained from dithionitereduction were in good agreement with those obtained directly. Reduction of the dissociated fragment (assumed Mb^+H_2O) by $SO_2^-$was 3 ± 1 x 10^6 $M^{-1}s^{-1}$ at pH of 8.2 for all Mb^+X species examined. Reduction of Mb^+ imidazole and Mb^+CN^- occurs directly with SO_2^-, and Mb^o CN^- (Mb^o, deoxymyoglobin) was characterised as an intermediatein reduction of the latter.

The reaction kinetics of native and carbodi-imide-modified tuna and horse heart cytochromes c with both a strong (dithionite) and a relatively weak (ascorbate) reducing agent were studied over a wide range of conditions (Mathews and Brittains, 1987). In their reactions with dithionite both the native and modified cytochromes exhibited single exponential time courses. The effects of

dithionite concentration and ionic strength on the rate of the reduction were complex and could best be explained in terms of the model proposed by Lambeth and Palmer (1973). According to this model, at low ionic strength the native proteins were reduced almost exclusively by $S_2O_4^{2-}$ whereas the modified proteins showed reactivity towards both $S_2O_4^{2-}$and SO_2^{-}. These findings were interpreted in terms of the different charge characteristics of the carbodi-imide-modified proteins relative to the native proteins. The findings that the modified proteins reacted with ascorbate in a biphasic manner were explained as arising from ascorbate binding to a reducible form of the protein, before electron transfer, with an equilibrium between the ascorbate-reducible form of the protein and a non-reducible form. Estimates were obtained for both the ascorbate equilibrium binding constant and the rate constant for the internal electron transfer for both the native and modified horse and tuna proteins. The effect of pH on the reactions indicated that the active reductant in all cases was ascorbate. The studies of ascorbate reactivity yielded important information concerning the proposed correlation between ascorbate reducibility and the presence of a 695 nm absorption band, and the study of dithionite reactivity illustrated the effect of protein charge and solution ionic strength on the relative contributions made by the species SO_2^{-} and $S_2O_4^{2-}$to the reduction of ferricytochrome c.

The kinetics of the oxidation of malachite green, MG^{+}, by dithionite ions, $S_2O_4^{2-}$have been studied spectrophotometrically in an aqueous acid free medium by Idris *et al.*,(2015). The investigation was carried out under pseudo- first order conditions of an excess of dithionite concentration. Reaction conditions were ionic strength of reaction medium, I = 0.1 mol dm^{-3}, λ_{max} = 620nm and T = 25.5±0.5°C. The stoichiometry of the reaction, determined by spectrophotometric titration, was 1:1. Reaction rates increased with increase in I and dielectric

constant (D) of reaction medium. Added ions catalysed the reaction and the result of the Michaelis - Menten analysis suggested that the reaction proceeded through the outer-sphere mechanistic pathway as shown in equations below.

2.5 Electron Transfer Reactions of Dithionate ion

The kinetics of the oxidation of dithionate ion, $S_2O_6^{2-}$, by *N, N′*-ethylenebis [salicylideneiminato] iron (III) complex ion,$[FeSalen(H_2O)_2]^+$, has been investigated at 28.5^{o}C over aqueous perchloric acid concentration range of $0.05 > [H^+] > 0.001$ mol dm^{-3}(Ukoha, *et al.,* 2010). Reduction of $[FeSalen(H_2O)_2]^+$was followed spectrophotometrically at 515nm. Spectrophotometric titration indicated that two moles of the oxidant was consumed for every mole of the reductant that was oxidized. Under pseudo-first order conditions of a large excess of dithionate ion, the rate of reaction increased with increase in concentration of dithionate ion but was not affected by variation in the concentration of the oxidant. The reaction was first order with respect to dithionate ion but zeroth-order with respect to $[FeSalen(H_2O)_2]^+$. The value of observed rate constant was found to be 1.92×10^{-2} dm^3 mol^{-1} s^{-1}. Spectroscopic and Michaelis – Menten plots

apparently tilted the reaction in favour of outer-sphere mechanistic pathway. The overall rate law for the equation was given as

$$-\frac{1}{2}\frac{d}{dt}[FeSalen] = k[S_2O_6^{2-}][H^+] \quad (2.42)$$

Atiga *et al* (2014) investigated the kinetics and mechanism of the reduction of the μ-adi-di[*N*,*N*′-bis{salicylideneethylenediaminatoiron(III)}] complex, $Fe(Salen))_2adi$, by dithionate ion, $S_2O_6^{2-}$, in aqueous perchloric acid at 29 °C, I = 0.05 mol dm^{-3} ($NaClO_4$) and $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}. Spectrophotometric titrations indicated that one mole of the reductant was oxidised per mole of oxidant. Kinetic profiles indicated first-order rate with respect to $[Fe(Salen))_2adi]$ but zeroth-order dependence on $[S_2O_6^{2-}]$. The rate of reaction increased with increase in $[H^+]$, decreased with increased dielectric constant, but was invariant to changes in ionic strength of the medium. Addition of small amounts of AcO^- and Mg^{2+} ions did not catalyse the reaction. A least-squares analysis of rate against $[H^+]^2$ was linear without intercept. The reaction was analysed on the basis of a proton-coupled outer-sphere electron transfer mechanism.

Babatunde and Ajayi (2013) investigated the kinetics of redox reduction of toluidine blue (hereafter referred to as TB^+) bydithionate ion. The studieswas carried out in acidic medium under pseudo-first order condition of excess $[S_2O_6^{2-}]$, at 31± 1°C, $[H^+] = 1 \times 10^{-2}$mol dm^{-3}, ionic strength (I) = 0.5 mol dm^{-3} (NaCl) and λ_{max} 600 nm. The redox reaction displays a 1:1 stoichiometry and the reaction was found to be first order and 3/2 order in the oxidant and the reductant respectively. The reaction was also catalysed by hydrogen ion with the empirical rate law given as:

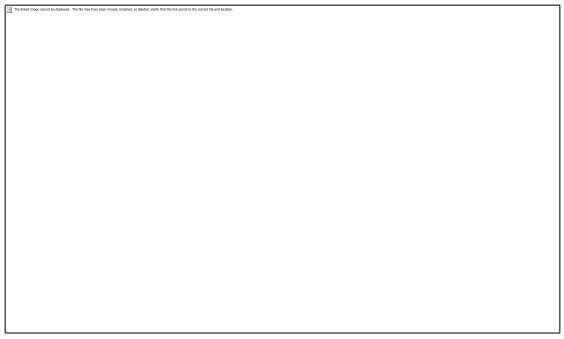
$$-d/dt[TB^+] = (a + b[H^+])[TB^+][S_2O_6^{2-}]^{3/2} \quad (2.43)$$

where a = 0.52 x 10^{-1} dm^3 $mol^{-1}s^{-1}$, b = 7.2 dm^6 mol^{-2} s^{-1}.

The rate of reaction decreased with increase in ionic strength and increased with increase in dielectric constant of the reaction mixture. Added anions and cations catalysed the reaction. The result of kinetic studies, spectroscopic investigations and Michealis-Mentens plot did not suggest the formation of intermediate complex. Outer-sphere mechanism was therefore postulated for the reaction.

2.6 Glutathione and Its Electron Transfer Reactions

This compound is an example ofthiol whichis an organosulphur compound that contains a carbon-bonded sulphydryl (-C-SH or R-SH) group (where R represents an alkane, alkene, or other carbon-containing group of atoms).The -SH functional group itself is referred to as either a thiol group or a sulphydryl group. They are often referred to as mercaptans.Glutathione (GSH) also known as γ-L-glutamyl-L-cysteinyl-glycine is a thiol with -SH functional group at cysteine. GSH is required for several cell processes interconnected with alterations in the maintenance and regulation of the thiol-redox status, due to its capability to exist in different redox specie (Forman*etal.*,2009). GSH is a major antioxidant in the brain (Dringen, 2000), with aconcentration of approximately 2-3 mM, which is much higher than that in blood or cerebrospinal fluid (Cooper and Kristal, 1997). It exerts its functions via several mechanisms.First, GSH non-enzymatically reacts withsuperoxide (Winterbourn and Metodiewa, 1994), NO (Clancy, 1994), hydroxyl radical (Bains and Shaw, 1997), and $ONOO^-$ (Koppal *et al.*, 1999).



Structure of glutathione

In particular, GSH has a higher ability to scavenge superoxide than cysteine (Hussaini *et al.,* 1996). Furthermore, there is no known enzymatic defense against hydroxyl radicals, making GSH the only compound capable of scavenging these radicals (Bains and Shaw, 1997). Furthermore, GSH serves as an essential cofactor for a number of enzymes. It works as an electron donor for the reduction of H_2O_2 or other peroxides catalysed by glutathione peroxidases (Chance*et al.,* 1979). The brain has a relatively high level of glutathione peroxidases as compared with that of catalase, while the liver has high levels of both (Maher, 2005). H_2O_2 is reduced to H_2O by thereaction of glutathione peroxidases with GSH, which is oxidised to GSH disulphide (GSSG) (Dringen, 2000). GSSG is then reduced back to GSH, a step catalysed by GSH reductase with NADPH, and is then reused as a glutathione peroxidases substrate. The relative ratio of the reduced /oxidised forms is over 100 under normal conditions, but is decreased to 49 under stressed conditions (Maher, 2005). It serves as an indicator of the cellular redox environment (Schafer and Buettner, 2001). GSH reacts with various endogenous and xenobiotic compounds mediated by glutathione-S-transferase (GST) (Commandeur*et al.,* 1995) to form mixed disulphides, which are exported to the outside of the cell. GSH can also react with 4-hydroxynonenal via the action of GST to form the GSH-hydroxynonenal adduct (Xie *etal.,* 1998). This process plays an important role in cellular detoxification. Another important role of

GSH is serving as a carrier /storage form for cysteine. Cysteine itself has neurotoxic effects mediated by free radical generation, increasing extracellular glutamate, and triggering overactivation of N-methyl-D-aspartate (NMDA) receptors (Janaky*et al.,* 2000). GSH is a non-toxic cysteine storage form with 10-100 times higher concentrations in mammalian tissues than cysteine (Cooper and Kristal, 1997). Approximately one-third to one-half of the total liver GSH serves as a cysteine reservoir that can be released, when necessary (Tateishi*et al.,* 1977).Moreover, GSH is the major redox buffer and maintains intracellular redox homeostasis. Under conditions of oxidative stress, GSH can lead to the reversible formation of mixed disulphides between protein thiol groups (S-glutathionylation), a process critical for preventingirreversible oxidation of proteins (Giustarini*et al.,* 2004). It therefore implies that GSH modulates a variety of certain outstanding protein functions via S-glutathionylation. Also, GSH can serve as a neuromodulator/neurotransmitter GSH binds via its gamma-glutamyl moiety to NMDA receptors (Janaky *et al.,* 1999). GSH is thought to exert dual (agonistic /antagonistic) actions on neuronal responses mediated by NMDA receptors in the brain. GSH also serves as an endogenous NO reservoir to form S-nitrosoglutathione (Singh *et al.,* 1996).

Abedinzadeh*et al.,* (1989) investigated the oxidation kinetics of glutathione (GSH) by hydrogen peroxide at neutral pH for different concentration ratios $[GSH]_o/[H_2O_2]_o$ between 0.2 and 2 (5×10^{-4} M $\leq[H_2O_2]_o\leq 2.5\times 10^{-3}$M; 4×10^{-4} M$\leq[GSH]_o\leq 2.5 \times 10^{-3}$M). In all cases studied, glutathione disulphide, GSSG was the main product formed via two different oxidation ways, each of them contributing respectively to 80-85% and 10-15%. The kinetic data indicated that an important fraction of hydrogen peroxide disappeared without oxidising the thiol function. Thatcould be attributed to a combination between GSH and H_2O_2 protecting the sulfide group. Chemical

evidences of the existence of a peroxide bond with GSSG were described. Under the experimental conditions, the overall stoichiometric equation was 2 moles GSH were oxidised by 1 mole H_2O_2 to give 1 mole of GSSG, given as;

The overall stoichiometric equation of the reaction was likened to the conversion of glutathione (GSH) to glutathione disulphide GSSG, *in vivo*, catalysed by glutathione peroxidase, which acts on hydrogen peroxide and otherperoxides.Concerning the reaction of H_2O_2 with GSH, McCormic *et al*., (1982) have shown that a UV chromophore having a maximalabsorption at 305 nm appeared during the reaction. But the kinetics of the reaction were not studied. The same observation was obtained when aerated aqueous solutions of GSH were irradiated with a 254 nm radiation.From several comparative studies with other thiols in the same conditions, they attributed the absorbance at 305 nm to a product which was formedon the N-acetylcysteinamide of GSH. Nevertheless, the mechanism of the oxidation of glutathione with hydrogen peroxide was not known until the kinetics of the reaction in question was carried out by Abedinzadeh *et al.,* (1989). Their experimental results could be explained by two separate kinetic pathways. Pathway I involves equations 2.45 and 2.46 and pathway II is composed of equations(2.47) to (2.50).

Pathway I

Pathway II

The palladium(II) catalysed electron transfer reaction between glutathione (reduced) (GSH) and pyridinium chlorochromate (PCC) has been studied spectrophotometrically over the range $2.00 \leq 10^3[GSH] \leq 6.00$; $0.01 \leq [H^+] \leq 0.03$ mol dm^{-3} , $2.83 \leq 10^5[Pd^{2+}] \leq 14.15$ and $20\ ^0C \leq T \leq 40\ ^0C$ (Das and Mohanty, 2013).The rate of reaction was found to increase with the increased in $[GSH]_T$, $[H^+]_T$ and $[Pd^{2+}]$. The reaction was found to exhibit first order dependence in $[GSH]_T$, $[H^+]_T$ and $[Pd^{2+}]_T$. The $\Delta H^{\neq}$ (kJ/mol) and $\Delta S^{\neq}$ (JK^{-1} mol^{-1}) for the electron transfer reaction were found to be -27.7 and -243.9 respectively. The product of the reaction was found to be glutathione disulphide (GSSG) as indicated by infrared spectrum. The negative values of activation parameters favoured the formation of the ordered transition state. The stoichiometry of the reaction was studied at 30^0C, where $[PCC]_T$ was kept constant at 4.0 $x10^{-4}$ mol dm^{-3} and [GSH] = 6.0$x10^{-3}$ $moldm^3$, the $[H^+]$ = 0.01 mol dm^{-3} and $[Pd^{2+}] = 2.83\times10^{-4}$ mol dm^{-3}. From the decrease in $[PCC]_T$ and $[GSH]_T$ the stoichiometry of thereaction was written as:

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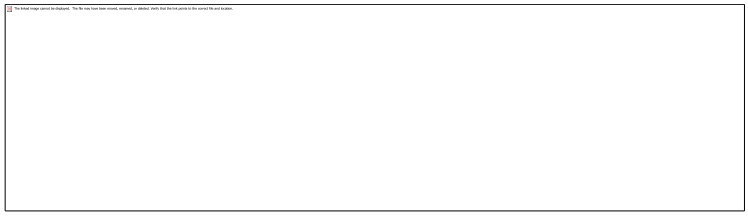
Moreover, Subudhi *et al.*,(2005) carried out kinetics and mechanistic study on the reaction of ferricytochrome c [cytc(III)] by subtrates namely glutathione (GSH) and L-cysteine (L-cys)

spectrophotometrically employing $[substrate]_T >> [cyt(III)]_T$. The reaction exhibited first order dependence on $[substrate]_T$ and $[cyt\ c(III)]_T$. The pseudo first order rate constant increased with an increase in pH, indicating that the conjugate base form of Hcyt c(III) was a better oxidant than the parent Hcyt c(III). The electron transfer rate constants between the oxidants and GSH for both k_1 and k_2 path were found to be greater than with L-cysteine. Hence, GSH was a better reductant of cyt c(III) as compared to L-cysteine. Stoichiometry of the reaction depicted that one mole of the substrate reacted with one moles of cyt c(III) and the product of reaction were GSSG and L-cystine. Nevertheless, reduction of cyt c(III) by GSH was 2.7 faster than L-cysteine. The physiological significance of higher rate of reduction of Cyt c(III) with GSH in comparison to L-cysteine could be because GSH is a tripeptide, the species in the activated state formed between GSH and Cyt c(III) was of lower potential energy than that of L-cysteine again. GSH lacks the toxicity associated with L-cysteine, making it suitable as a cellular redox buffer to maintain a given thiol/disulfide redox potential (Halliwell and Gutterridge, 1999). Possibly that is why all through ages cells selects GSH as better reductant than L-cysteine.

2.7Diphenylcarbazides and Semicarbazides

In chemistry, a carbazide is a functional group with the general formula RNH-NH(C=O)NH-NHR and can be derived from the condensation of carbonic acid with a hydrazine.Semicarbazide or carbohydrazide is the simplest carbazide, diphenylcarbazide is another common carbazide which is being used as an analytical reagent(Crossley, 1936).The sulphur analog is called a thiocarbazide, of which thiocarbohydrazide is the simplest example. Semicarbazideis awater-soluble white solid chemical compound with the formula $OC(N_2H_2)(NH_3)$. Diphenylcarbazides and semicarbazides are derivatives of hydrazine. The molecular formular of diphenylcarbazide is

$C_{13}H_{14}N_4O$. The colour reaction between diphenylcarbazide and chromium(VI) has long been used for the colourimetric determination of chromium (Pflaum and Howick, 1956).



Structure of diphenylcarbazide

Structure of semicarbazide

The kinetics of oxidation of semicarbazide by 12-tungstocobaltate(III) ion in aqueous acidic medium at 300K and a constant ionic strength of 0.3 mol dm^{-3} was studied spectrophotometrically at λ_{max} 624nm under pseudo first-order conditions (Nagolkar*et al.,* 2015). The reaction exhibited 1:2 stoichiometry (semicarbazide:12-tungstocobaltate(III)). The main oxidative products were identified by spot test and spectral studies. The effect of $[H^+]$ ion and ionic strength of the reaction medium have been investigated. The rate of reaction decreased as the concentration of hydrogen ion increased, but increased as the as the ionic strength of the reaction medium increase. The rate constants involved in the different steps of the mechanism were calculated. From the logk versus 1/T values of activation parameters have been evaluated. The activation parameters with respect to the slow steps of the mechanism were computed and discussed. The stoichiometric equation and the overall rate law of the reaction can be represented are represented in equation 2.52 and 2.53 respectively.

$$\text{Rate} = \frac{K_1 k_1}{(K_1 + [H^+])}[\text{semicarbazide}]_T[Co^{III}W_{12}O_{40}]^{5-} \quad (2.53)$$

Moreover, there is no report in literature with respect to the electron transfer reactions of diphenylcarbazide. In this study diphenylcarbazide and semicarbazide are hereafter refer asDH_2 andEH_2 respectively.

CHAPTER THREE

3.0 EXPERIMENTAL

3.1 Materials and Reagents

All chemical reagents and solvents used were of analytical grade (BDH, Kermel, Sigma-Aldrich) and were used without further purification. Singly distilled water was used throughout for all solutions preparation.

3.1.1 Synthesis and characterisation of tetrakis(2,2'- bipyridine)-μ-oxo-diiron(III) chloride

The oxo-bridged binuclear complex, $[Fe_2(bpy)_4O]Cl_4$, hereafter referred to as Fe_2O^{4+} was prepared, purified and characterised following the method of David (1973).An aqueous solution of ferric chloride was prepared by dissolving 3.0g of $FeCl_3.6H_2O$ in 25cm^3 of water, to which was added 3.5g of 2, 2□-bipyridine. The 2, 2□-bipyridine dissolved to give dark brown solution. This solution was filtered and to the filtrate was added saturated aqueous solutionof KCl. The resulting brown precipitate was allowed to settle overnight, filtered under suction, washed with cold water followed by n-hexane, and dried at room temperature in a vacuum desiccator.Electronic and fourier transform infrared spectra agreed with literature results. The complex was stored in amber coloured bottle that was wrapped with aluminium foil and kept in dark cupboard. The uv-visible spectrum of the synthesized complex had λ_{max} at 29,0700cm^{-1} ≈ 344nm (literature: 29,000 cm^{-1} ≈ 345 nm), whereas the FTIR spectrum of the Fe-O-Fe absorbed at 826 cm^{-1}(literature: 830cm^{-1}).A standard solution,1.0 × 10^{-3} mol $dm^{-3}$of the binuclear complex of iron(III) ion was prepared by dissolving 2.234× 10^{-2} g of the synthesised complex in a 25 cm^3 volumetric flask with distilled water and made up to the mark with distilled water.

3.1.2 Thiourea solution

A Stock solution, 0.5 mol dm^{-3} of thiourea was prepared by dissolving 3.80g of thiourea (Sigma–Aldrich) in a 100 cm^3 volumetric flask containing distilled water and made up to the mark with distilled water.

3.1.3 *N*□-methylthiourea ($CH_3HNCSNH_2$) solution

A stock solution, 0.05 mol dm^{-3} of *N*□ – methyl thiourea was prepared by dissolving 0.450g of *N*-methylthiourea (Sigma–Aldrich) in a 100 cm^3 volumetric flask containing distilled water and made up to the mark with distilled water.

3.1.4 *N, N*□– dimethylthiourea ($CH_3HNCSNHCH_3$) solution

A stock solution,0.05 mol dm^{-3} of *N,N'*-dimethyl thiourea was prepared by dissolving 0.520g of *N, N'*-dimethylthiourea ((Sigma–Aldrich)) in a 100 cm^3 volumetric flask containing distilled water and made up to the mark with distilled water.

3.1.5 *N*-allylthiourea (CH_2=$CHCH_2HNSNH_2$) solution

A stock solution, 0.5 mol dm^{-3} of *N* – allylthiourea was prepared by dissolving 5.81g of *N* – allylthiourea (Sigma-Aldrich) in a 100 cm^3 volumetric flask containing distilled water and made up to the mark with distilled water.

3.1.6 *N, N*- diethylthiourea (CH_2=$CHCH_2HNSNH_2$) solution

A stock solution, 0.5 mol dm^{-3} of *N, N* – allylthiourea was prepared by dissolving 5.81g of *N* – allylthiourea (Sigma-Aldrich) in a 100 cm^3 volumetric flask containing distilled water and made up to the mark with distilled water.

3.1.7 Sodiumdithionite ($Na_2S_2O_4$) solution

A stock solution, 0.1 mol $dm^{-3}$of $Na_2S_2O_4$ was prepared by dissolving 8.75g of $Na_2S_2O_4$ (May and Baker, Analar grade) in distilled water in a 50cm^3 volumetric flask and made up to the mark with distilled water.

3.1.8 Sodium dithionate ($Na_2S_2O_6$) solution

A stock solution, 0.5 mol $dm^{-3}$of $Na_2S_2O_6$ was prepared by dissolving 10.30g of $Na_2S_2O_6$ (Sigma-Aldrich, Analar grade) in distilled water in a 100cm^3 volumetric flask and made up to the markwith distilled water.

3.1.9 Semicarbazide hydrochloride($OC(NH_2)(N_2H_3)$ HCl) solution

A stock solution,0.5 mol $dm^{-3}$of semicarbazide was prepared by dissolving 1.393g of semicarbazide hydrochloride in distilled water in a 25cm^3volumetric flask and made up to the mark with distilled water.

3.1.10 Diphenylcarbazide ($C_{13}H_{14}N_4O$) solution

A stock solution, 0.05 mol $dm^{-3}$of diphenyl carbazide was prepared by dissolving 1.21g of the compound in a mixed solvent which comprised 25cm^3distilled methanol and 75cm^3 distilled water in a 100cm^3 volumetric flask. With recourse to the dielectric constant of methanol which is 32.6, the dielectric constant of the mixed solvent was 68.9. It is worthy to note that methanol did not reduced the oxidant that was why it was used in the mixed solvent.

3.1.11 Glutathione($C_{10}H_{17}N_3O_6S$) solution

A stock solution, 0.5 mol $dm^{-3}$of glutathione was prepared by dissolving 7.675g of glutathione in distilled water in a 50cm^3 volumetric flask and made up to the mark with distilled water.

3.1.12 Preparation of standard solutions of magnesium chloride, potassium chloride, sodium sulphate, sodium nitrate, sodium chloride, sodium ethanoate and sodium formate

Astandard solution, 1.00 mol dm^{-3} each of these compounds was prepared by dissolving 2.375g ($MgCl_2$), 1.863g (KCl), 3.55g (Na_2SO_4), 2.125g ($NaNO_3$), 1.46g (NaCl), 2.05g (CH_3COONa) and 1.70g (HCOONa) in distilled water and made up to the mark in 25cm^3 volumetric flask.

3.1.13 Preparation of standard solution of hydrochloric acid

Stock solutions of 2.00 mol dm^{-3}(HCl) was made by diluting 8.5cm^3 of 36% HCl (specific gravity 1.18) in 50cm^3 standard flask then made up to mark with distilled water. The solution was standardized titrimetrically with standard solution of previously dried Na_2CO_3 using methyl red as indicator.

3.2 Methods

3.2.1 Stoichiometric study

The stoichiometry of each system was determined by spectrophotometric titration using the mole ratio method (Iyun, 1990; Iyun and Adegite, 1990; Vaidya *et al.*, 1991; Iyun *et al.*,1995a, 1996; Iyun and Tinuoye, 1998; Ukoha, 1999; Iyun and Ukoha, 1999; Ukoha and Iyun, 2001, 2002; Ukoha and Ibrahim, 2004). The concentration of the oxo-bridged iron complex was kept constant while that of the reductants were varied between the mole ratio 1: 0.2 to 1:3 ([reductant]/ [oxidant]) as follows:

For thiourea (TU) as reductant:$[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, TU] = (2.0 – 24) $\times 10^{-5}$mol dm^{-3},$[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3} and I = 0.3 mol dm^{-3}(NaCl) and T = 27 $\pm 1.0^oC$.

For *N*-methylthiourea (MTU) as reductant: $[Fe_2O^{4+}] = 1.0\times 10^{-4}$ mol dm^{-3}, [MTU] = (2.0 – 24.0) × 10^{-5} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3}(NaCl) and T = 27 ±1.0°C.

For *N*-allylthiourea (ATU) as reductant: $[Fe_2O^{4+}] = 1.0 \times 10^{-5}$ mol dm^{-3}, [ATU] = (3.0 – 30.0) × 10^{-5} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3}(NaCl) and T = 27 ±1.0°C

For *N,N'*-dimethylthiourea (DMTU) as reductant: $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, [DMTU] = (3.0 – 30.0) × 10^{-5} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl) and T = 27 ±1.0°C

For *N,N'*-diethylthiourea (DETU) as reductant: $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, [DETU] = (2.0 – 24.0) × 10^{-4} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl) and T = 30 ±1.0°C

For $S_2O_4^{2-}$ as reductant: $[Fe_2O^{4+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[S_2O_4^{2-}] = (1.0 – 12.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3}(NaCl) and T = 26 ±1.0°C

For $S_2O_6^{2-}$ as reductant: $[Fe_2O^{4+}] = 2.0\times 10^{-4}$ mol dm^{-3}, $[S_2O_6^{2-}] = (6.0 – 48.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl) and T = 26 ±1.0°C

For semicarbazide (EH_2) as reductant: $[Fe_2O^{4+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[EH_2] = (1.0 -12.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl) and T = 26 ±1.0°C

For diphenylcarbazide (DH_2) as reductant: $[Fe_2O^{4+}] = 1.0 \times 10^{-5}$ mol dm $^{-3}$, $[DH_2] = (2.0 – 18.0) \times 10^{-6}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl) and T = 27 ±1.0^{o}C

For glutathione (GSH) as reductant:$[Fe_2O^{4+}] = 6.7 \times 10^{-5}$ mol dm $^{-3}$, [GSH] = (2.68 – 29.5) $\times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl) and T = 26 ±1.0^{o}C

The reactions were allowed to go to completion and the absorbances of the completely reacted mixtures (A_∞) were monitored at 520 nm using Corning Colorimeter 253. The absorbances obtained were plotted against the mole ratios of the reactants. Points of sharp breaks in these plots gave the stoichiometries of the reactions.

3.2.2 Products analysis

At the completion of the reaction, the reaction mixtures were analysed for organic and inorganic products formed in each system. The products were confirmed by chemical test and infrared spectroscopy as follows:

The FTIR spectra of the binuclear complex of iron(III), thiourea substituted thioureas and all other reductants were obtained separately with a Shimadzu FTIR-84008 spectrophotometer in the region 500-4000 cm^{-1} prior to the reactions and after the completion of the reactions for all the systems. The spectra thus obtained, were compared for possible shifts in stretching/vibrational frequencies.

For the reactions where thiourea and substituted thioureas were used as reductants TLC and PTLC were carried out prior to the FTIR as follows: PTLC was carried out using Fluka silica gel precoated glass plates 20×20cm with layer thickness of 0.25mm. A thin line of about 1.5cm from

the bottom of the plate was drawn with a pencil. The sample to be separated was dissolved in minimum amount of solvent to give an approximate concentration of 20mg/ml. It was then applied uniformly along the thin line using capillary tube. The plate was allowed to dry after which it was developed using chloroform and methanol solvent system. The developed plate was air dried in a fume cupboard and the position of the band of interest was marked with pencil and scraped off the back of the plate on to a foil. The scraped sorbent was size reduced using pestle and mortar, transferred to a sintered glass funnel and washed repeatedly with acetone 100% and the solution obtained was evaporated to give the isolated compound (Richard, 1998). Addition of dilute alkaline $CuSO_4$ solution to the products was done to test for presence of urea/urea derivatives.

For the reactions where thiol(glutathione) was used as a reductant, test for the presence of disulphide formed was carried out according to literature (McAuley and Gomwalk, 1968, 1969). The thiol was reacted with a little excess of the oxidant in acid medium and ionic strength of reaction. At the completion of the reaction, the mixture was extracted six times with diethyl ether. The combined ether extracts were washed and dried with anhydrous Na_2SO_4 and left overnight to dry. The crystals product was analysed by the use of FTIR. Spectroscopic technique was used to test for the possible products involved in the reaction of Fe_2O^{4+} and carbazides (semicarbazide and diphenylcarbazide).

3.2.3 Kinetic measurements

The rates of reactions of the Fe_2O^{4+} with the reductants were studied by monitoring the increase in absorbance of the reaction mixture at its λ_{max} (520 nm)using Corning Colorimeter 253. All kinetic measurements were carried out under pseudo-first order conditions with respective

reductant concentrations in excess of the reductant concentration at stated temperature. Ionic strength as well as $[H^+]$ were maintained constant for each system unless otherwise stated (Iyun and Adegite, 1990;Iyun and Shehu, 2004; Iyun *et al.*, 1992a, 1992b, 1992c, 1992d, 1995a, 1995b, 1996; Ukoha, 1999; Ukoha and Iyun, 2001, 2002; Ukoha and Ibrahim, 2004).

The pseudo – first order plots of log $(A_\infty - A_t)$ against time were made and the slopes of the plots gave the pseudo – first order rate constants, k_{obs}. The second order rate constants, k_2, were determined from k_{obs} as k_{obs}/ [reductant] (Iyun and Adegite, 1990; Vaidya *et al.*, 1991; Iyun *et al.*, 1992a; Lohdip*et al.*, 1998; Lohdip, 1999;Ukoha and Ibrahim, 2004).

3.2.4 Effect of change in hydrogen ion concentration on rate of reaction

The effect of changes in the hydrogen ion concentration on the reaction rate was investigated by keeping the concentrations of the oxidant and the reductants constant while that of the hydrogen ion concentration was varied(4.0- 14.0) $\times 10^{-3}$ mol dm^{-3}(HCl). Ionic strength, I was maintained constant at the stated temperature at 0.30 mol dm^{-3} (NaCl). Order of reaction with respect to acid concentration was obtained as the slope of the plot of $logk_{obs}$ against log $[H^+]$. Variation of acid dependent second order rate constant, $k_2(H^+)$ with $[H^+]$ was obtained by plotting $k_2(H^+)$against $[H^+]$ (Vaidya *et al.*, 1991; Ukoha and Iyun, 2001, 2002, Ukoha and Ibrahim, 2004).

3.2.5 Effect of change in ionic strength of reaction medium on rate of reaction

The ionic strength of the reaction mixture was varied (0.1- 0.6) mol dm^{-3}(NaCl) while maintaining the concentrations of the oxidant, reductant and hydrogen ion constant at stated reaction temperature.

3.2.6 Dielectric constant dependence

The effect of medium dielectric constant, D, on the rate of reactions was investigated by carrying out the reactions in medium of varying dielectric constants. The medium dielectric constants were varied using a binary solvent mixture of water and acetone while keeping all other conditions constant. The dielectric constant was calculated (Ukoha and Iyun, 2001) as follows:

$$D_{mixture} = \frac{(V(cm^3) \text{ of acetone x D of acetone}) + (V(cm^3) \text{ of water x D of water})}{\text{Total volume of solution}} \quad (3.1)$$

3.2.7 Effect of addition of ions to reaction medium on rateof reaction

The effect of added ions on the reaction rate was observed by the addition of various amounts of ions (Mg^+, K^+, NO_3^-, SO_4^{2-},CH_3COO^-, and $HCOO^-$) while maintaining the oxidant, reductant and hydrogen ion concentrations constant. The ionic strength and temperature were maintained constant, also (Ukoha, 1999; Ukoha and Iyun, 2001, 2002; Ukoha and Ibrahim, 2004).

3.2.8 Test for participation of free radicals in the course of reaction

Test for free radicals was carried out by adding 2 g of acrylamide to a partially oxidised reaction mixture containing various concentrations of oxidant, reductant and hydrogen ion for each system. A large excess of methanol was added to the reaction mixture. Control experiment was carried out by adding acrylamide to solutions of oxidant and reductant separately at the same conditions of $[H^+]$, I and temperature. Any polymerisation as indicated by gel formation suggested the presence of free radicals in the reaction mixture (Iyun and Adegite, 1990; Vaidya *et al.,* 1991; Iyun *et al.,* 1992a, 1992b, 1992c, 1992d, 1995a, 1995b, 1996; Ukoha, 1999; Ukoha and Iyun, 2001, 2002; Ukoha and Ibrahim, 2004).

3.2.9 Test for formation of intermediate complex prior to electron transfer

Test for the presence of stable, detectable intermediate complexes formed in the course of the reaction was carried out by recording the electronic spectra of partially reacted reaction mixtures at various time intervals depending on the speed of the reaction. Similar runs were made for reactants separately in each case. A shift in, or consistent, λ_{max} and/ or enhancement of peak as the reaction progressed was determined. Furthermore, identification or non identification of intercepts in the Michaelis–Menten plots of 1/ k_{obs} versus 1/[reductant] would give an idea of the presence or absence of intermediate complex formation (Ukoha, 1999; Ukoha and Iyun, 2001, 2002; Ukoha and Ibrahim, 2004).

CHAPTER FOUR

4.0 RESULTS

4.1 Stoichiometry

Results of stoichiometric studies for the reduction of Fe_2O^{4+} by thiourea (TU) and its derivatives i.e. *N*-methylthiourea (MTU), *N*-allylthiourea (ATU), *N*,*N*-dimethylthiourea (DMTU) and *N*,*N*-diethyl thiourea (DETU) show that one mole of each of the reductants was consumed by one mole of Fe_2O^{4+}. The titration curves of each of the systems were determined and are presented in Figures 4.1 to 4.5.

Based on the above findings, the stoichiometric equations for the five systems can be represented by equations 4.1 – 4.5.

$$Fe_2O^{4+} + (NH_2)_2C{=}S \rightarrow 2Fe^{2+} + (NH_2)_2C{=}O + S \quad (4.1)$$

$$Fe_2O^{4+} + CH_3NH(NH_2)C{=}S \rightarrow 2Fe^{2+} + CH_3NH(NH_2)C{=}O + S \quad (4.2)$$

$$Fe_2O^{4+} + CH_3NH(NHCH_3)C{=}S \rightarrow 2Fe^{2+} + CH_3NH(NHCH_3)C{=}O + S \quad (4.3)$$

$$Fe_2O^{4+} + H_2N(NHR)C{=}S \rightarrow 2Fe^{2+} + H_2N(NHR)C{=}O + S \quad (4.4)$$

where $R = CH_2CH{=}CH_2$

$$Fe_2O^{4+} + RNH(NHR)C{=}S \rightarrow 2Fe^{2+} + RNH(NHR)C{=}O + S \quad (4.5)$$

where $R = CH_2CH_3$

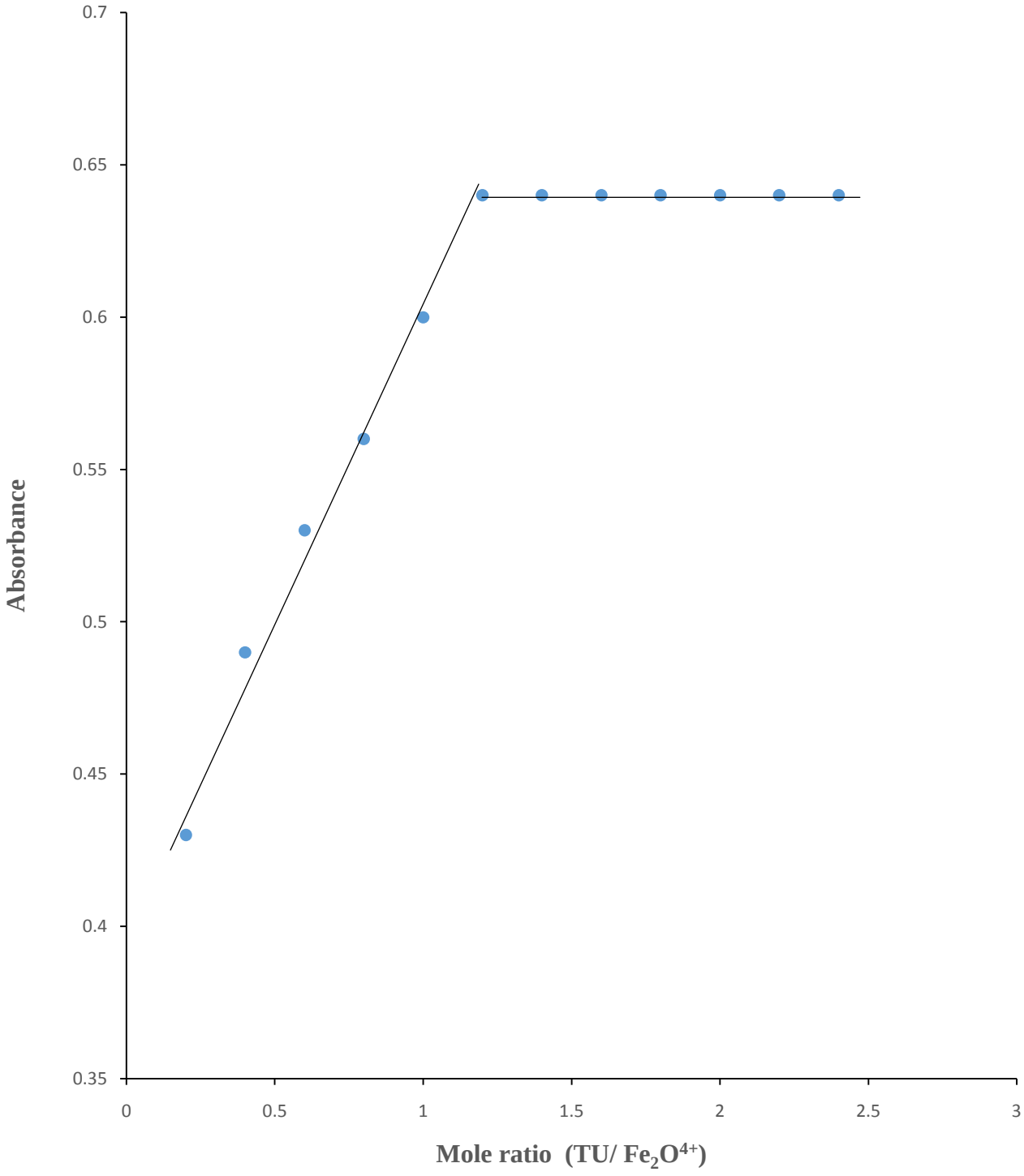


Figure 4.1: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of TU by Fe_2O^{4+} at $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, [TU] = (2.0 – 24.0) × 10^{-5} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm

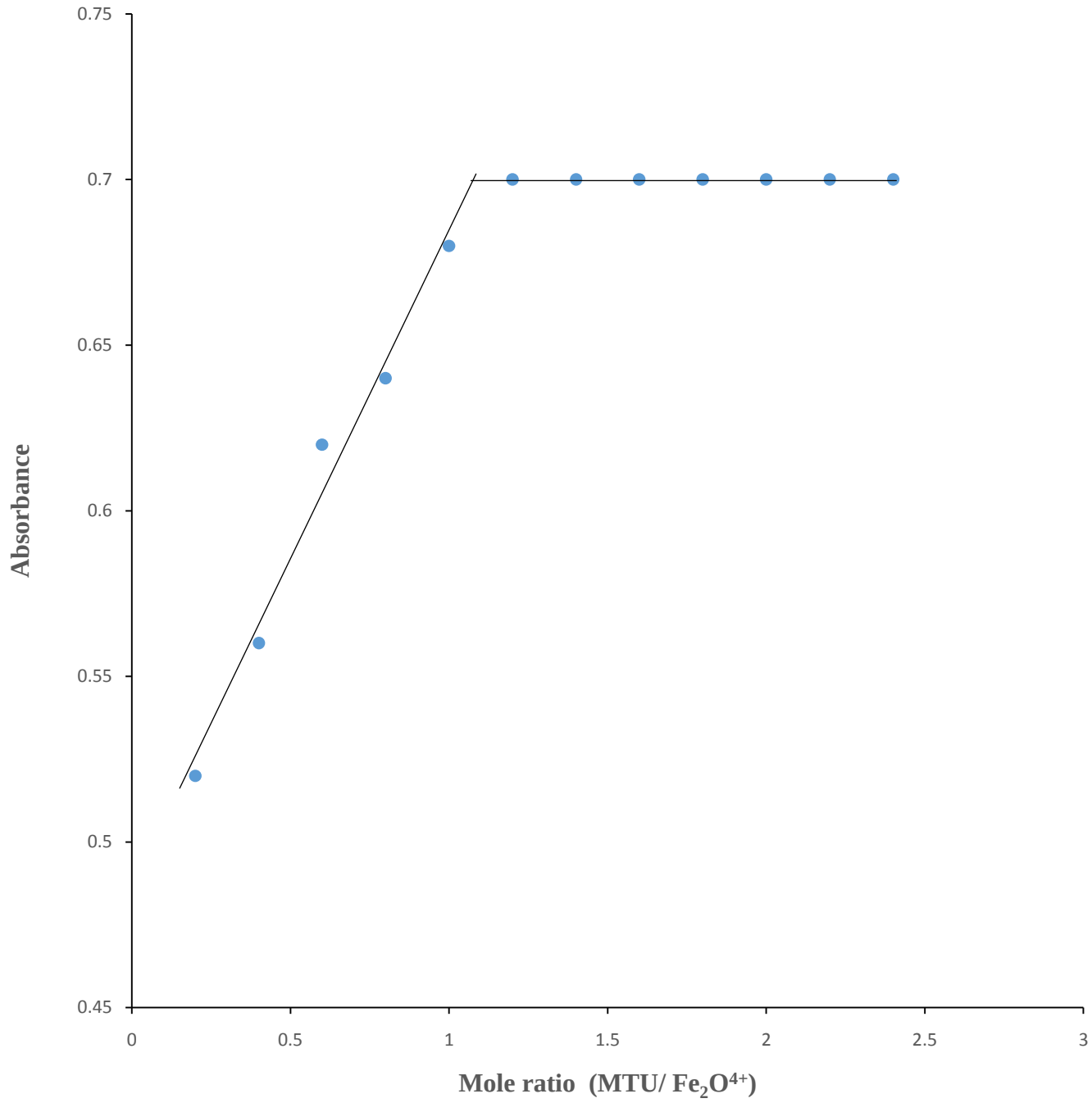


Figure 4.2: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of MTU byFe_2O^{4+}at $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, [MTU] = (2.0 – 24.0) $\times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0^oC and λ_{max} = 520 nm

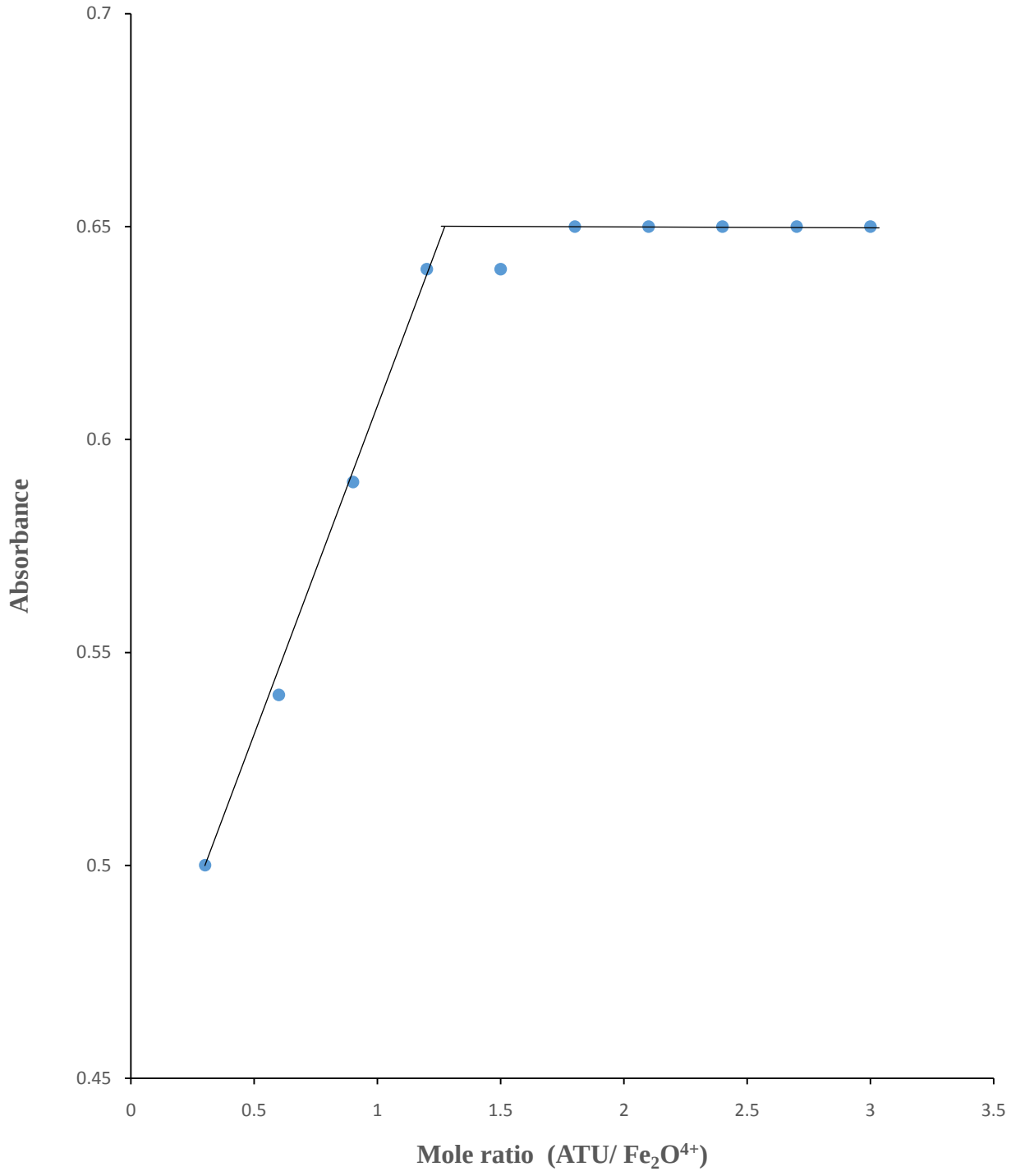


Figure 4.3: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of ATU byFe_2O^{4+}at $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, [ATU] = (3.0 – 30.0) $\times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0^oC and λ_{max} = 520 nm

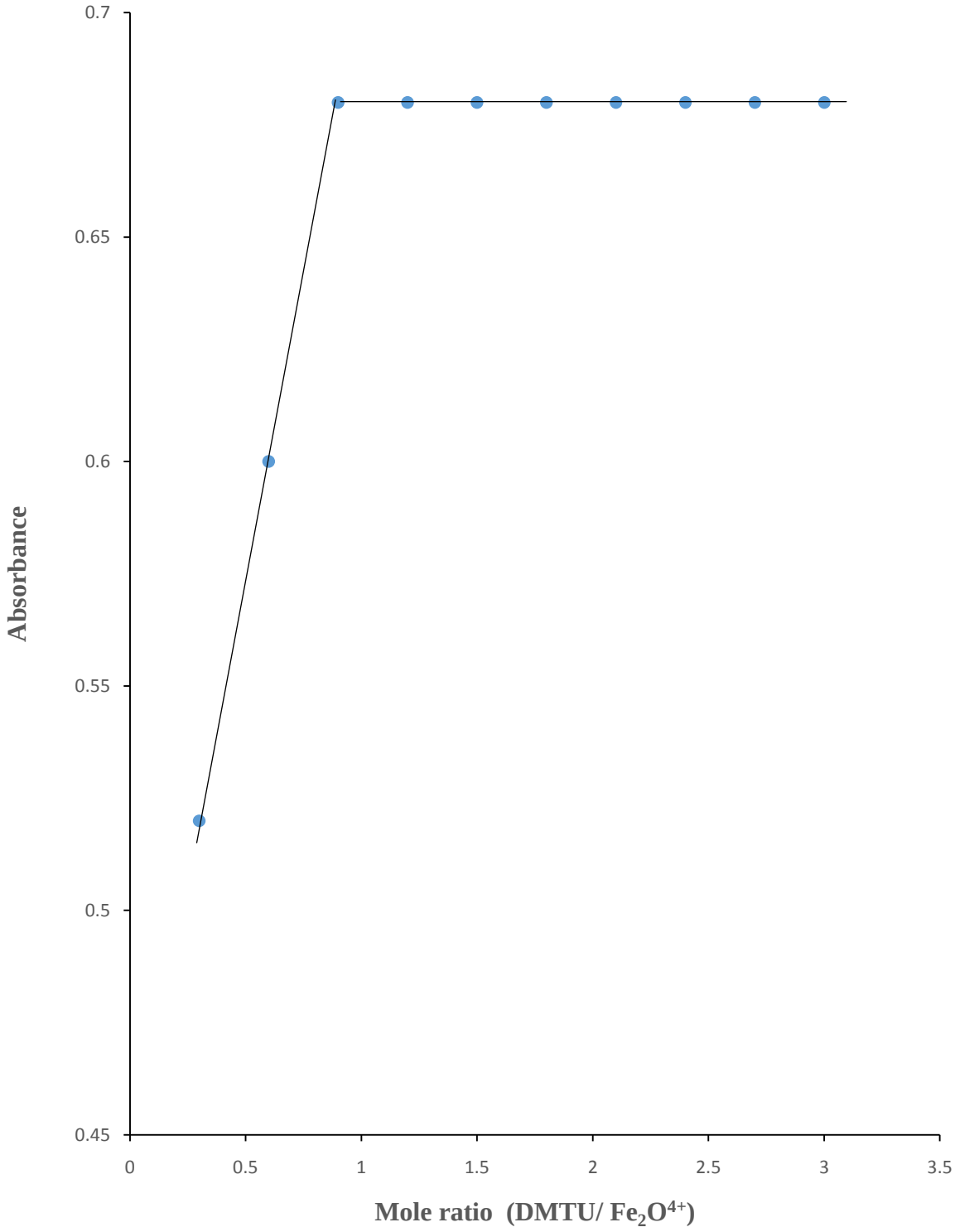


Figure 4.4: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of DMTU by Fe_2O^{4+} at $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, [DMTU] = (3.0–30.0) $\times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm

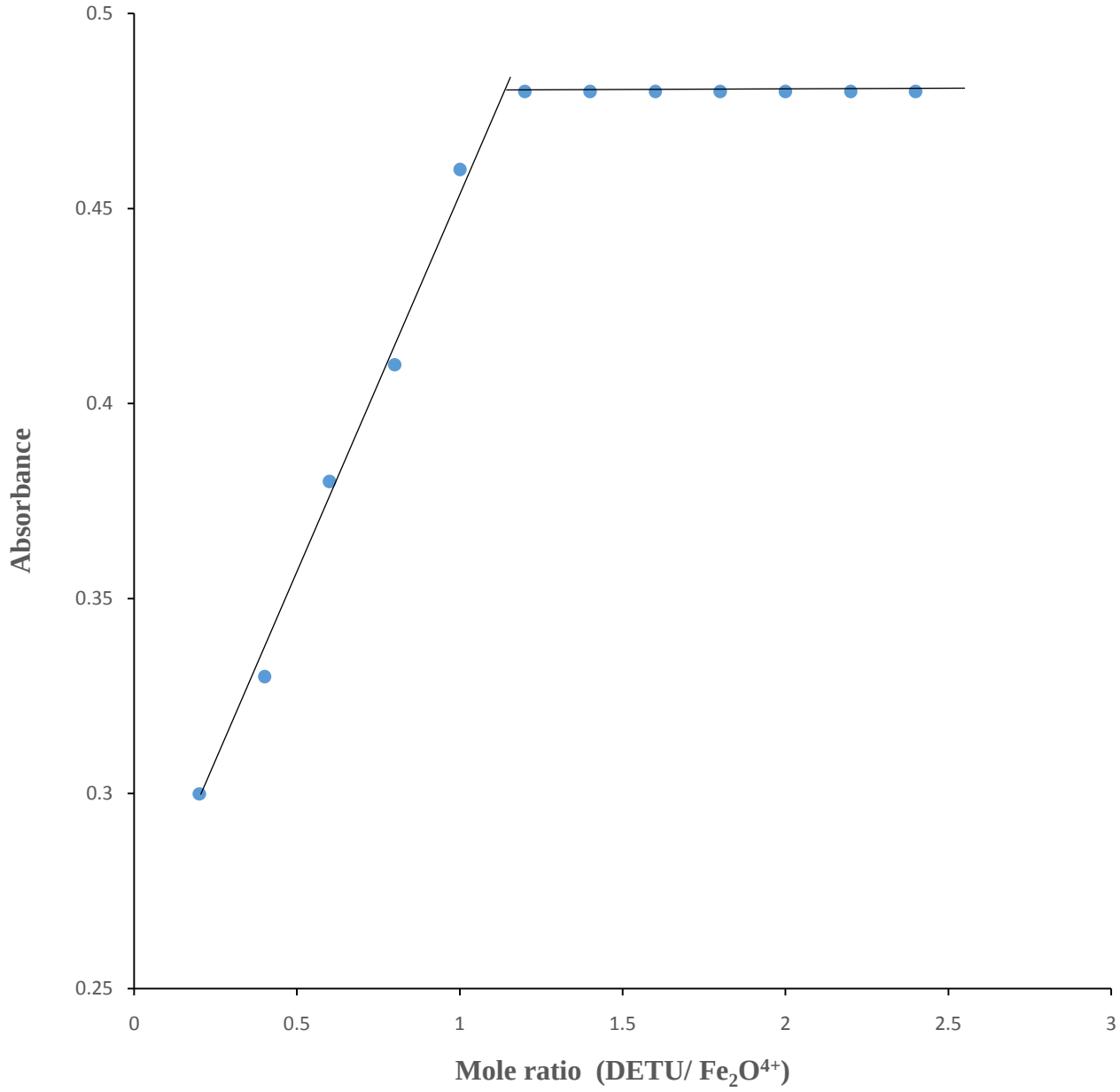


Figure 4.5: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of DETU by Fe_2O^{4+}at $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, [DETU] = (2.0–24.0) $\times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 30.0 ± 1.0°C and λ_{max} = 520 nm

Results of stoichiometric studies for the reduction of Fe_2O^{4+} by dithionite ion ($S_2O_4^{2-}$), dithionate ion ($S_2O_6^{2-}$), semicarbazide (EH_2) and diphenyl carbazide (DH_2) show that one mole of each of the reductants was consumed by one mole of Fe_2O^{4+}. The titration curves of each of the systems was determined and are presented in Figures 4.6- 4.9, whereas one mole of Fe_2O^{4+} was consumed by two moles glutathione (GSH) the titration curve is represented in Figure 4.10. The stoichiometric equations for the five systems above can be represented by equations 4.6 – 4.9

$$Fe_2O^{4+} + S_2O_4^{2-} + H_2O + O_2 \rightarrow 2Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (4.6)$$

$$Fe_2O^{4+} + S_2O_6^{2-} + H_2O \rightarrow 2Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (4.7)$$

$$Fe_2O^{4+} + RH_2 \rightarrow 2Fe^{2+} + R + H_2O \quad (4.8)$$

$$Fe_2O^{4+} + 2GSH \rightarrow 2Fe^{2+} + GSSG + H_2O \quad (4.9)$$

where RH_2 are carbazides(EH_2 and DH_2) and GSH is glutathione

4.2 Products Analysis

The results of the different types of products formed in each system represented in equations 4.1 – 4.9 at the completion of the reaction are as follows:

a.) A pinkish-violet colour which gradually turned bluish was obtained with the addition of dilute alkaline $CuSO_4$ solution to the products of thiourea and its derivatives. This shows the presence of urea or its derivatives.

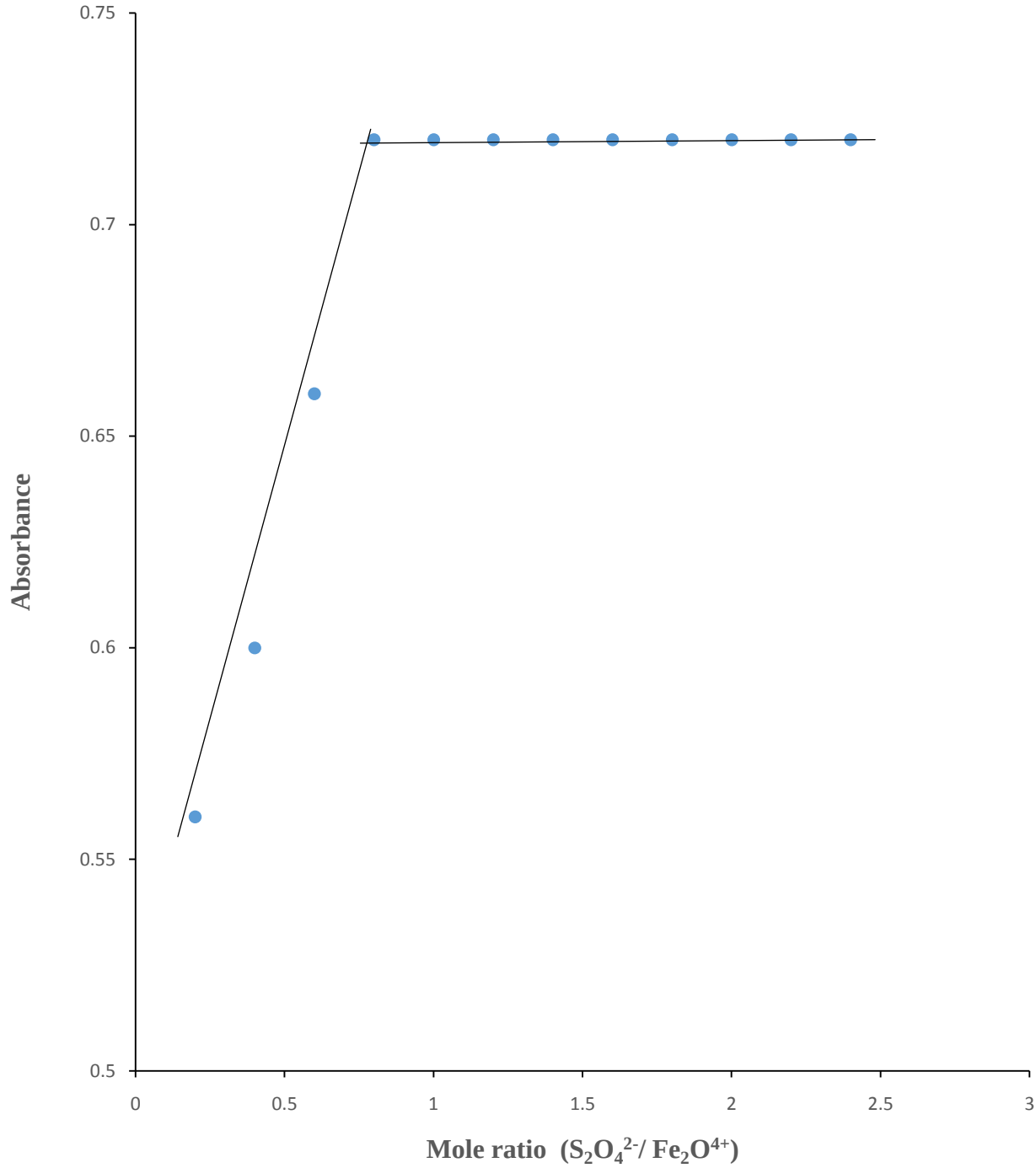


Figure 4.6: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of $S_2O_4^{2-}$by Fe_2O^{4+}at $[Fe_2O^{4+}] = 5.0 \times 10^{-5}$ mol dm^{-3},$[S_2O_4^{2-}] = (1.0 - 12.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 26.0 ± 1.0^oC and λ_{max} = 520 nm

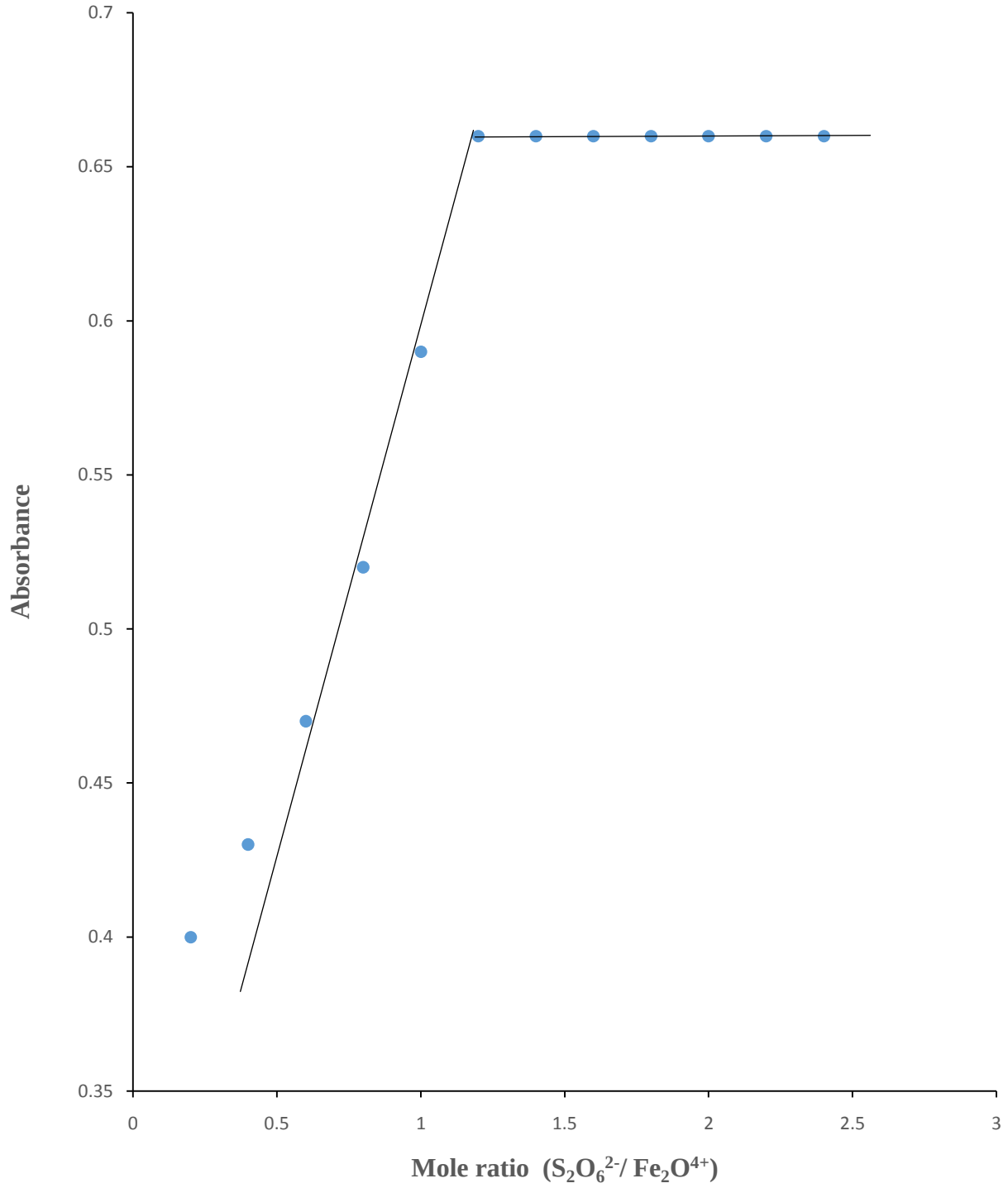


Figure 4.7: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of $S_2O_6^{2-}$ by Fe_2O^{4+}at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3},$[S_2O_6^{2-}] = (4.0 – 48.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 26.0 ± 1.0^oC and λ_{max} = 520 nm

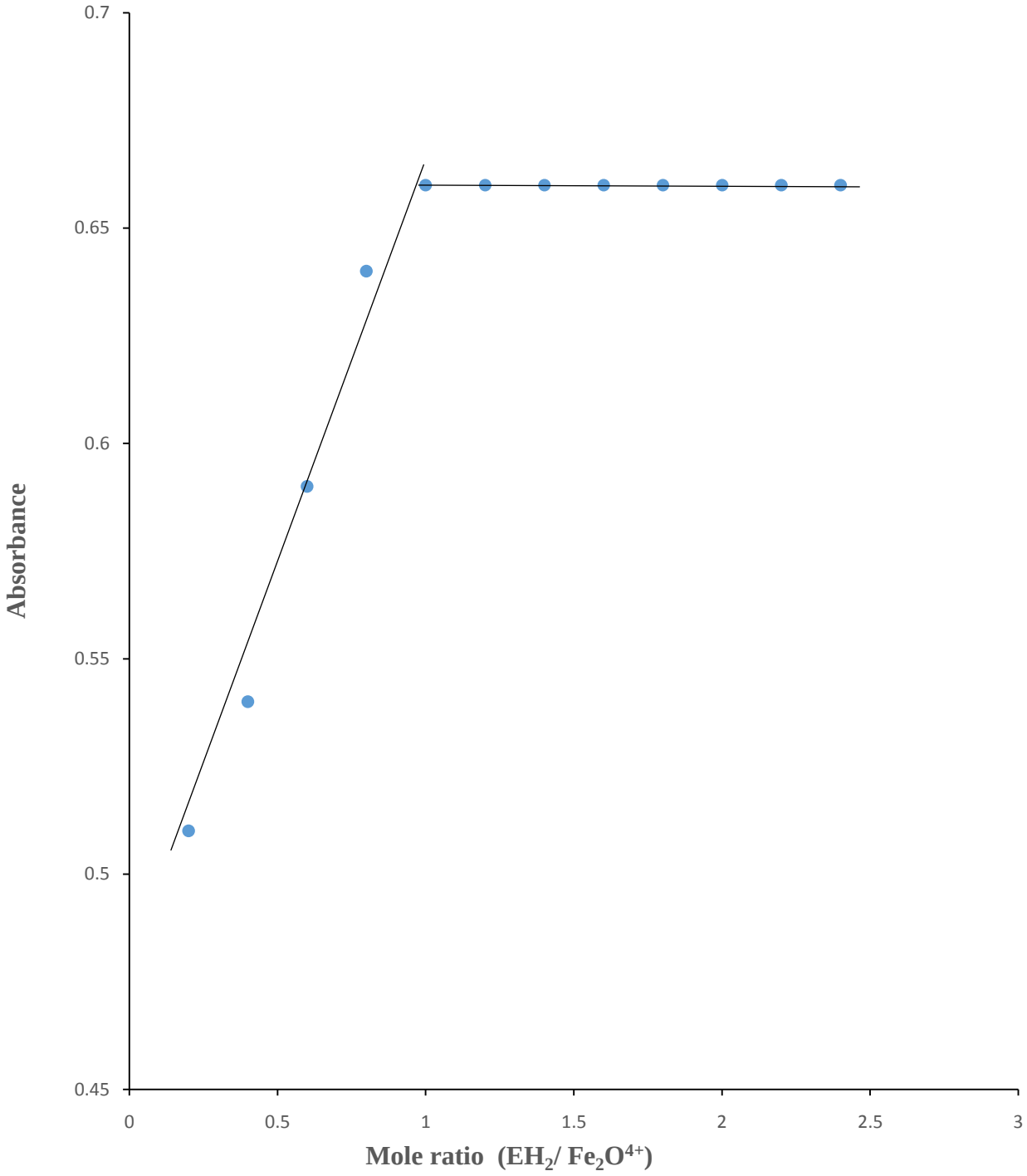


Figure 4.8: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of EH_2 by Fe_2O^{4+} at $[Fe_2O^{4+}] = 5.0 \times 10^{-5}$ mol dm^{-3}, $[EH_2] = (1.0 - 12.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 26.0 ± 1.0°C and λ_{max} = 520 nm

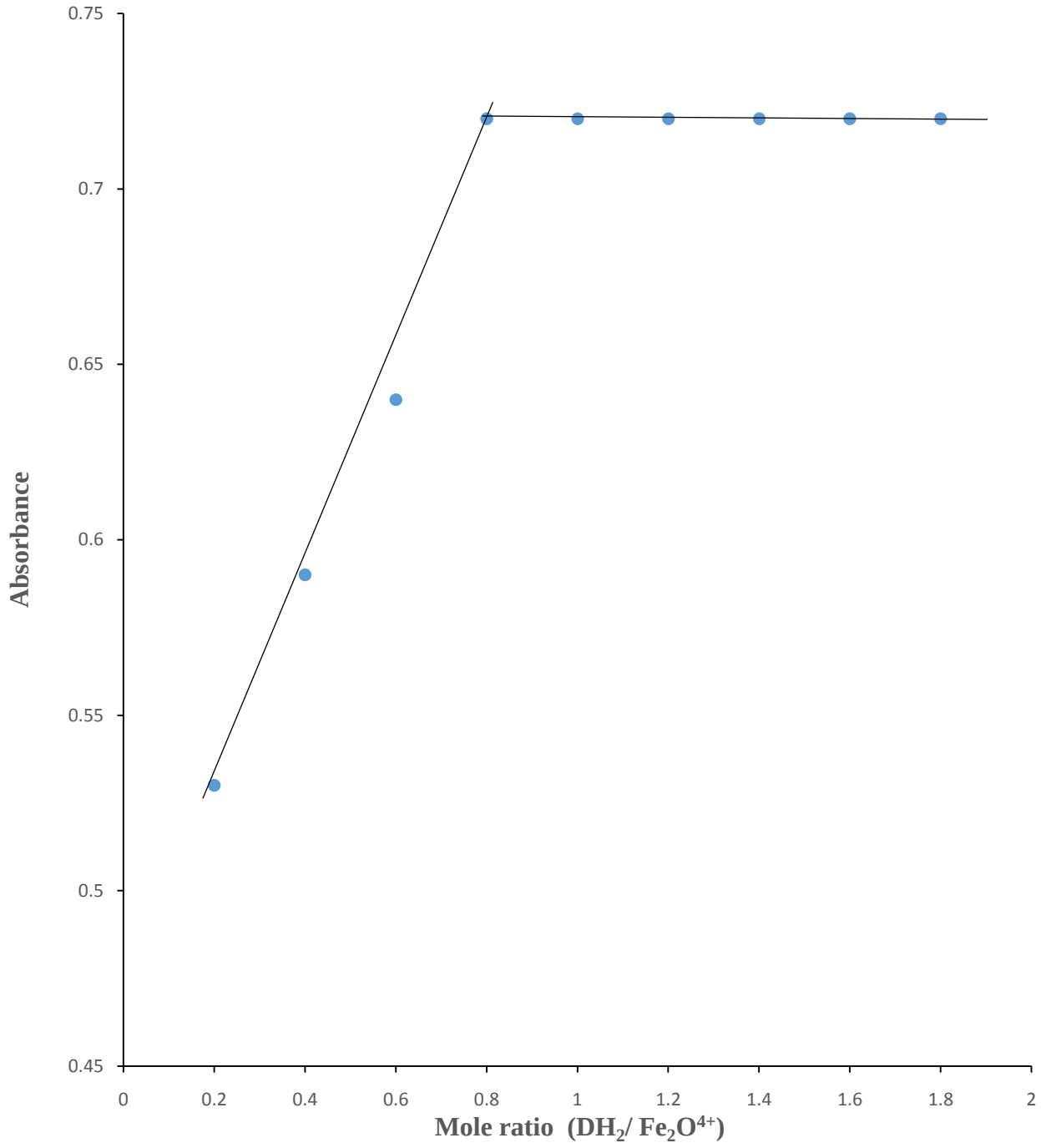


Figure 4.9: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of DH_2 by Fe_2O^{4+} at $[Fe_2O^{4+}] = 1.0 \times 10^{-5}$ mol dm^{-3}, $[DH_2] = (2.0 – 18.0) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 26.0 ± 1.0°C and λ_{max} = 520 nm

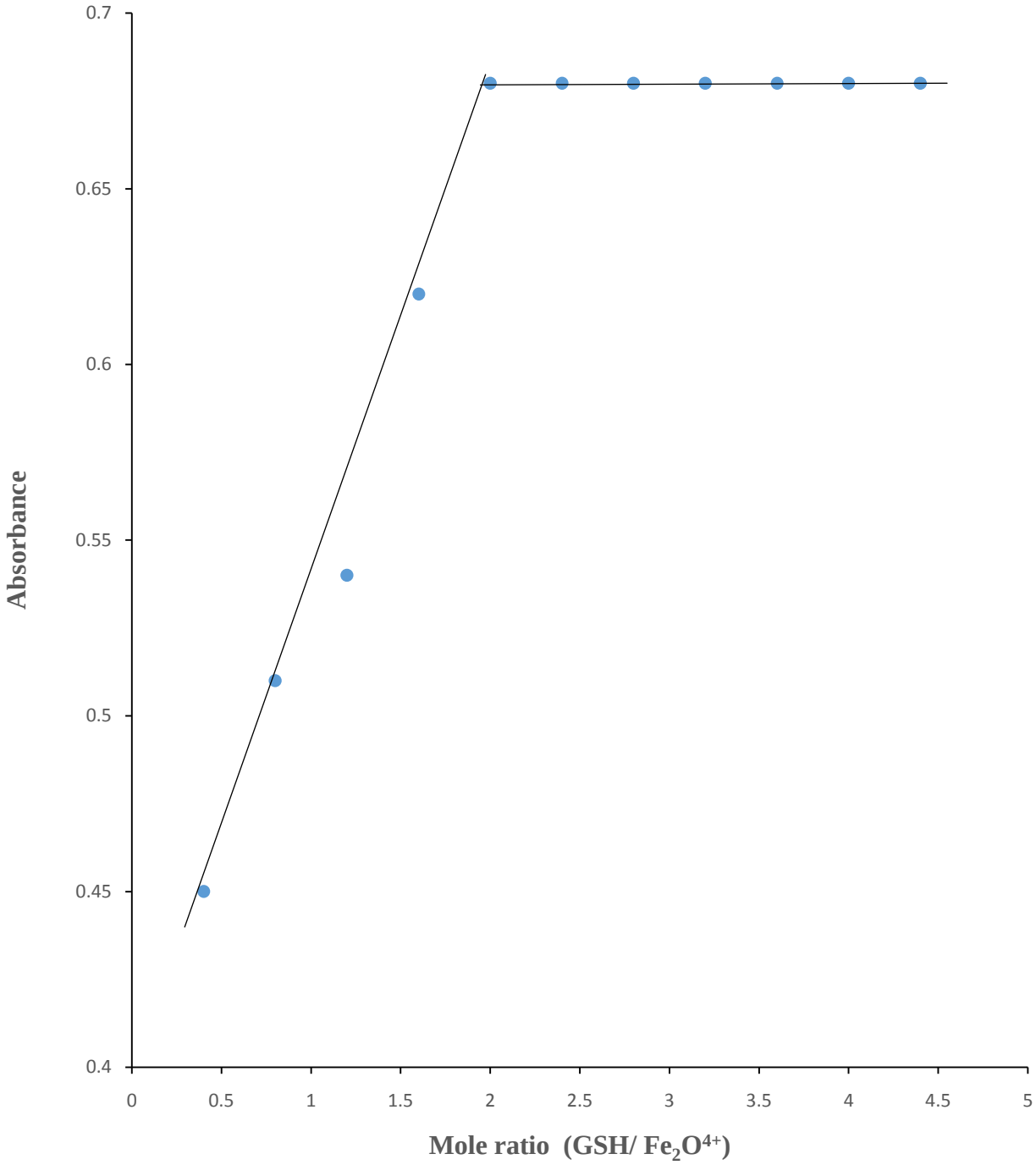


Figure 4.10: Plot of absorbance versus mole ratio for the determination of stoichiometry of the oxidation of GSH by Fe_2O^{4+}at $[Fe_2O^{4+}] = 6.7 \times 10^{-5}$ mol dm^{-3},$[GSH^-] = (2.68 – 29.5) \times 10^{-5}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 26.0 ± 1.0°C and λ_{max} = 520 nm

b.) The Fourier Transform infrared (FTIR) spectra of thiourea and those of the substituted thioureas were obtained separately with a Shimadzu FTIR-84008 spectrophotometer in the region 500-4000 cm^{-1} prior to the reactions and at completion of the reactions, Figure (4.11-4.20) indicates a new stretching frequency at 1644 ± 30 cm^{-1} which has been assigned to υ (C=O) of urea (Al-Majthouls and Salman, 2012) as against 700 ± 50 cm^{-1} of υ (C=S) of the thioureas (Begum *et al.,* 2009). In the reaction of Fe_2O^{4+}/thioureas sulphur was qualitatively identified as one of the inorganic products by formation of violet colour on addition of sodium nitroprusside to the product on a tile (Murugan, 2013).

c.) The spectra of Fe_2O^{4+}/ reductants reactions over a wide range of wavelength (400-700nm) indicated that the Fe^{2+} in the products absorbed maximally at 520nm which is analogous to literature values of 522nm (Ayoko *et al.,* 1993c, 1996), 530nm (Ayoko *et al.,* 1993a and b) and 520nm (Hazra and Lahiri, 1975; Iyun *et al.,* 1996, 1dris *et al.*, 2004, Yusuf *et al.,* 2004). Addition of $K_3[Fe(CN)_6]$ to the products of all the systems gave a blue black colour, also confirmed the presence of Fe^{2+}in all the products. Addition of acidified $BaCl_2$ solution to the products of Fe_2O^{4+}/ $S_2O_4^{2-}$ and Fe_2O^{4+}/ $S_2O_6^{2-}$ gave a white precipitate which is insoluble in excess dilute HCl, an indication that SO_4^{2-} ion is in the reaction products of the two systems.

The formation of disulphides as the only organic products in the reactions of Fe_2O^{4+} was confirmed using the method of McAuley and Gomwalk (1968 and 1969). FTIR spectroscopic method was also carried out on the crystals formed to ascertain the formation of disulphides (Figures 4.21 – 4.22) and on carbazides (semicarbazide and diphenyl carbazide) (Figures 4.23- 4.26).

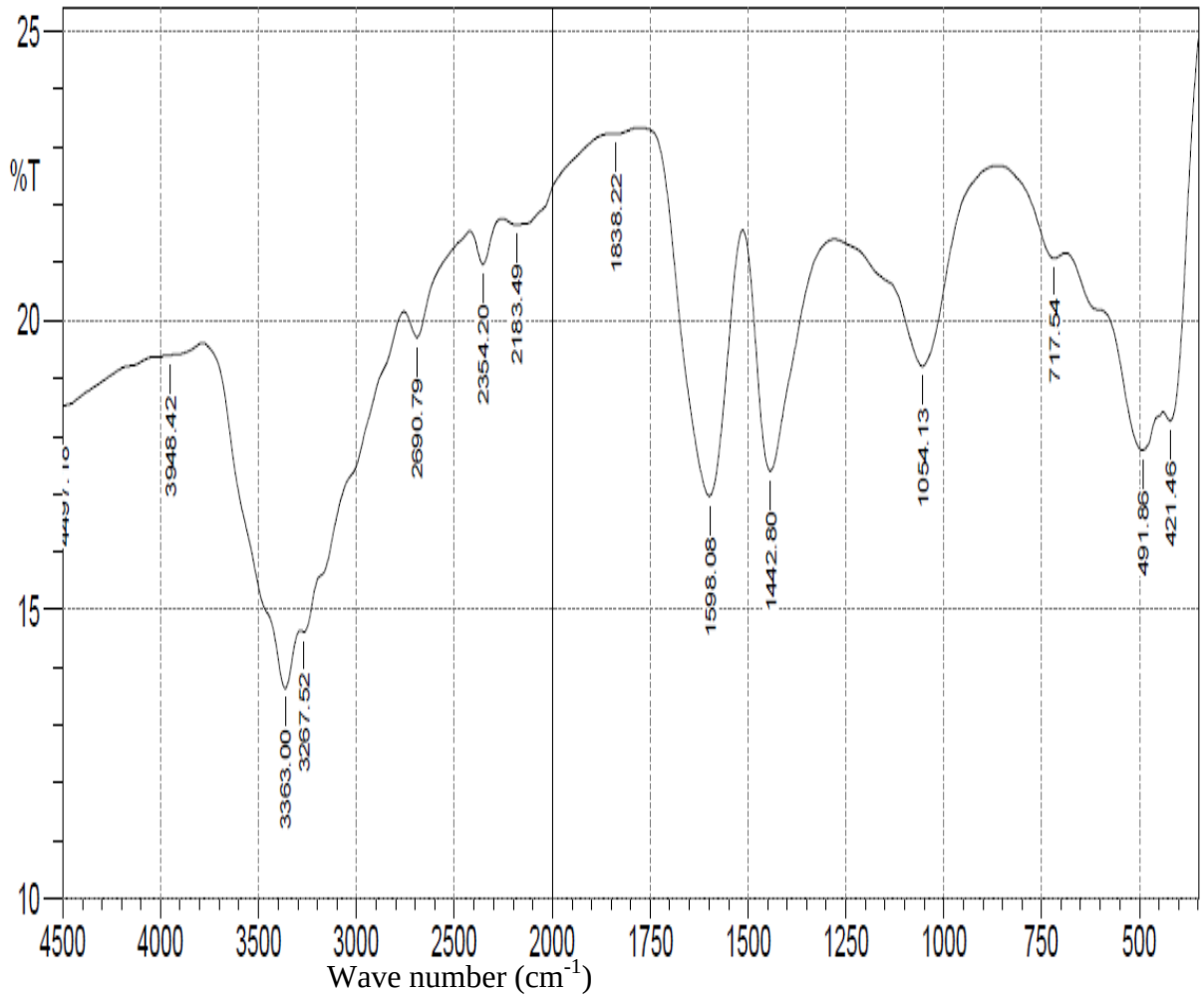


Figure 4.11 : FTIR spectrum of TU

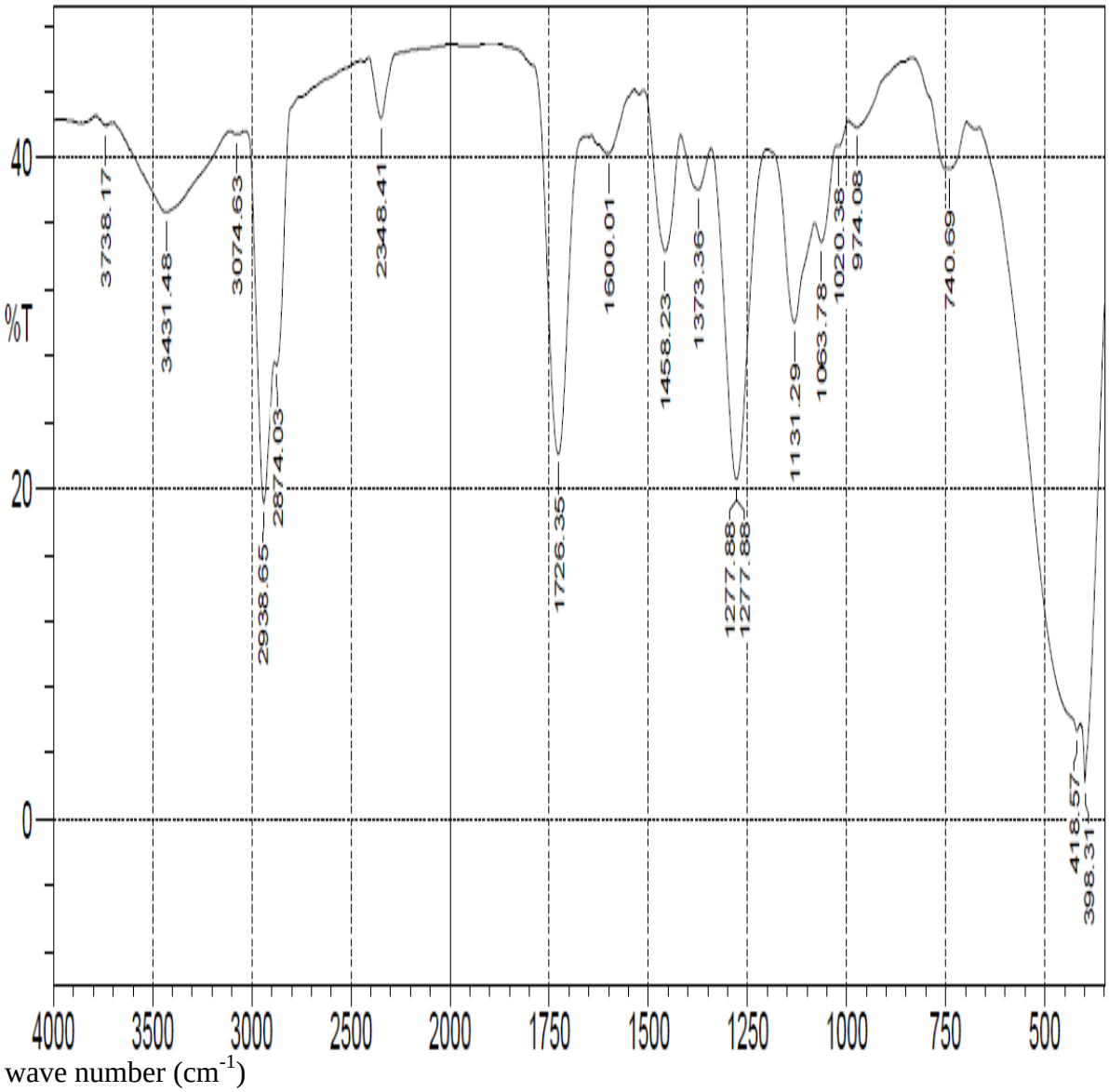


Figure 4.12 : FTIR spectrum of MTU

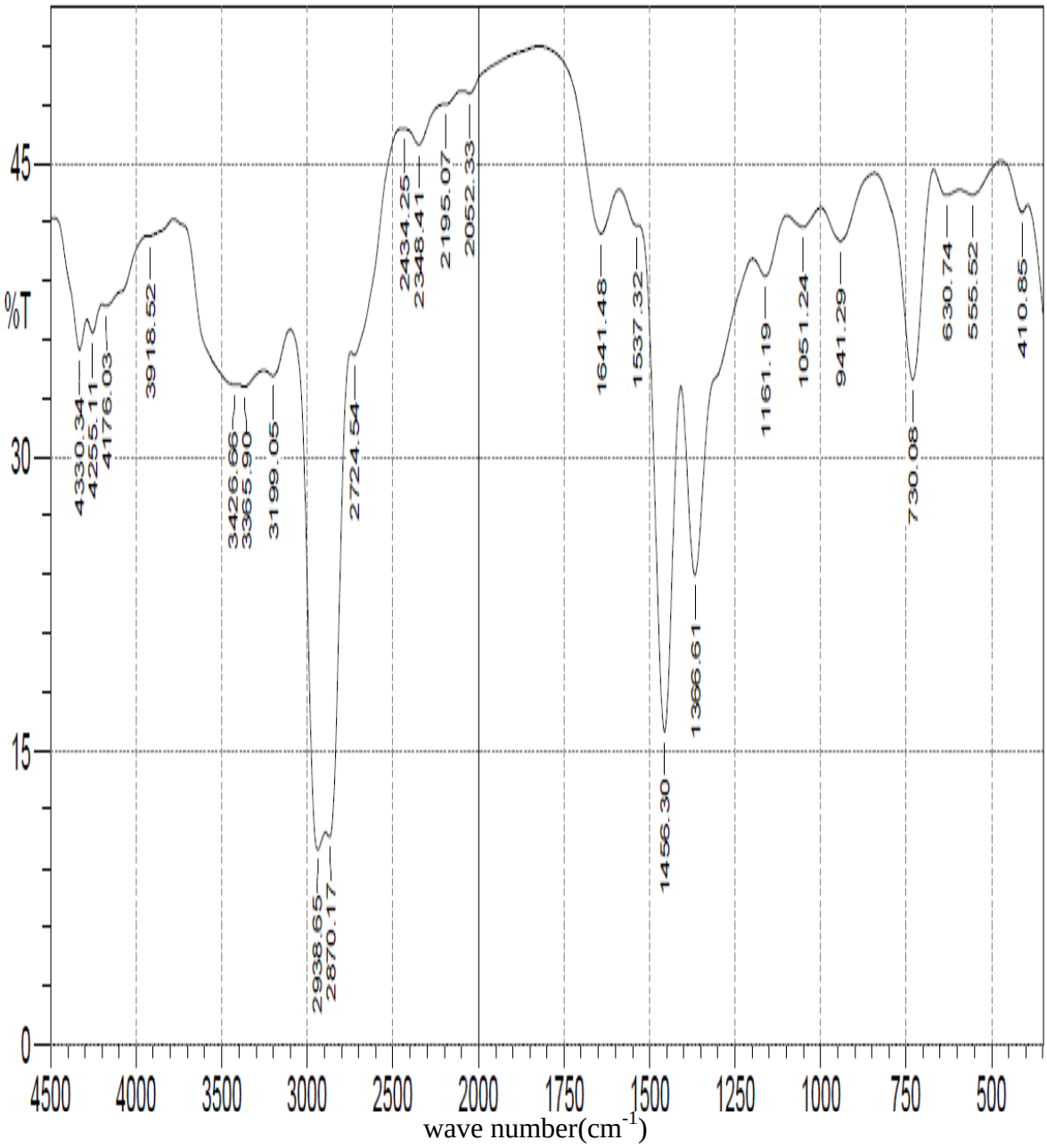


Figure 4.13 : FTIR spectrum of ATU

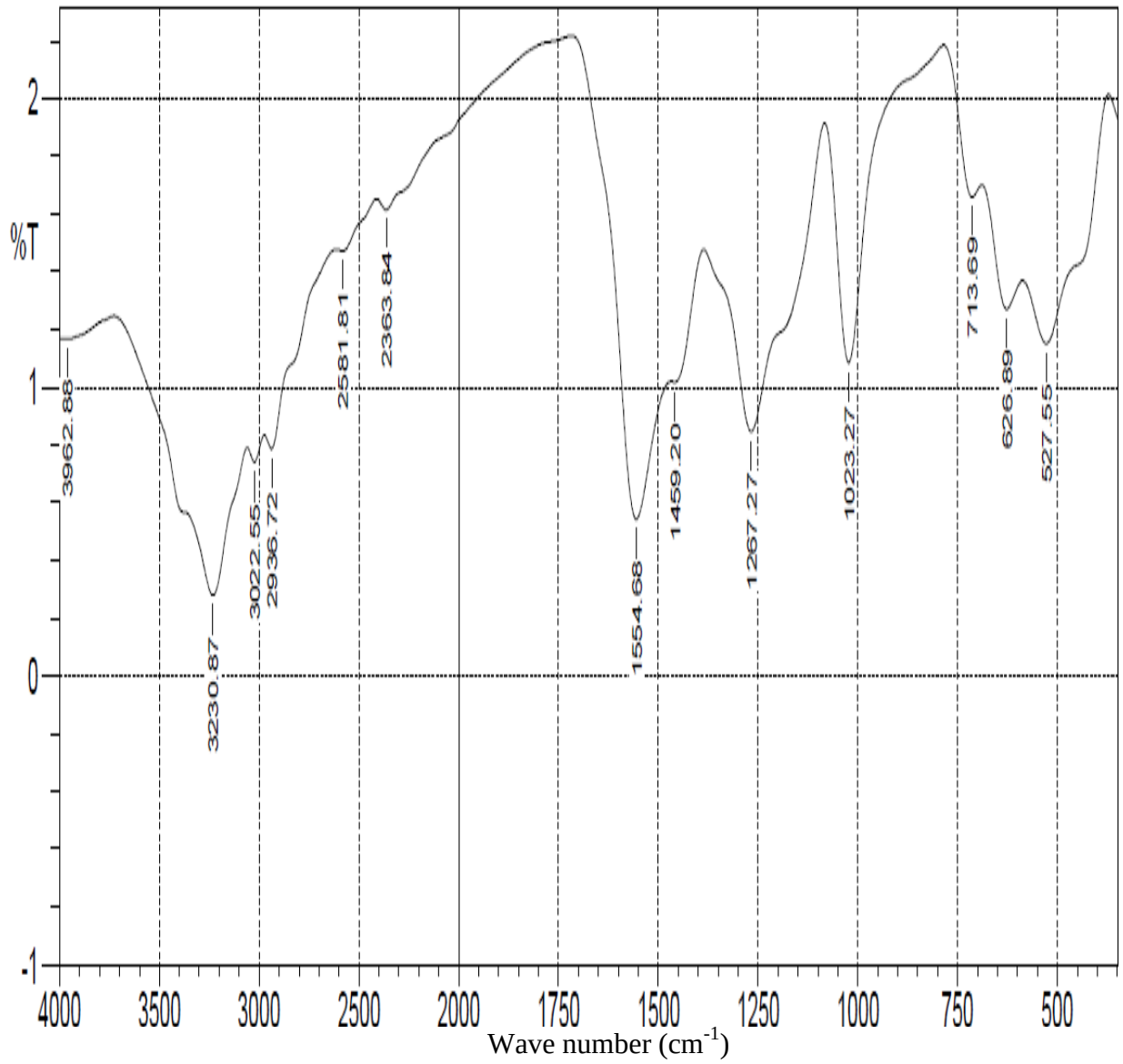


Figure 4.14 : FTIR spectrum of DMTU

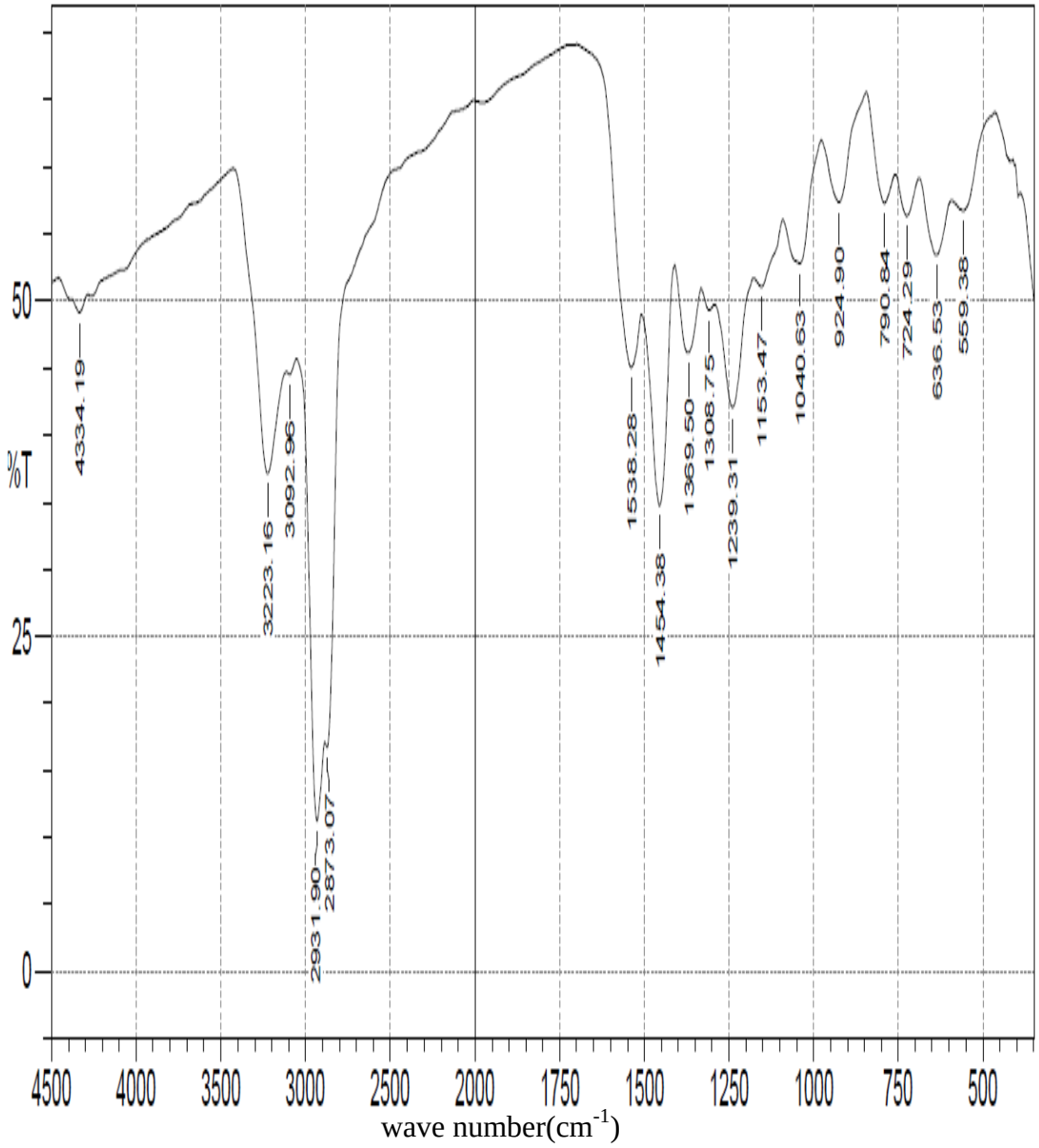


Figure 4.15 : FTIR spectrum of DETU

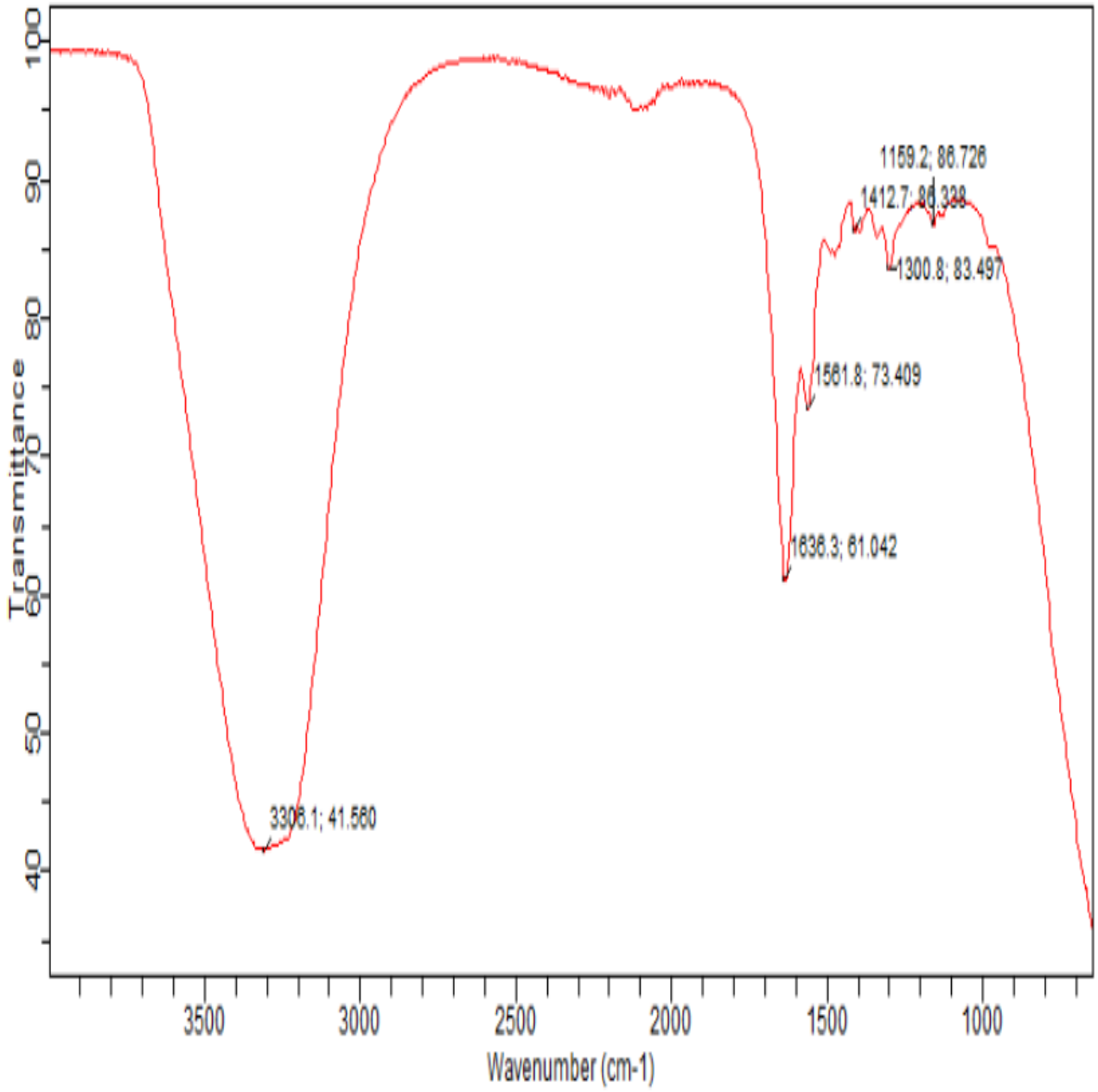


Figure 4.16: FTIR spectrum of the product of reaction of Fe_2O^{4+}/TU

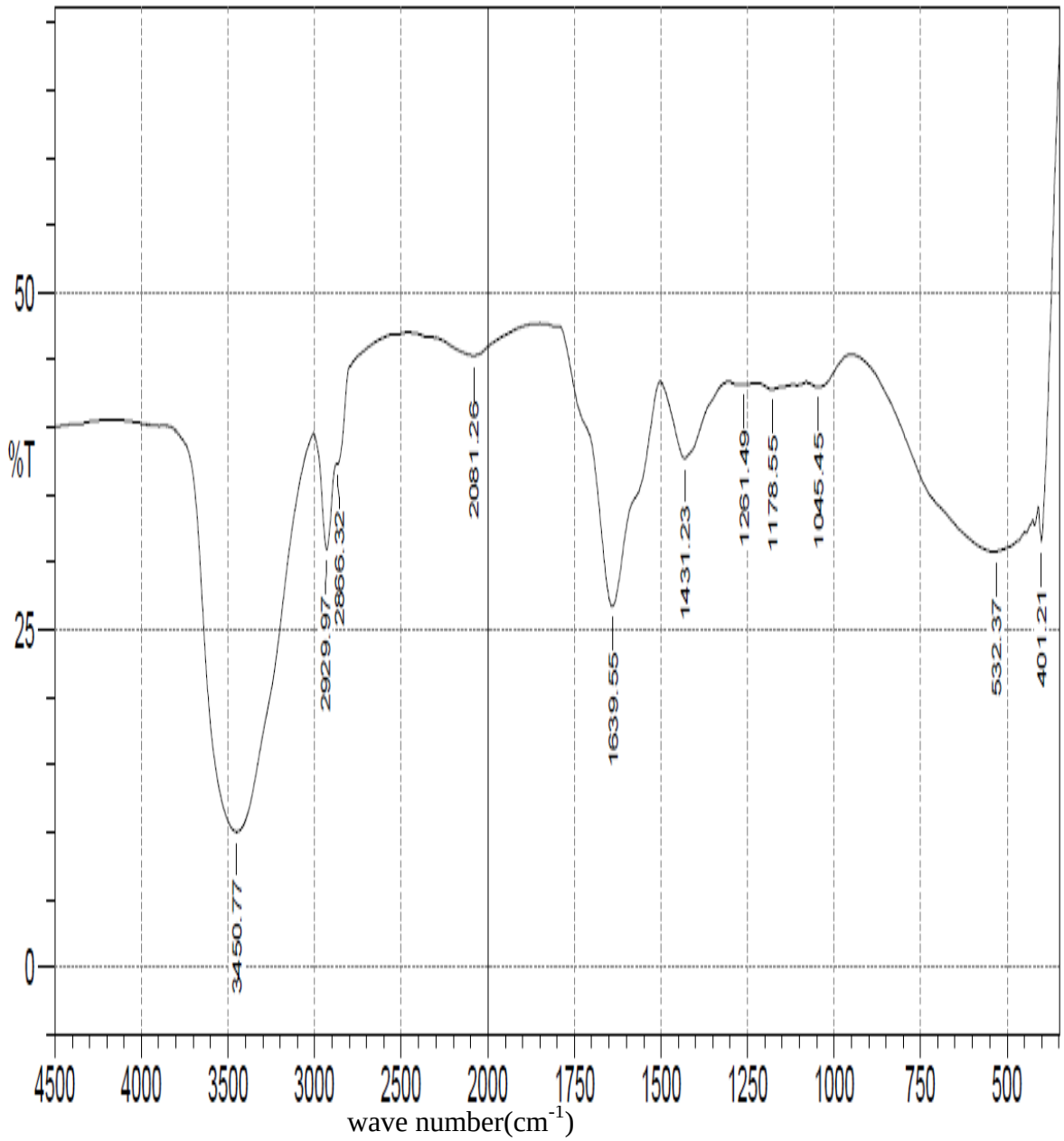


Figure 4.17 : FTIR spectrum of the product of reaction of Fe_2O^{4+}/MTU

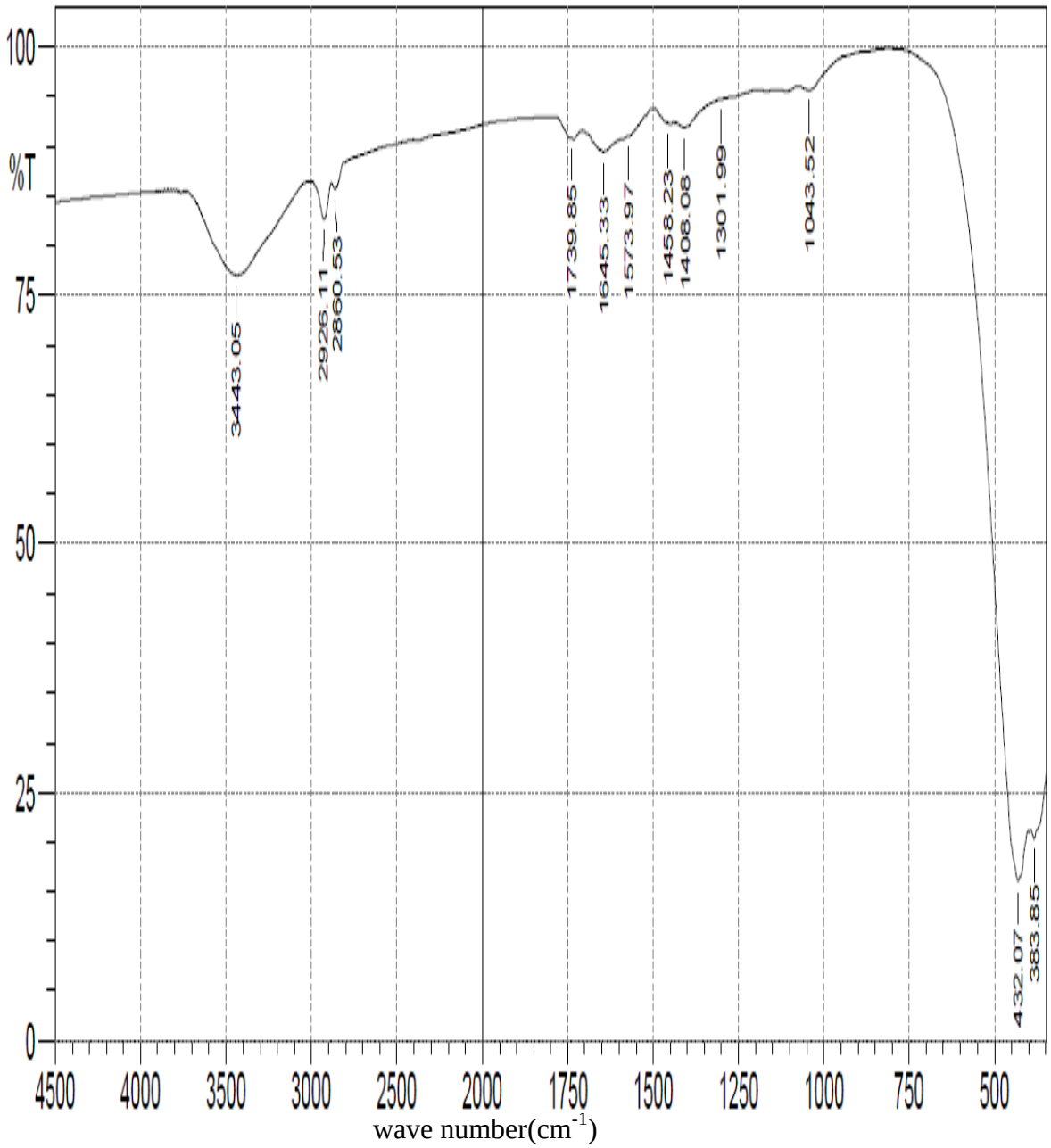


Figure 4.18 : FTIR spectrum of the product of reaction of Fe_2O^{4+}/ATU

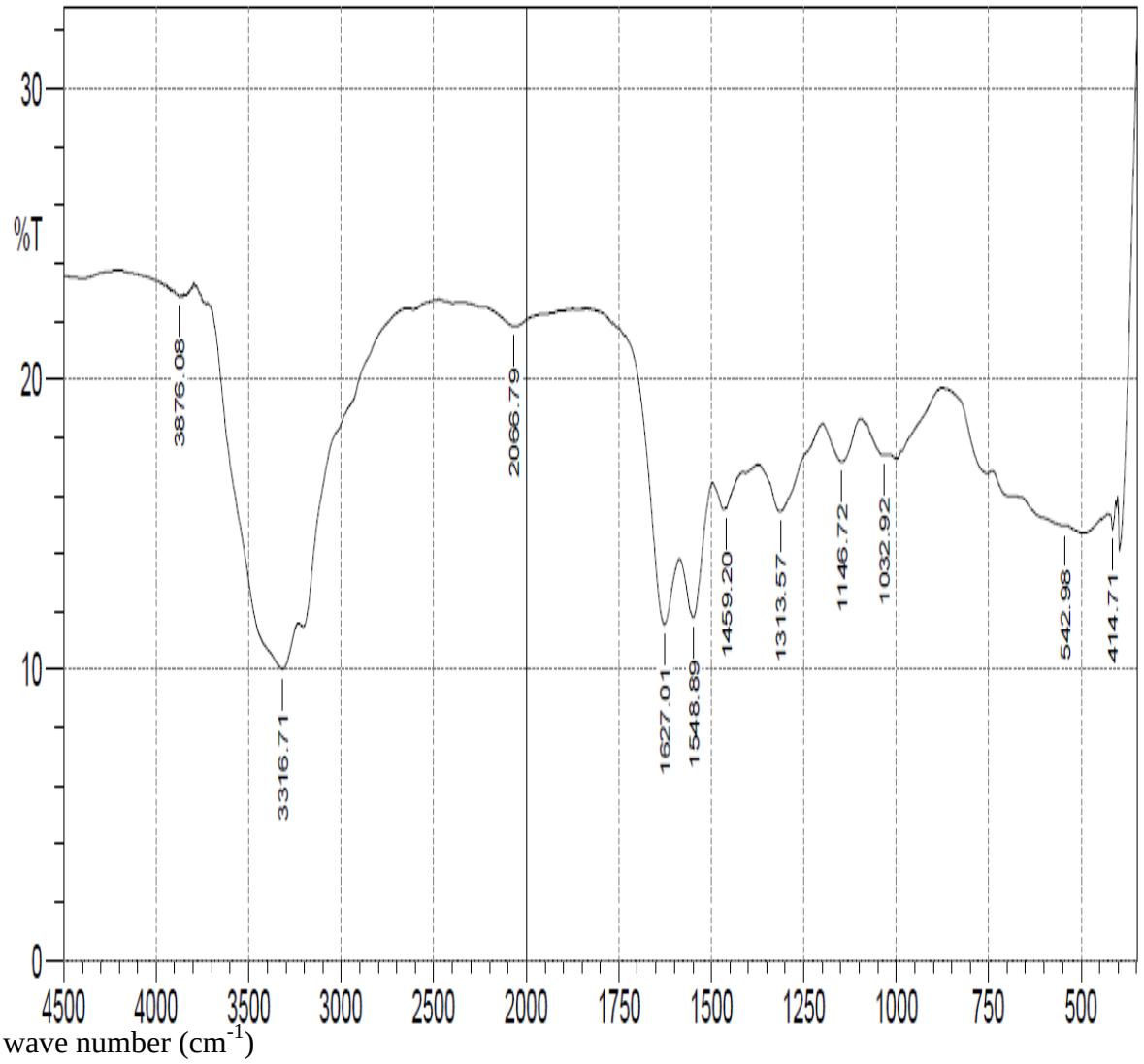


Figure 4.19 : FTIR spectrum of the product of reaction of Fe_2O^{4+}/DMTU

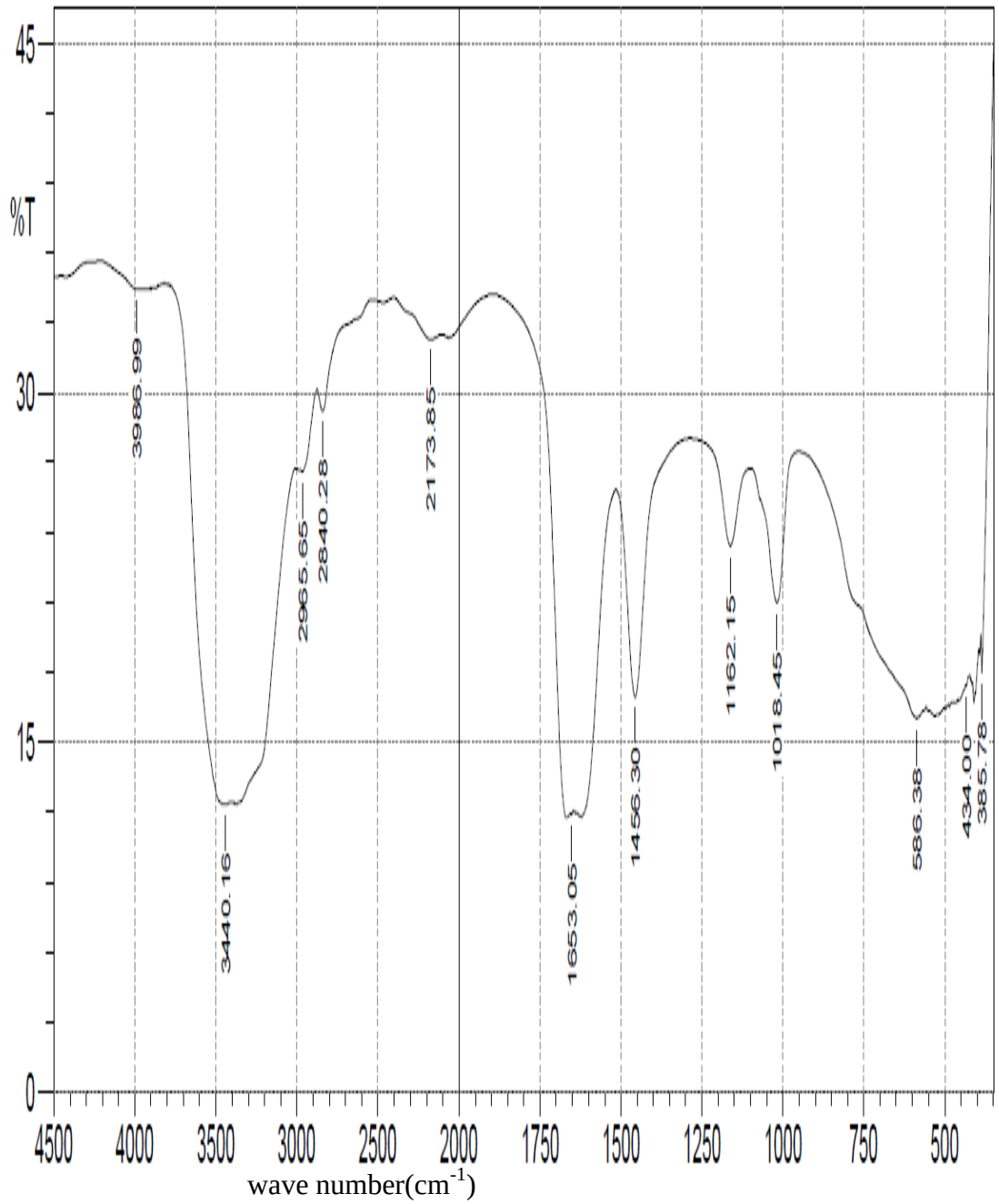


Figure 4.20: FTIR spectrum of the product of reaction of Fe_2O^{4+}/DETU

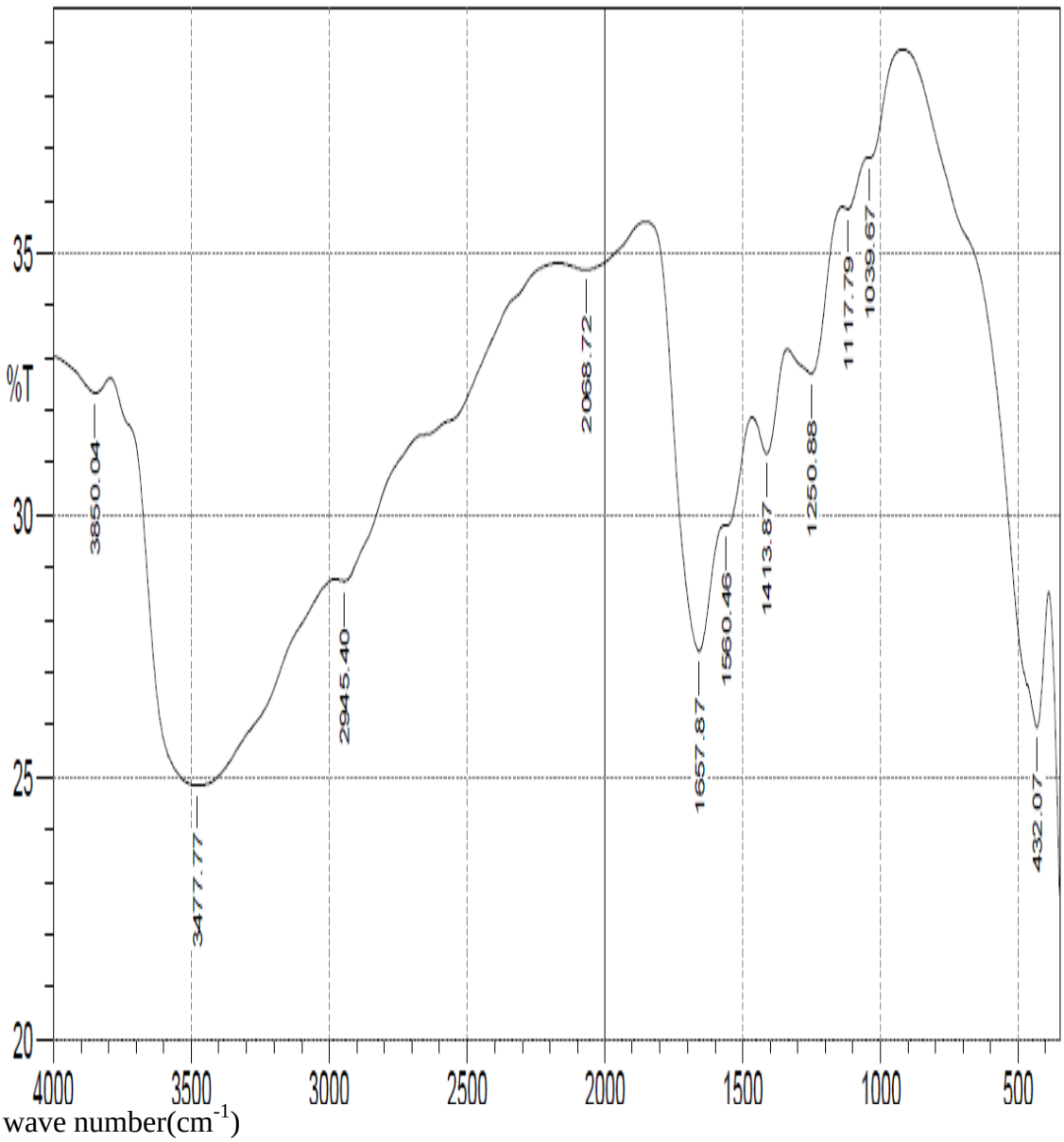


Figure 4.21 : FTIR spectrum of GSH

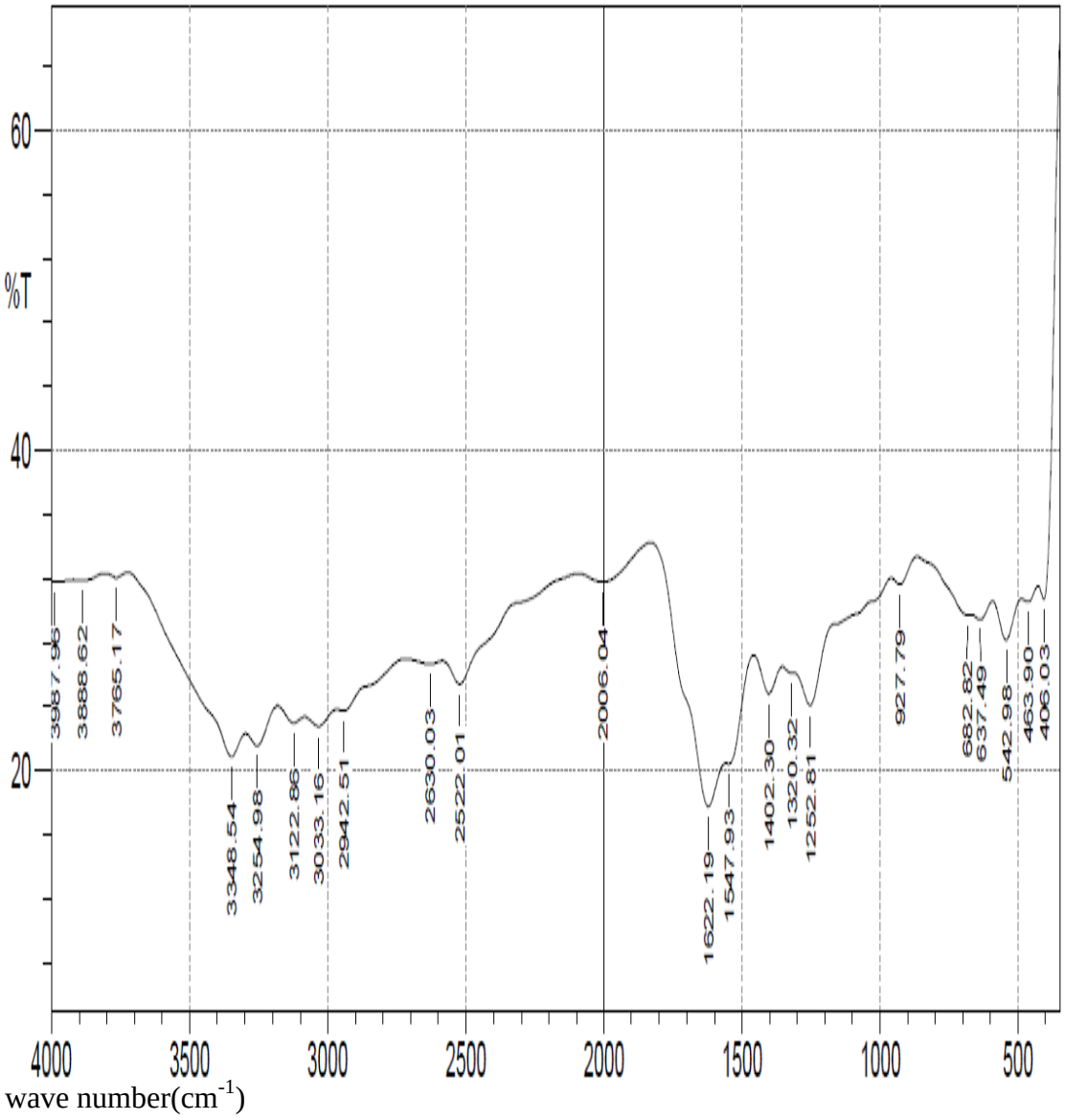


Figure 4.22 : FTIR spectrum of the product of reaction of Fe_2O^{4+}/GSH

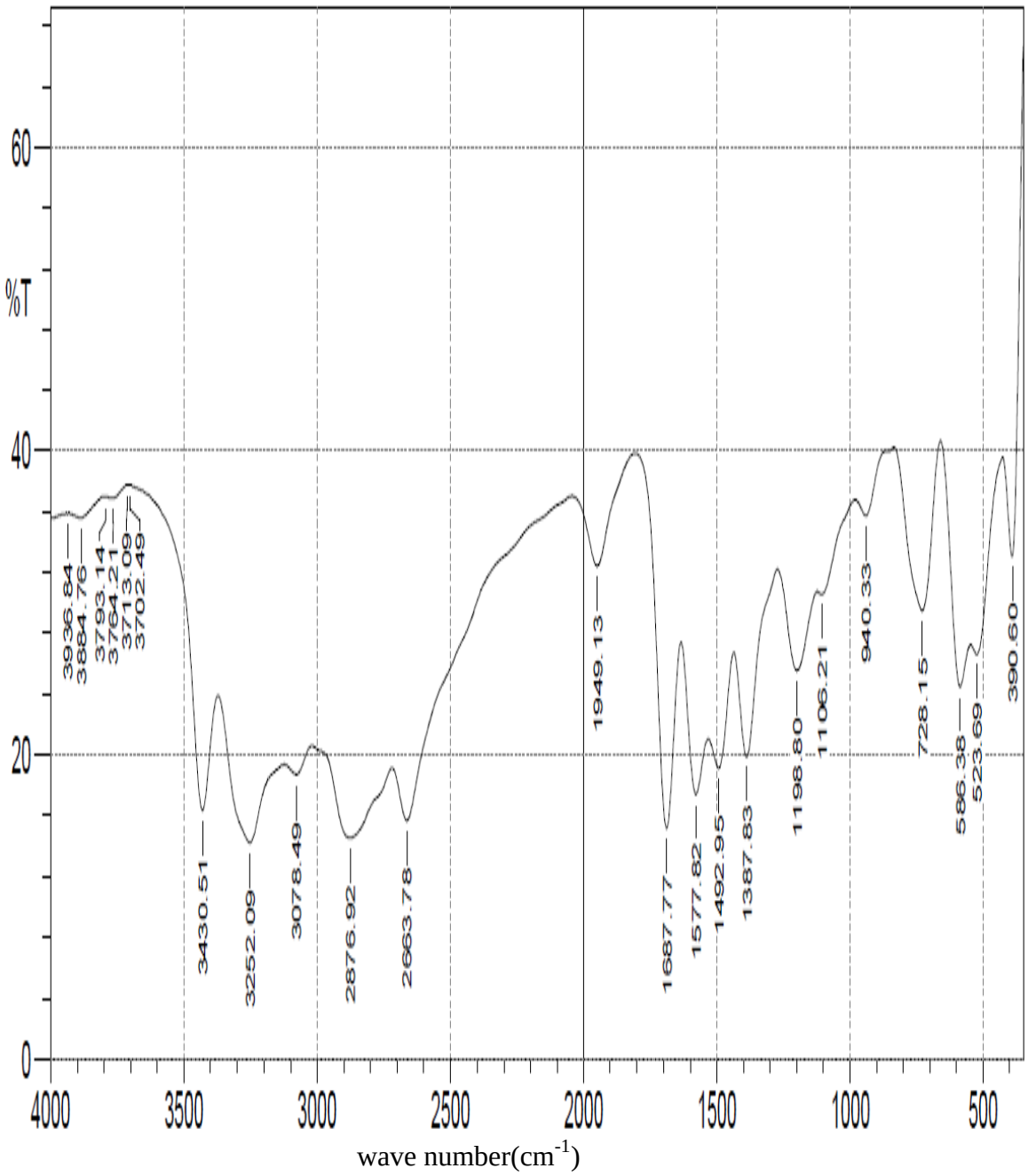


Figure 4.23 : FTIR spectrum of EH_2

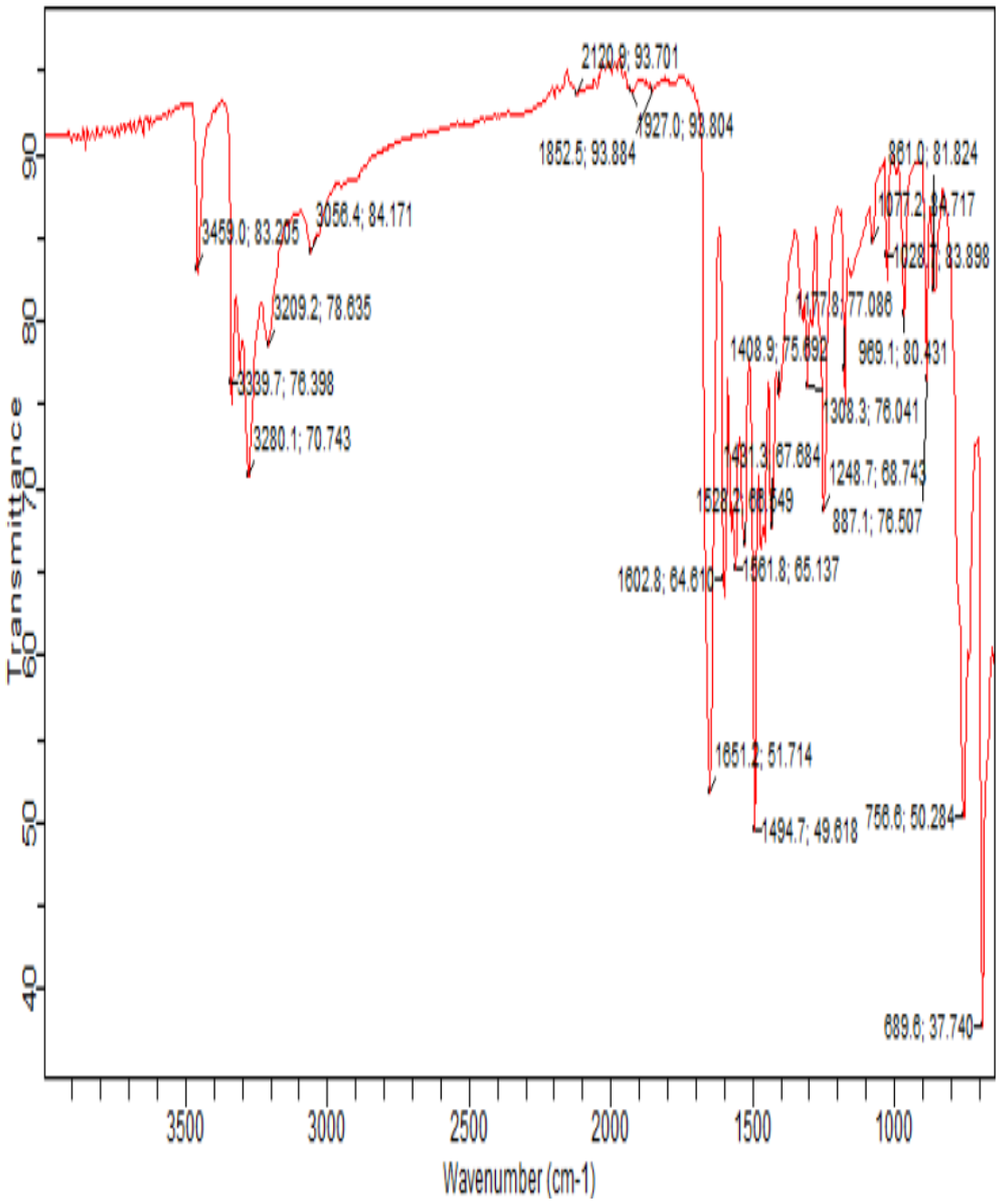


Figure 4.24 : FTIR spectrum of the of DH_2

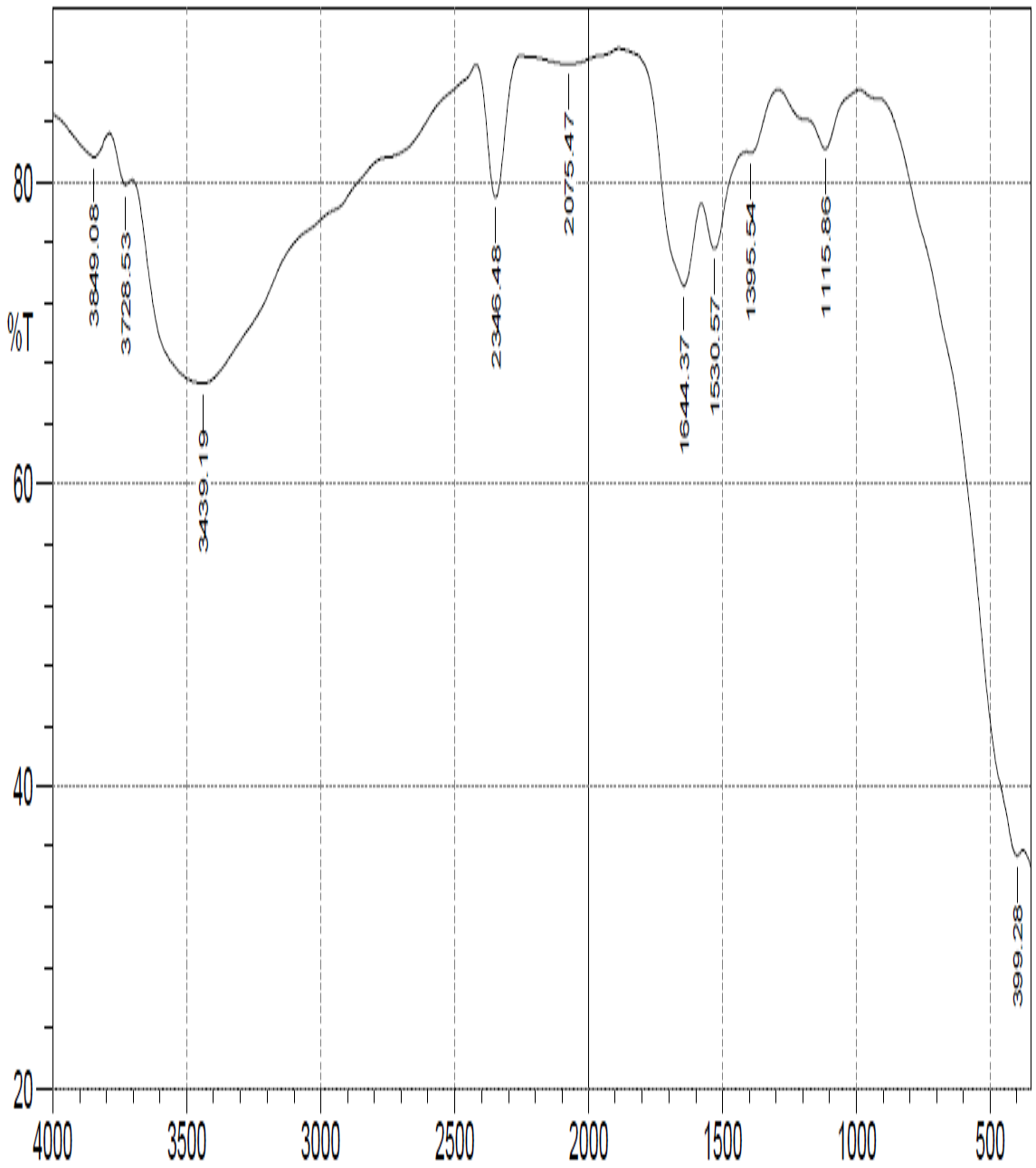


Figure 4.25: FTIR spectrum of the product of reaction of Fe_2O^{4+}/EH_2

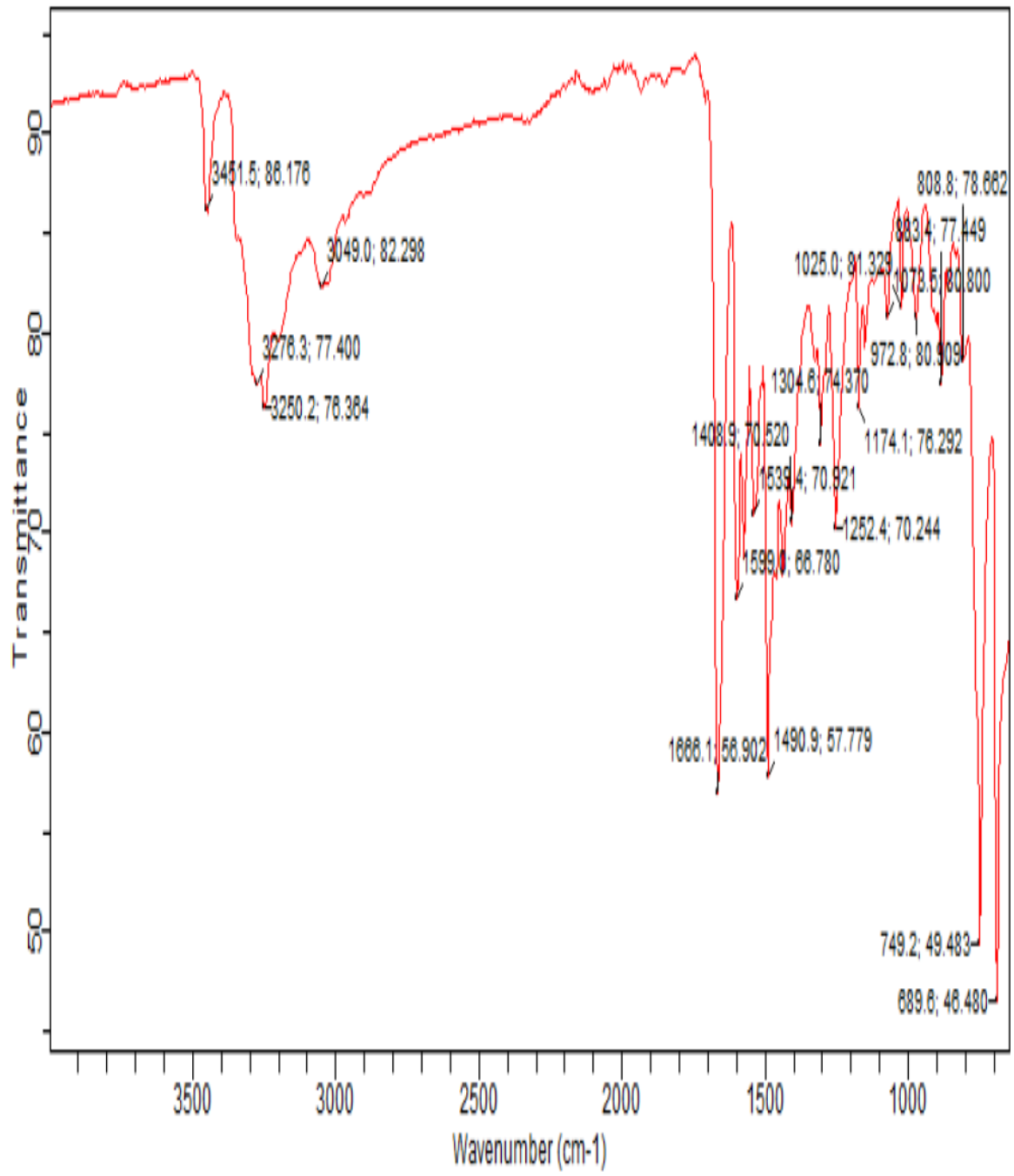


Figure 4.26: FTIR spectrum of the product of reaction of Fe_2O^{4+}/DH_2

4.3 Determination of Pseudo-first Order and Second Order Rate Constants and Order of Reaction

4.3.1 Fe_2O^{4+} reaction with thiourea and thiourea derivatives (*N*-methylthiourea, *N,N'*-dimethylthiourea and *N*-allylthiourea)

Pseudo-first order plots of log (A_∞-A_t) versus time (where A_t and A_∞ are absorbances at time't' and at infinity, respectively) were linear to more than 80% extent of reaction. This suggests first order dependence of rate on [Fe_2O^{4+}] for all the systems. Typical pseudo – first order plots for the reactions of the oxo- bridged iron(III) complex and the thioureas are presented as Figures 4.27- 4.31. The slopes of the plots gave the pseudo-first order rate constants, k_{obs}. The values of k_{obs} for each of the systems are presented in Tables 4.1 – 4.5. The second order rate constants, k_2, were determined as the ratio of k_{obs} to [reductants], and were found to be fairly constant (Tables 4.1 – 4.5). The second order rate constants for the five systems were found to be (2.58 ± 0.02) × 10^{-2} (Fe_2O^{4+}/ TU); (27.99 ± 0.03) × 10^{-2} (Fe_2O^{4+} / MTU); (6.25 ± 0.02) × 10^{-2} (Fe_2O^{4+} / ATU); (36.3 ± 0.03) × 10^{-2} (Fe_2O^{4+}/ DMTU) and (2.76 ± 0.05) × 10^{-2} (Fe_2O^{4+} / DETU) dm^3 mol^{-1} s^{-1}. Order of reaction with respect to [TU], [MTU], [ATU] , [DMTU] and [DETU] as obtained from the slopes of the plots of log k_{obs} versus log [reductant] at constant [H^+] and constant ionic strength were found to be 1.01 (TU), 1.0 (MTU), 0.98 (ATU),1.04 (DMTU) and 1.03(DETU), indicating first order dependence of the rates of reaction on [TU], [MTU], [ATU], [DMTU] and [DETU] (Figures 4.32 – 4.36) .

The rate law at constant [H^+] for the reaction of Fe_2O^{4+} and the thioureas can be represented as equation 4.10

$$\frac{d}{dt}[Fe_2O^{4+}] = k_2[Fe_2O^{4+}][\text{reductant}] \qquad (4.10)$$

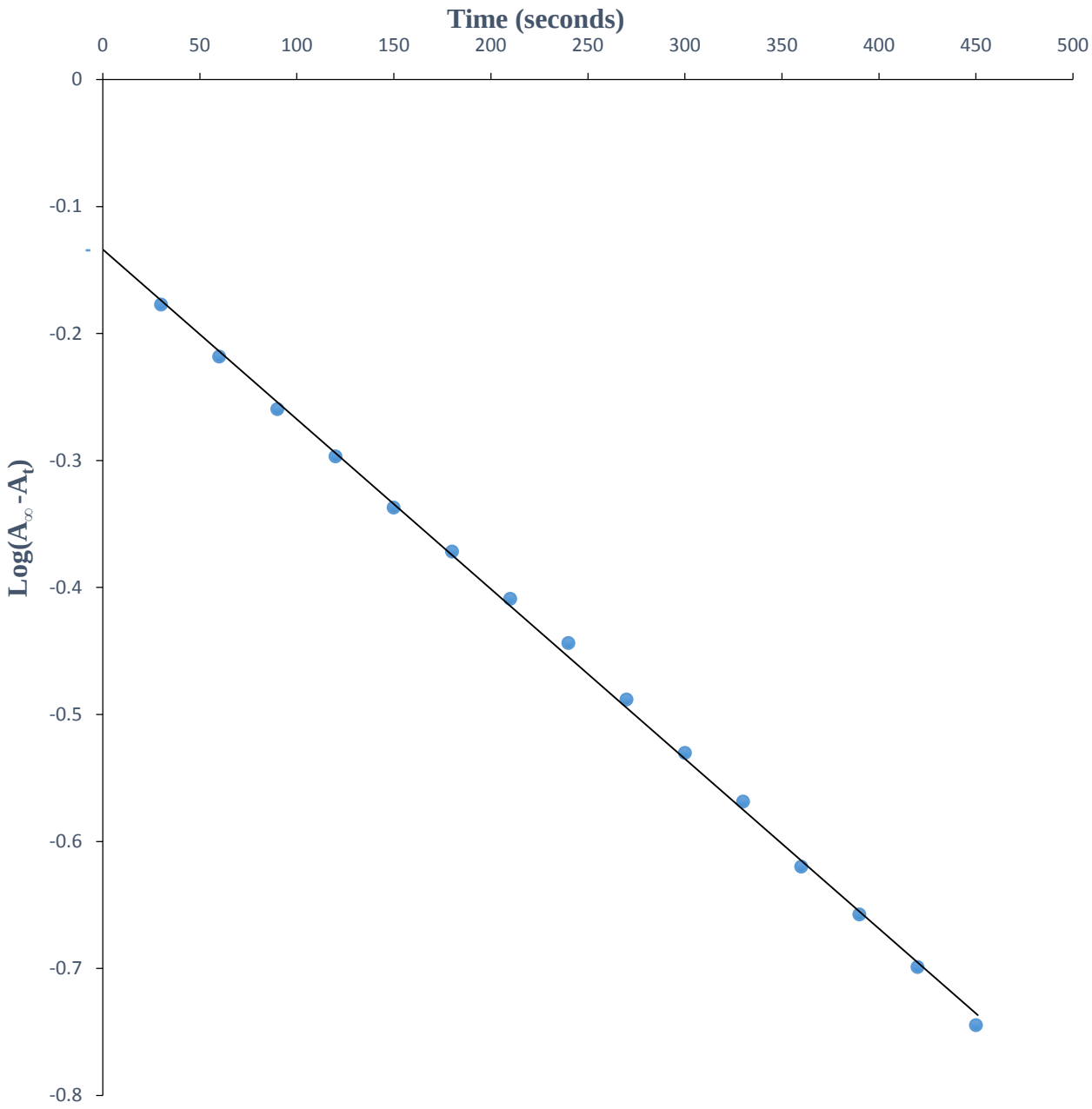


Figure 4.27: Typical pseudo-first order plot for the redox reaction of Fe_2O^{4+} with TU at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[TU] = 4.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm

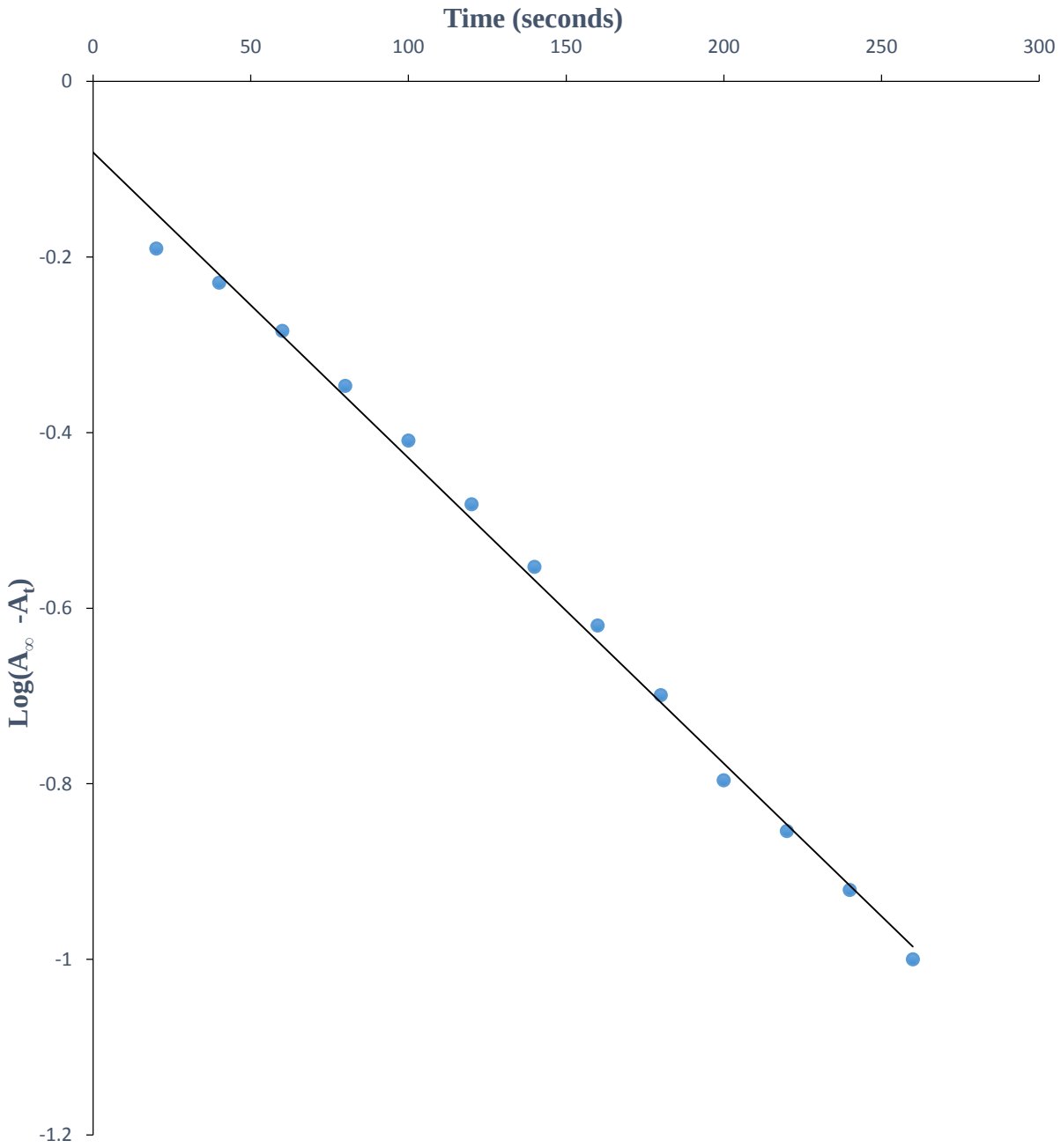


Figure 4.28: Typical pseudo-first order plot for the redox reaction of Fe_2O^{4+} with ATU at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[ATU] = 5.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm

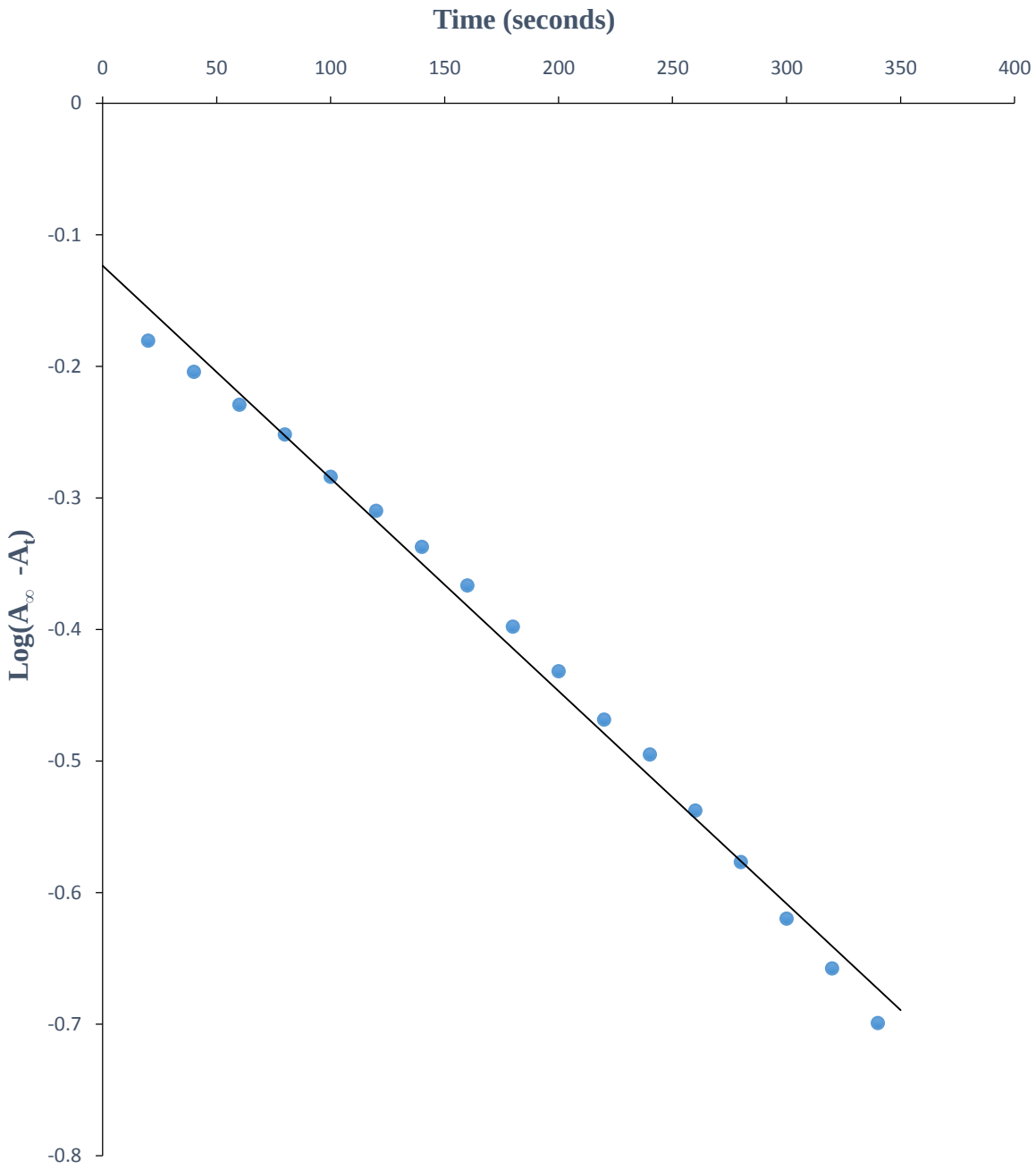


Figure 4.29: Typical Pseudo-first order plot for the redox reaction of $Fe_2O^{4+}$with MTU at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[MTU] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm

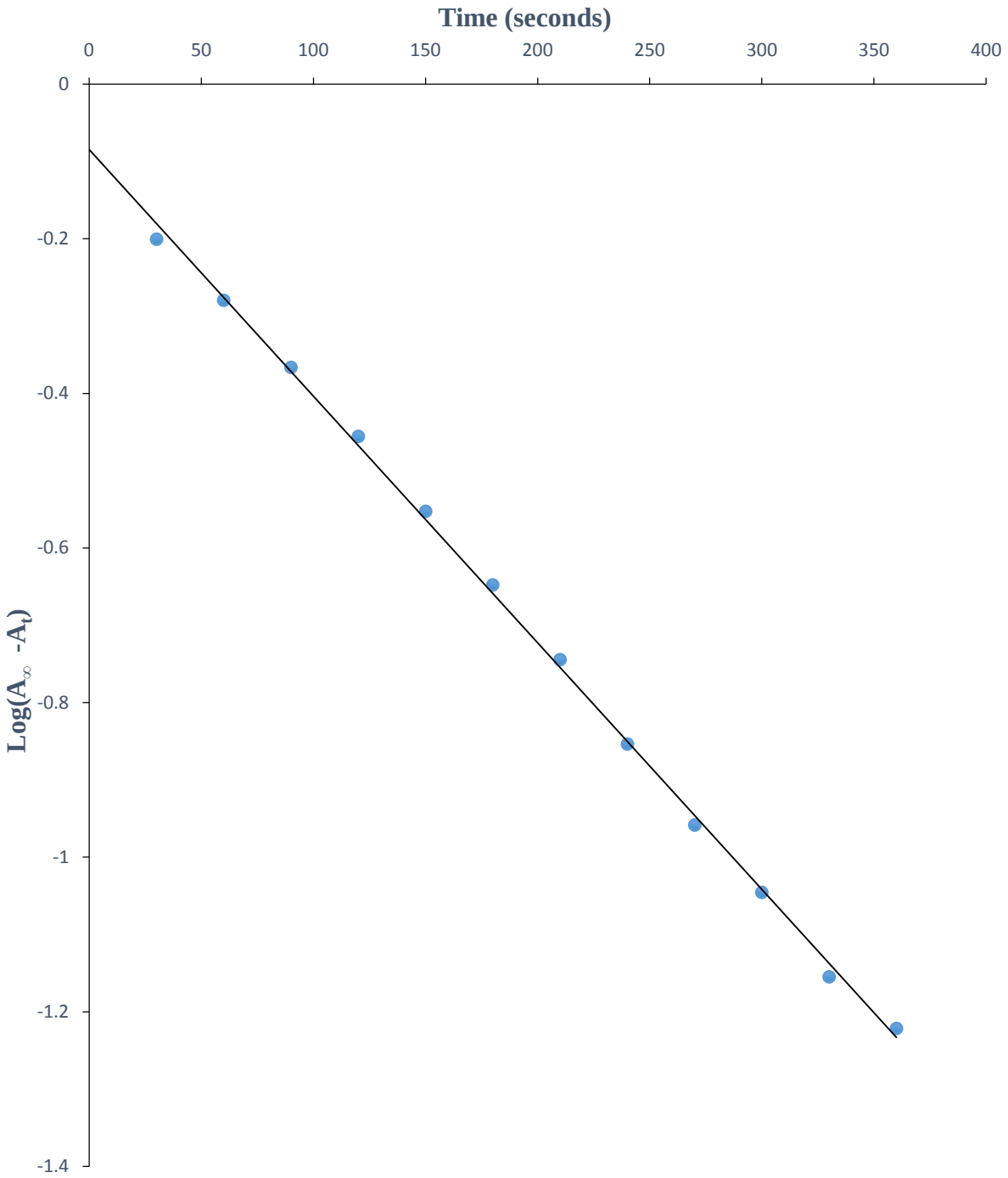


Figure 4.30: Typical Pseudo-first order plot for the redox reaction of $Fe_2O^{4+}$with DMTU at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, [DMTU] = 8.0×10^{-3} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C andλ_{max} = 520 nm

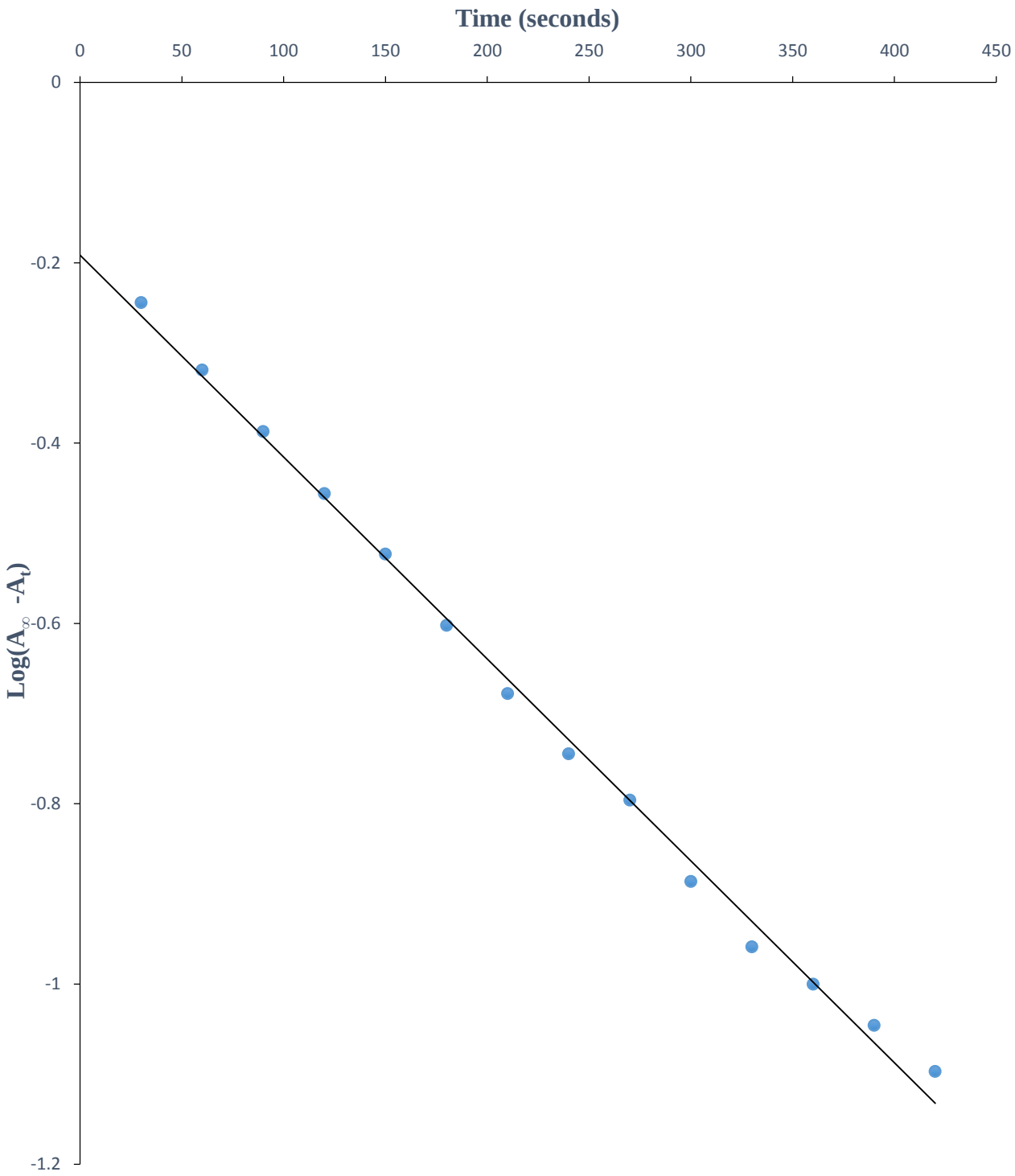


Figure 4.31: Typical Pseudo-first order plot for the redox reaction of $Fe_2O^{4+}$with DETU at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, [DETU] = 8.0×10^{-3} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 30.0 ± 1.0°C and λ_{max} = 520 nm

Table 4.1 : Pseudo-first and second order rate constants for the redox reaction of TU by Fe_2O^{4+} in aqueous HCl medium, T =27.0 ±1.0°C I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}]= 2 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520nm

10^2[TU] (mol dm^{-3})	$10^3[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3}	10^3 k_{obs} (s^{-1})	10^2k_2 ($dm^3mol^{-1}s^{-1}$)
2.4	1.0	3.0	6.09	2.53
4.0	1.0	3.0	10.02	2.51
5.0	1.0	3.0	12.87	2.57
6.0	1.0	3.0	16.14	2.69
7.0	1.0	3.0	18.02	2.60
8.0	1.0	3.0	20.58	2.57
12.0	1.0	3.0	30.67	2.56
5.0	0.4	3.0	12.70	2.54
5.0	0.6	3.0	12.65	2.53
5.0	0.8	3.0	12.58	2.52
5.0	1.0	3.0	12.62	2.53
5.0	1.2	3.0	12.57	2.52
5.0	1.4	3.0	12.76	2.55
5.0	1.0	1.0	12.00	2.40
5.0	1.0	2.0	12.98	2.59
5.0	1.0	3.0	13.00	2.60
5.0	1.0	4.0	13.68	2.73
5.0	1.0	5.0	12.74	2.55
5.0	1.0	6.0	12.71	2.54

Table 4.2: Pseudo-first and second order rate constants for the redox reaction of MTU by Fe_2O^{4+} in aqueous HCl medium, T = 27.0 ±1.0°C, I = 0.30 mol dm^{-3}(NaCl), $[Fe_2O^{4+}]= 2 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520nm

10^3[MTU] (mol dm^{-3})	$10^3[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	k_2 ($dm^3mol^{-1}s^{-1}$)
2.0	1.0	3.0	5.58	0.279
3.0	1.0	3.0	8.37	0.279
4.0	1.0	3.0	11.20	0.280
5.0	1.0	3.0	14.00	0.280
6.0	1.0	3.0	16.70	0.278
7.0	1.0	3.0	19.40	0.277
8.0	1.0	3.0	22.90	0.286
5.0	0.4	3.0	14.20	0.284
5.0	0.6	3.0	14.30	0.286
5.0	0.8	3.0	14.50	0.290
5.0	1.0	3.0	14.30	0.286
5.0	1.2	3.0	14.30	0.286
5.0	1.4	3.0	13.00	0.260
5.0	1.0	1.0	14.30	0.286
5.0	1.0	2.0	13.70	0.274
5.0	1.0	3.0	14.10	0.282
5.0	1.0	4.0	14.10	0.282
5.0	1.0	5.0	13.40	0.268
5.0	1.0	6.0	13.70	0.274

Table 4.3: Pseudo-first and second order rate constants for the redox reaction of ATU by Fe_2O^{4+} in aqueous HCl medium, T = 27.0 ±1.0°C, I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}]= 2 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520nm

10^3[ATU] (mol dm^{-3})	$10^3[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^2k_2 ($dm^3mol^{-1}s^{-1}$)
2.0	1.0	3.0	12.50	6.25
3.0	1.0	3.0	18.90	6.30
4.0	1.0	3.0	24.90	6.22
5.0	1.0	3.0	30.80	6.16
6.0	1.0	3.0	37.30	6.22
7.0	1.0	3.0	44.20	6.31
8.0	1.0	3.0	50.20	6.28
5.0	0.4	3.0	31.70	6.34
5.0	0.6	3.0	30.50	6.10
5.0	0.8	3.0	30.90	6.18
5.0	1.0	3.0	31.20	6.24
5.0	1.2	3.0	31.10	6.22
5.0	1.4	3.0	30.70	6.14
5.0	1.0	1.0	29.90	5.98
5.0	1.0	2.0	30.70	6.14
5.0	1.0	3.0	30.20	6.04
5.0	1.0	4.0	31.00	6.20
5.0	1.0	5.0	30.30	6.06
5.0	1.0	6.0	29.80	5.96

Table 4.4 : Pseudo-first and second order rate constants for the redox reaction of DMTU by Fe_2O^{4+} in aqueous HCl medium, T =27.0 ±1.0°C, I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}]= 2 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520nm

10^3[DMTU] (mol dm^{-3})	$10^3[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	k_2 ($dm^3mol^{-1}s^{-1}$)
4.0	1.0	3.0	14.52	0.363
6.0	1.0	3.0	21.50	0.359
8.0	1.0	3.0	29.20	0.366
10.0	1.0	3.0	35.00	0.350
12.0	1.0	3.0	44.60	0.372
14.0	1.0	3.0	50.40	0.360
16.0	1.0	3.0	59.20	0.370
8.0	0.4	3.0	28.80	0.360
8.0	0.6	3.0	28.70	0.359
8.0	0.8	3.0	29.40	0.368
8.0	1.0	3.0	28.90	0.361
8.0	1.2	3.0	29.10	0.364
8.0	1.4	3.0	28.50	0.356
8.0	1.0	1.0	27.30	0.341
8.0	1.0	2.0	28.70	0.359
8.0	1.0	3.0	29.30	0.366
8.0	1.0	4.0	28.70	0.359
8.0	1.0	5.0	27.90	0.349
8.0	1.0	6.0	29.40	0.367

Table 4.5 : Pseudo-first and second order rate constants for the redox reaction of DETU by Fe_2O^{4+} in aqueous HCl medium, λ_{max} = 520nm, T = 30.0 ±1°C, I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}] = 2 \times 10^{-4}$ mol dm^{-3}

10^3[DETU] (mol dm^{-3})	$10^3[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^4 k_{obs} (s^{-1})	10^2k_2 ($dm^3mol^{-1}s^{-1}$)
30	1.0	3.0	7.75	2.58
40	1.0	3.0	11.30	2.83
50	1.0	3.0	14.50	2.90
60	1.0	3.0	15.70	2.62
70	1.0	3.0	19.60	2.80
80	1.0	3.0	23.20	2.90
90	1.0	3.0	24.50	2.72
80	0.4	3.0	21.30	2.66
80	0.6	3.0	21.70	2.71
80	0.8	3.0	23.00	2.88
80	1.0	3.0	23.30	2.91
80	1.2	3.0	22.50	2.81
80	1.4	3.0	24.00	3.00
80	1.0	1.0	21.90	2.62
80	1.0	2.0	23.10	2.88
80	1.0	3.0	23.20	2.90
80	1.0	4.0	23.10	2.89
80	1.0	5.0	23.20	2.90
80	1.0	6.0	23.30	2.91

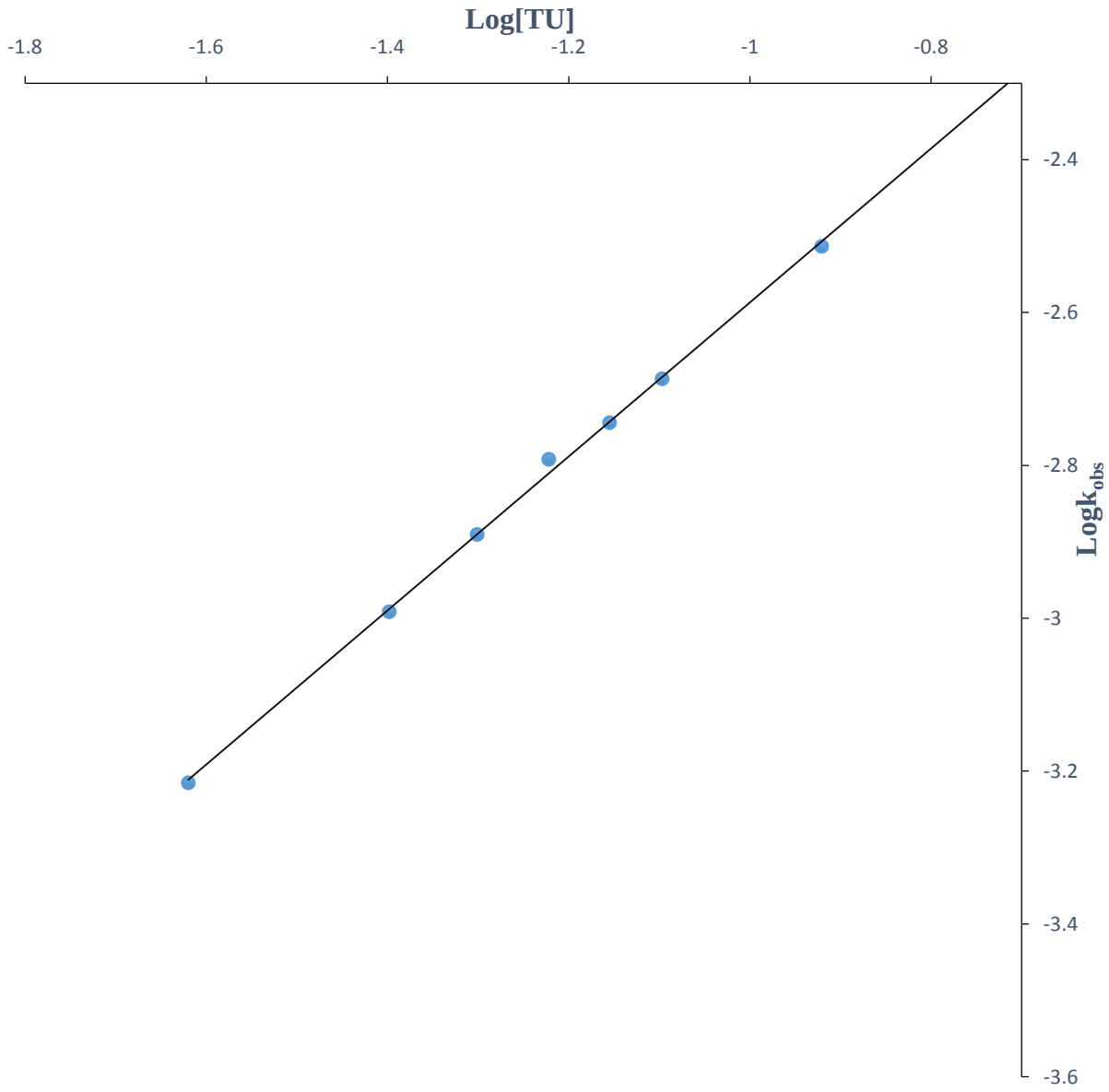


Figure 4.32: Plot of log k_{obs} versus log [TU] for the redox reaction of Fe_2O^{4+} with TU at $[Fe_2O^{4+}]$ = 2×10^{-4} mol dm^{-3}, [TU] = $(2.4 – 12.0) \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3mol dm^{-3} (NaCl), T = 27.0 ± 1.0^oC and λ_{max} = 520 nm

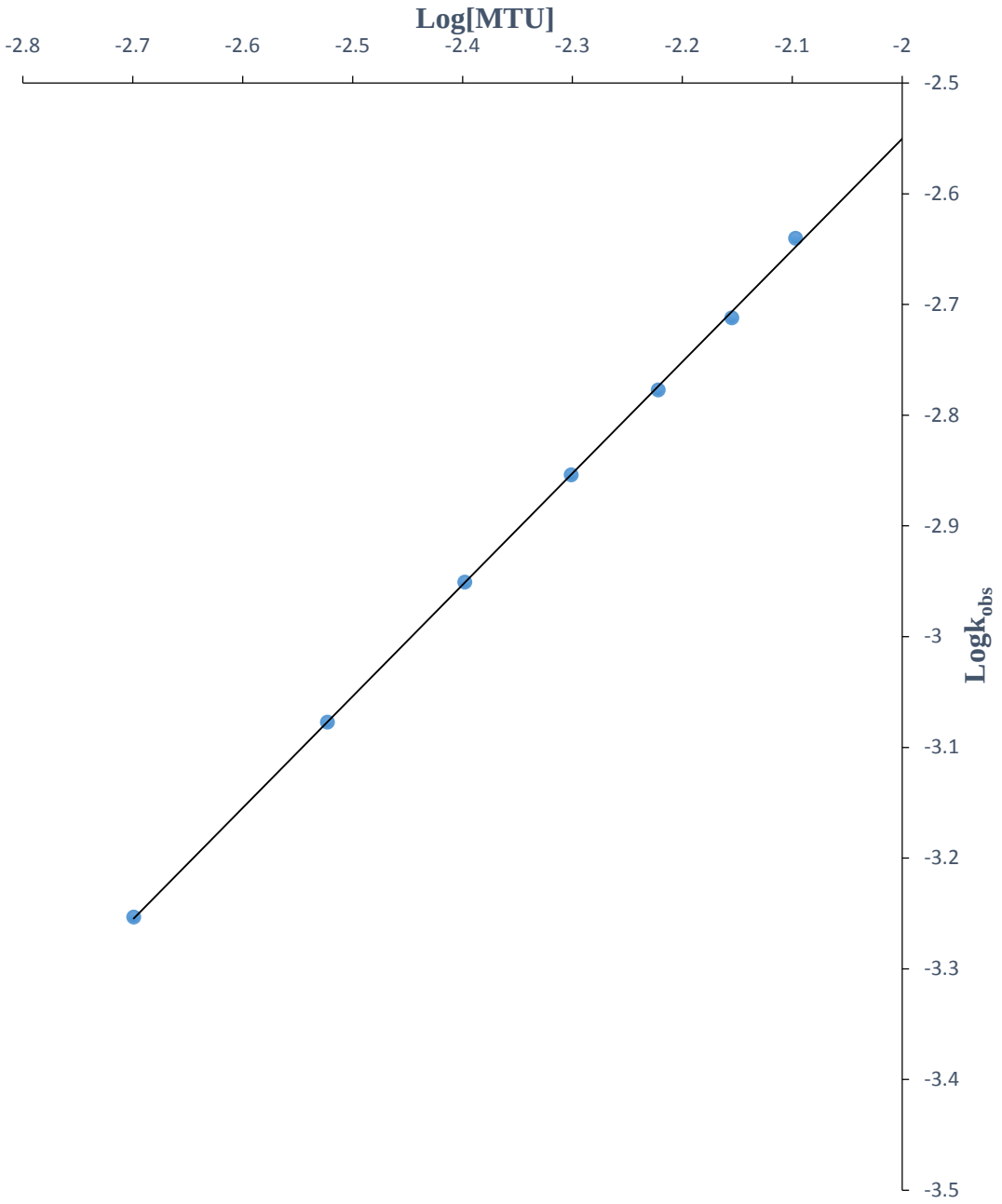


Figure 4.33: Plot of log k_{obs} versus log [MTU] for the redox reaction of $Fe_2O^{4+}$with MTU at $[Fe_2O^{4+}] = 2 \times 10^{-4}$ mol dm^{-3}, [MTU] = (2.0 – 8.0) × 10^{-3} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0^{o}C and λ_{max} = 520 nm

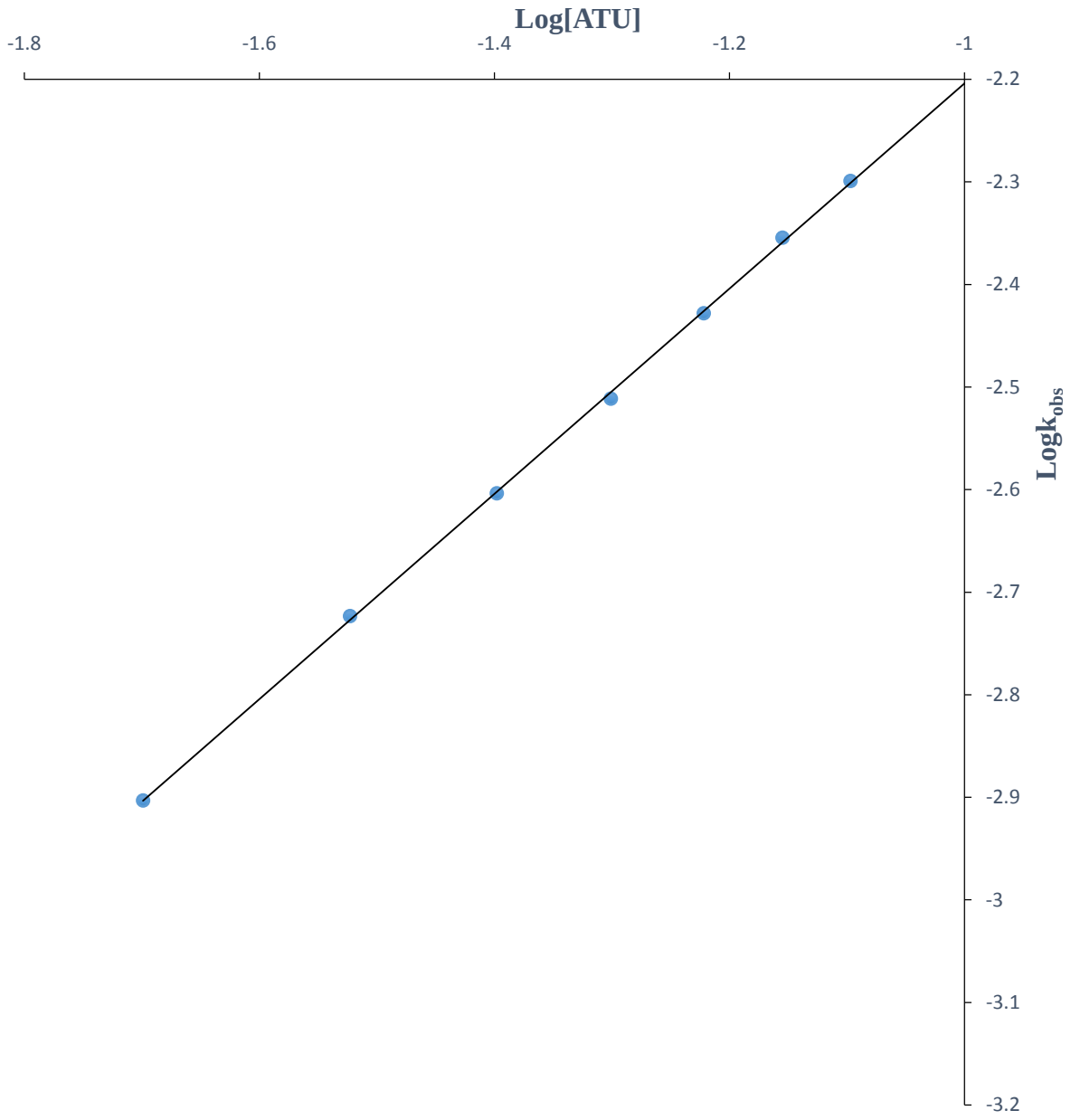


Figure 4.34: Plot of log k_{obs} versus log [ATU] for the redox reaction of $Fe_2O^{4+}$with ATU at $[Fe_2O^{4+}] = 2 \times 10^{-4}$ mol dm^{-3}, [ATU] = (2.0 – 8.0) × 10^{-2} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0^{o}C and λ_{max} = 520 nm

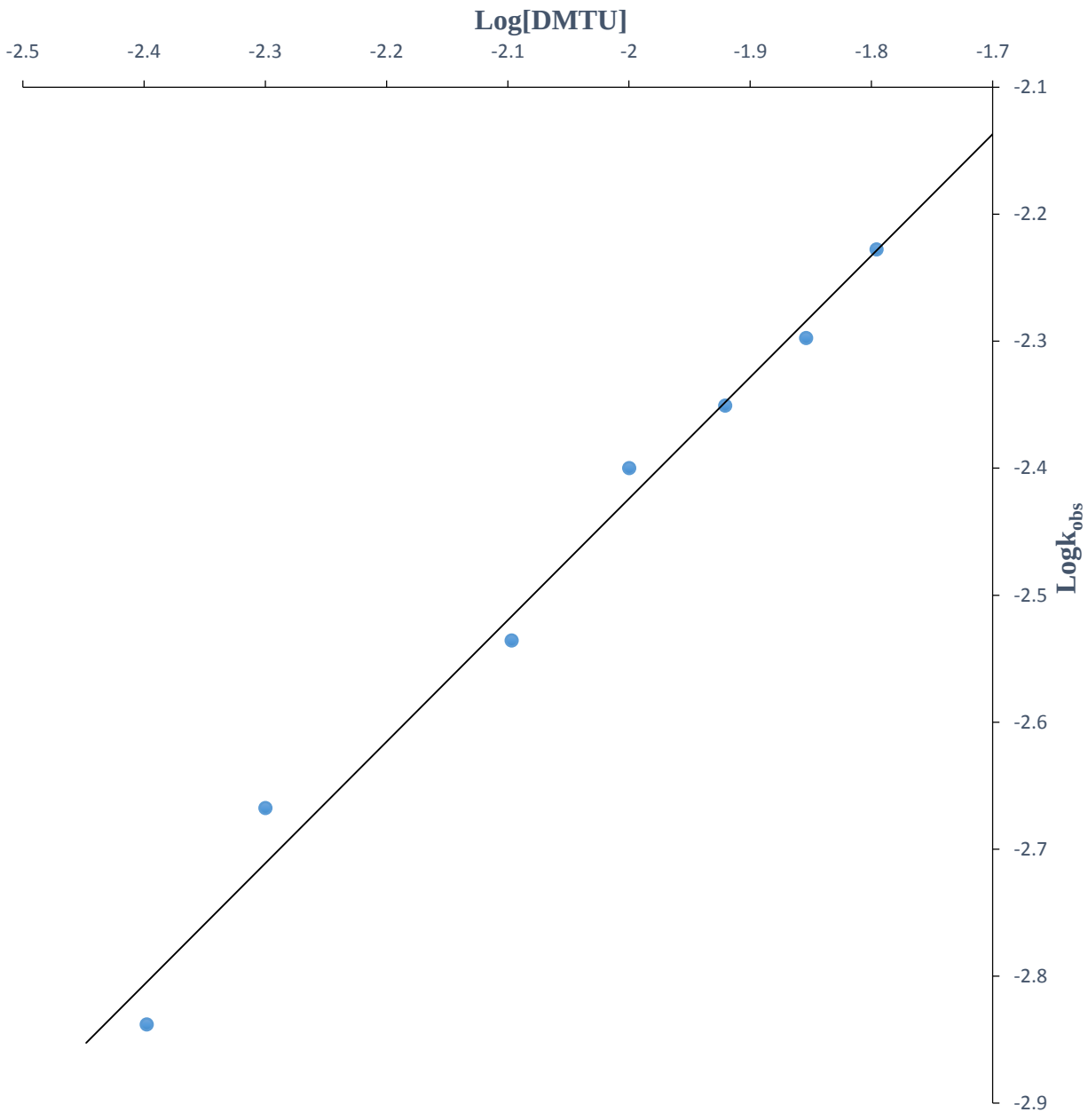


Figure 4.35: Plot of log k_{obs} versus log [DMTU] for the redox reaction of $Fe_2O^{4+}$with DMTU at $[Fe_2O^{4+}] = 2 \times 10^{-4}$ mol dm^{-3}, [DMTU] = (4.0 – 16.0) × 10^{-3} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0^{o}C and λ_{max} = 520 nm

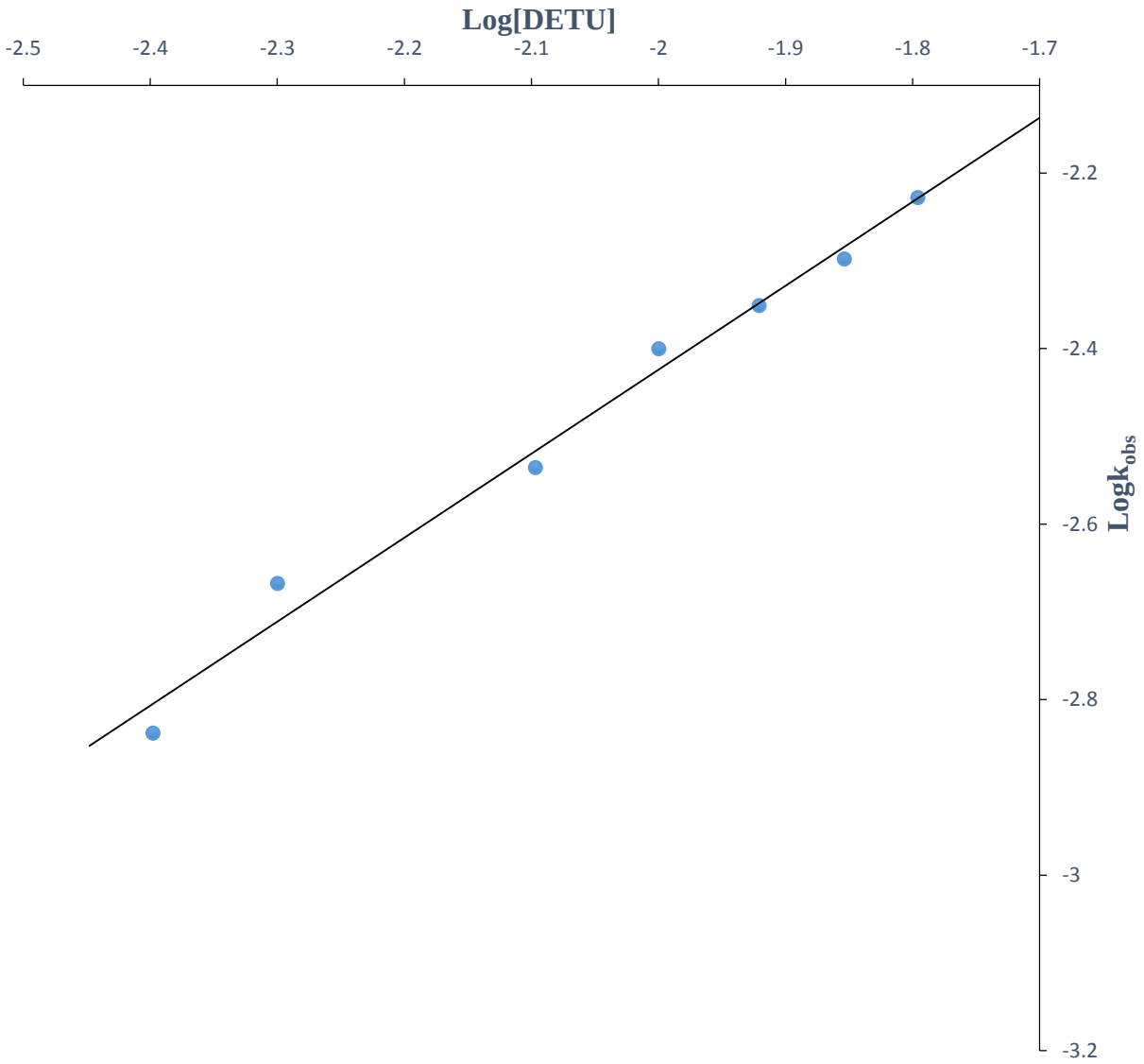


Figure 4.36: Plot of log k_{obs} versus log [DETU] for the redox reaction of $Fe_2O^{4+}$with DETU at $[Fe_2O^{4+}] = 2 \times 10^{-4}$ mol dm^{-3}, [DETU] = $(3.0 – 9.0) \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^3$mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 30.0 ± 1.0^{o}C and λ_{max} = 520 nm

where the reductants are thiourea (TU), *N*-methylthiourea (MTU), *N*-allylthiourea (ATU), *N*, *N*□-dimethylthiourea (DMTU) and *N*,*N*□ - diethyl thiourea. The values of the second order rate constants, k_2 , in $dm^3\ mol^{-1}\ s^{-1}$ are the same as the ones reported in Tables 4.1 – 4.5.

4.3.2 Fe_2O^{4+} reaction with $S_2O_4^{2-}$, $S_2O_6^{2-}$, EH_2, DH_2 and GSH

Pseudo-first order plots of log (A_∞ - A_t) versus time were linear for over 80% extent of reaction. This suggests that the reaction is first order with respect to [Fe_2O^{4+}] for all the systems above under discussion, typical pseudo – first order plots for the reactions of the oxo- bridged iron(III) complex and the reductants above are presented as Figures 4.37- 4.41. The slopes of the pseudo-first order plots gave the pseudo-first order rate constants, k_{obs}.First order rate constants, k_{obs} were constant over the concentration range studied in all the systems, indicating that the k_{obs} was independent of reductants' concentrations (Tables 4.6- 4.10). This suggest zero order dependence on all the reductants above and that the reaction was first order overall. The first order rate constants for the five systems were found to be (3.11 ± 0.035) × 10^{-3}($Fe_2O^{4+}/S_2O_4^{2-}$), (1.98 ± 0.041) ×10^{-3}($Fe_2O^{4+}/S_2O_6^{2-}$), (1.58 ± 0.015) × 10^{-3}(Fe_2O^{4+}/EH_2), (1.35 ± 0.020) × 10^{-3}(Fe_2O^{4+}/DH_2) and (4.05 ± 0.050) × 10^{-3}(Fe_2O^{4+}/GSH) s^{-1}. At constant [H^+], the experimental rate law can therefore be represented by the equation:

$$\frac{d}{dt}[Fe_2O^{4+}] = k_{obs}\,[Fe_2O^{4+}] \qquad (4.11)$$

4.4 Effect of Changes in Hydrogen Ion Concentration, [H^+], on Rates of Reaction

4.4.1: Fe_2O^{4+} reaction with thiourea and thiourea derivatives (MTU, ATU, DMTU, DETU), $S_2O_4^{2-}$, $S_2O_6^{2-}$, EH_2, DH_2 and GSH

Within the hydrogen ion concentration [H^+] range, $4.0 \times 10^{-4} \leq [H^+] \leq 14.0 \times 10^{-4}$ mol dm^{-3}, kinetic runs were carried out at constant ionic strength, while keeping oxidant and reductant

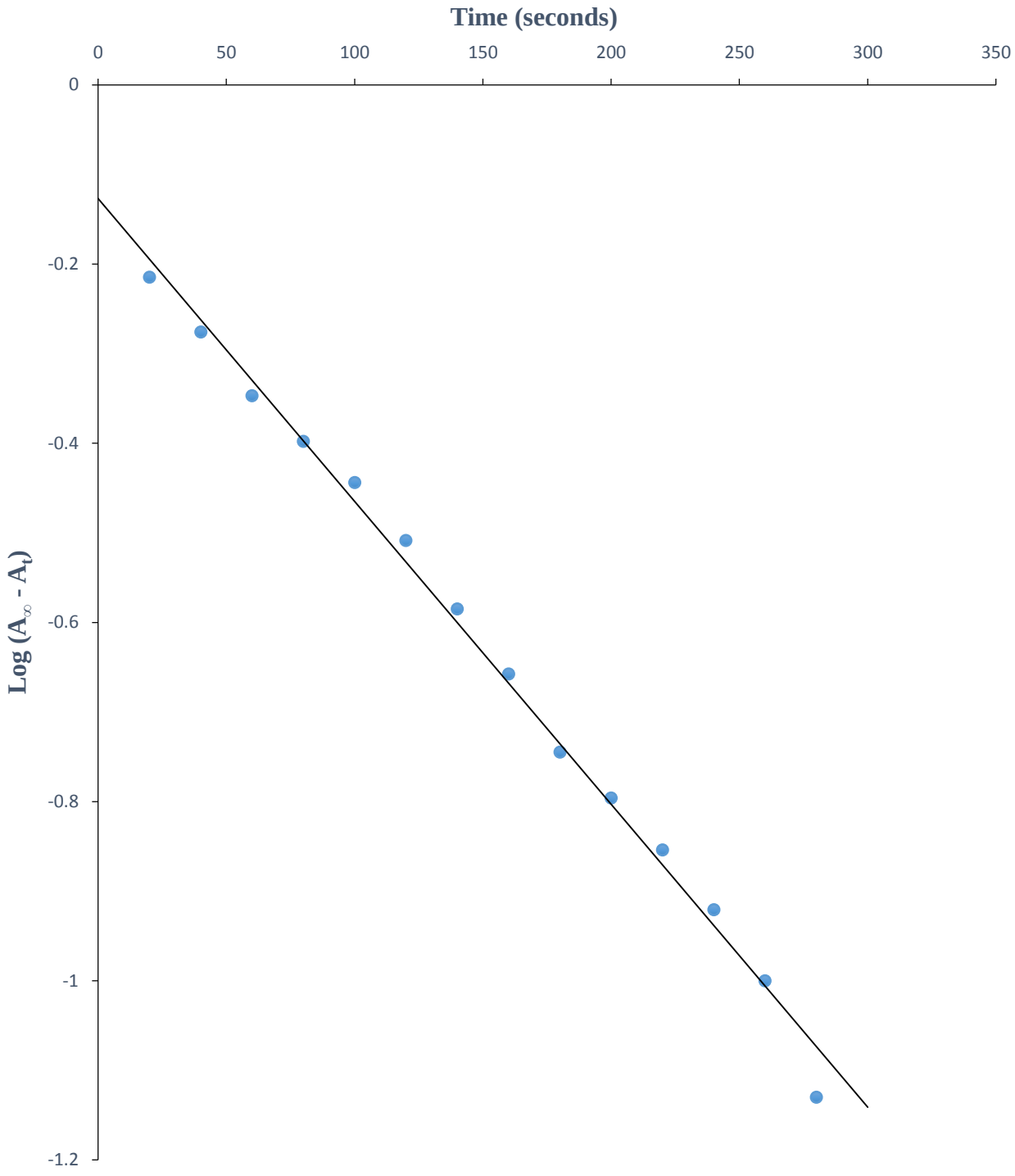


Figure 4.37: Typical pseudo-first order plot for the redox reaction of Fe_2O^{4+} with $S_2O_4^{2-}$ at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[S_2O_4^{2-}] = 7.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 26.0 ± 1.0^{o}C and λ_{max} = 520 nm

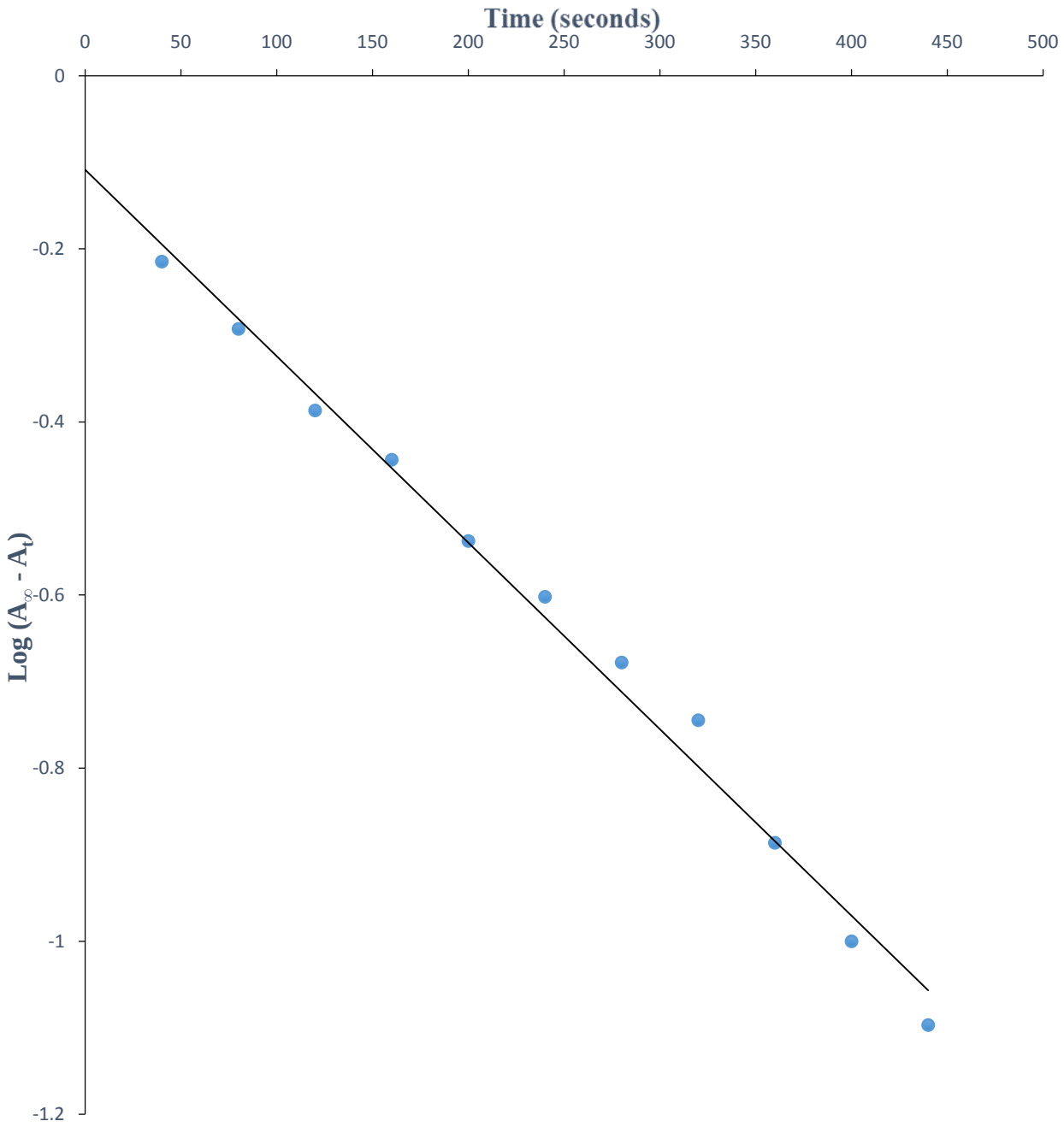


Figure 4.38: Typical pseudo-first order plot for the redox reaction of Fe_2O^{4+} with $S_2O_6^{2-}$ at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[S_2O_6^{2-}] = 14.0 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 26.0 ± 1.0^{o}C and λ_{max} = 520 nm

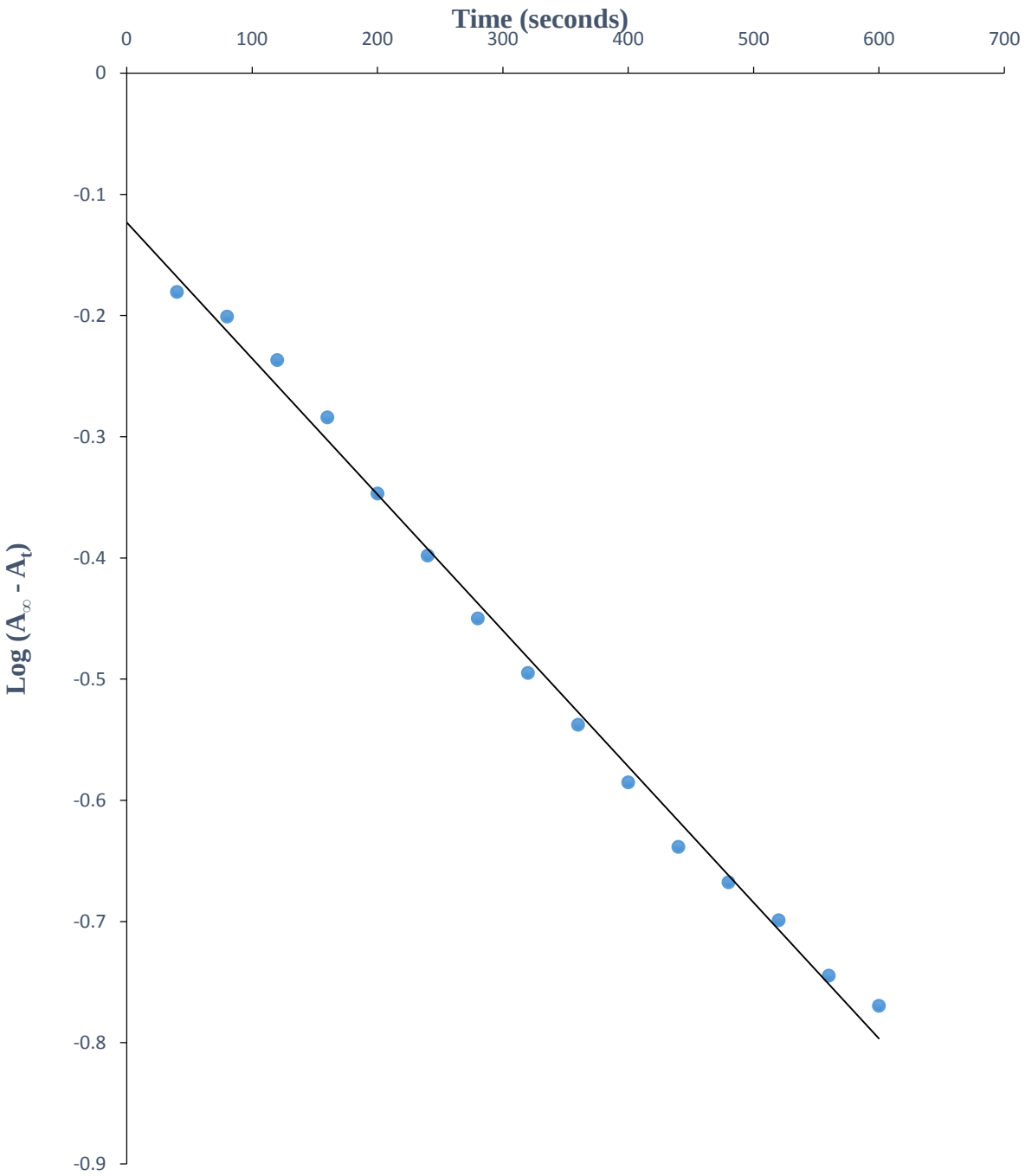


Figure 4.39: Typical pseudo-first order plot for the redox reaction of Fe_2O^{4+} with EH_2 at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[EH_2] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 26.0 ± 1.0^{o}C and λ_{max} = 520 nm

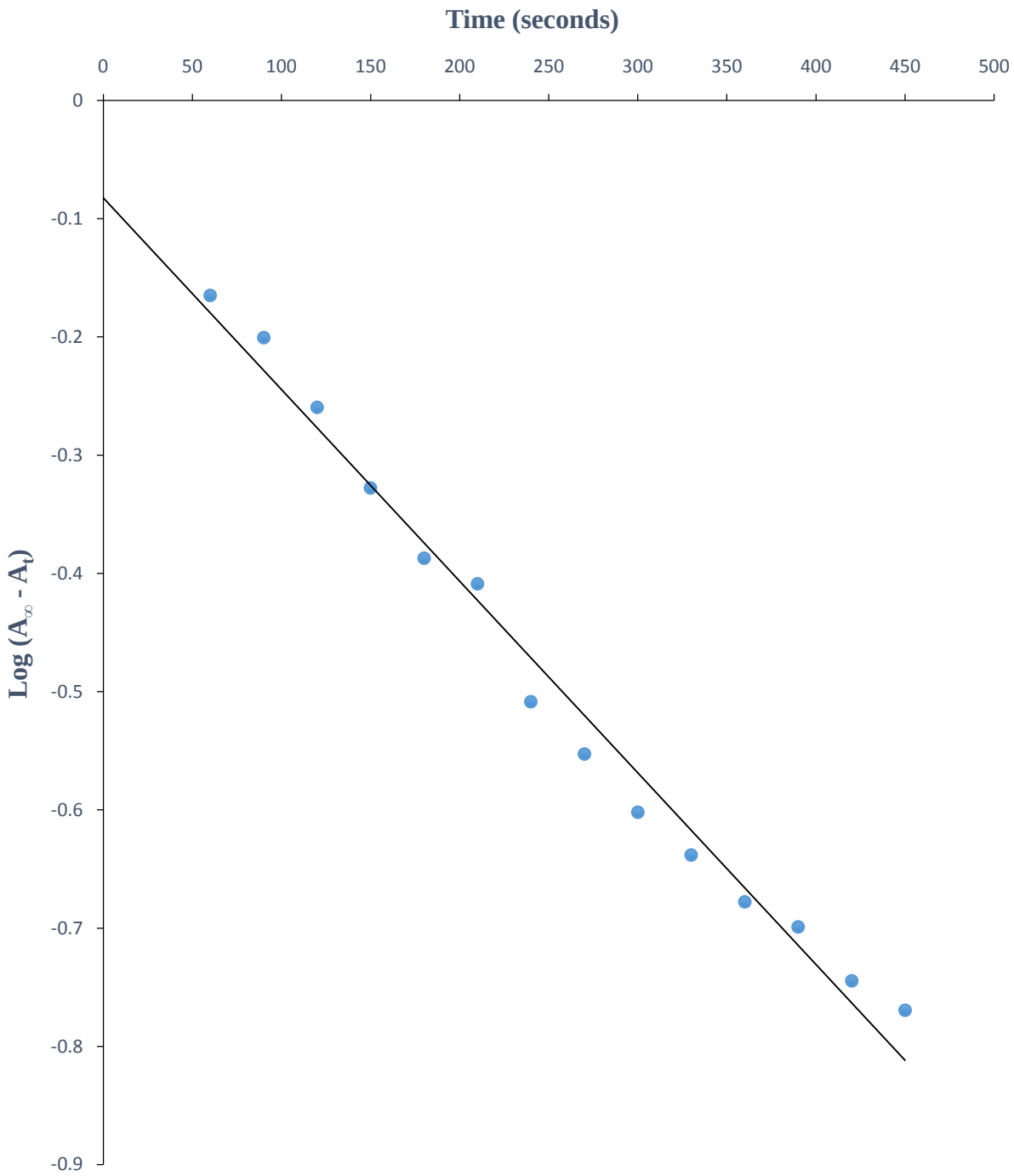


Figure 4.40: Typical pseudo-first order plot for the redox reaction of $Fe_2O^{4+}$with DH_2 at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[DH_2] = 5.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 26.0 ± 1.0^{o}C and λ_{max} = 520 nm

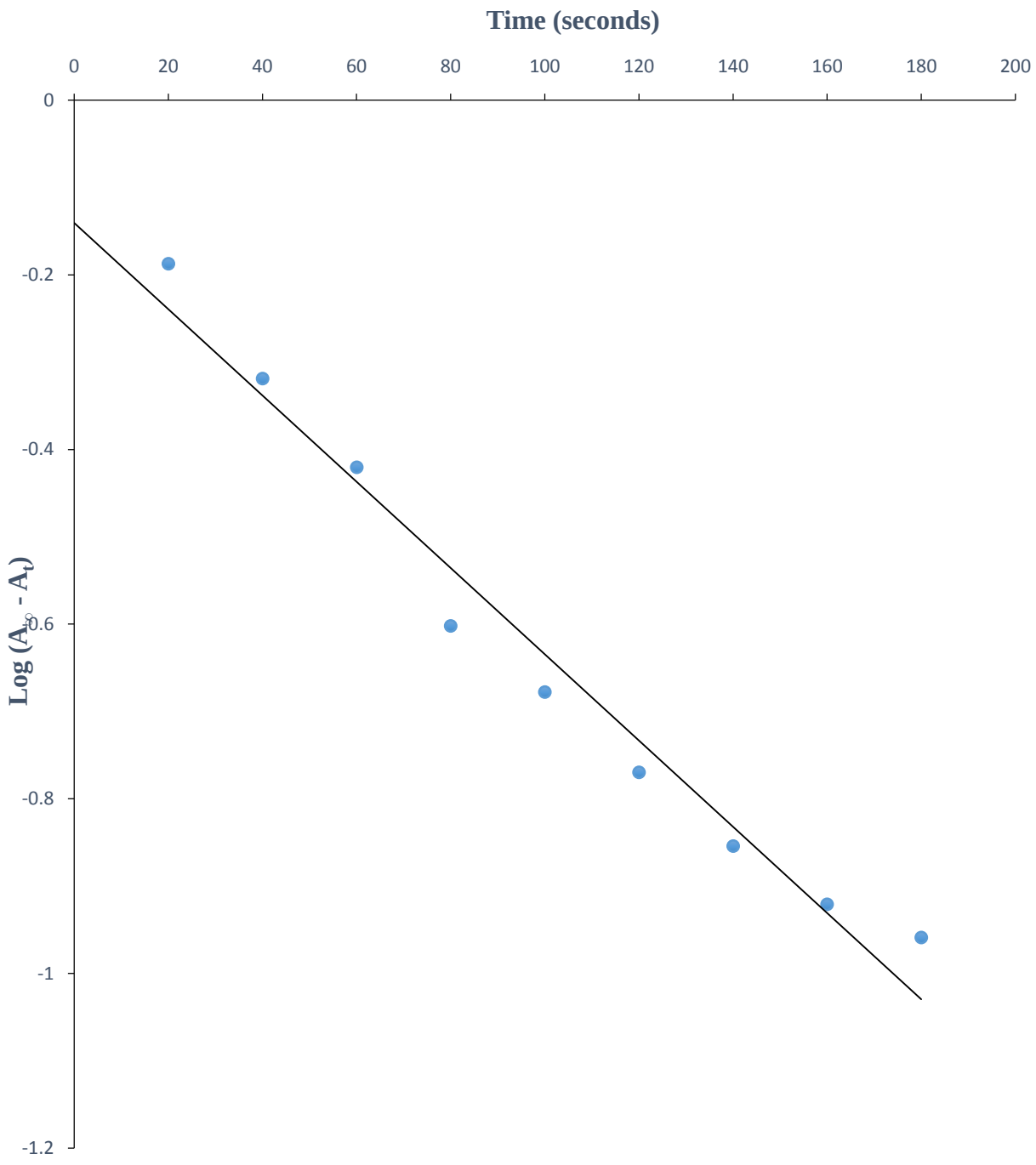


Figure 4.41: Typical pseudo-first order plot for the redox reaction of Fe_2O^{4+} with GSH at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, [GSH] = 5.0×10^{-3} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl), T = 26.0 ± 1.0^{o}C and λ_{max} = 520 nm

Table 4.6: Pseudo-first order rate constants for the redox reaction of Fe_2O^{4+} – $S_2O_4^{2-}$ in aqueous HCl medium, λ_{max} = 520nm, I = 0.30 mol dm^{-3} (NaCl), [Fe_2O^{4+}] = 1 × 10^{-4} mol dm^{-3} , T = 26.0 ±1.0°C

$10^3[S_2O_4^{2-}]$ (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^3k_{obs} (s^{-1})
3.0	1.0	3.0	3.20
5.0	1.0	3.0	3.08
7.0	1.0	3.0	3.20
9.0	1.0	3.0	3.06
11.0	1.0	3.0	3.15
13.0	1.0	3.0	2.94
15.0	1.0	3.0	3.16
7.0	0.4	3.0	3.07
7.0	0.6	3.0	3.08
7.0	0.8	3.0	2.98
7.0	1.0	3.0	3.10
7.0	1.2	3.0	3.10
7.0	1.4	3.0	3.04
7.0	1.0	1.0	3.05
7.0	1.0	2.0	2.95
7.0	1.0	3.0	3.10
7.0	1.0	4.0	3.04
7.0	1.0	5.0	3.01
7.0	1.0	6.0	3.04

Table 4.7: Pseudo-first order rate constants for the redox reaction of Fe_2O^{4+} – $S_2O_6^{2-}$ in aqueous HCl medium, λ_{max} = 520nm, I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}]$= 2 × 10^{-4} mol dm^{-3} , T = 26.0 ±1.0°C

$10^3[S_2O_6^{2-}]$ (mol dm^{-3})	10^2 $[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^3 k_{obs} (s^{-1})
2.0	1.0	3.0	1.88
4.0	1.0	3.0	1.88
6.0	1.0	3.0	1.92
8.0	1.0	3.0	2.01
12.0	1.0	3.0	2.06
14.0	1.0	3.0	2.06
6.0	1.0	3.0	2.02
6.0	0.4	3.0	1.90
6.0	0.6	3.0	1.81
6.0	0.8	3.0	1.85
6.0	1.0	3.0	1.90
6.0	1.2	3.0	1.89
6.0	1.4	3.0	1.91
6.0	1.0	1.0	1.97
6.0	1.0	2.0	2.01
6.0	1.0	3.0	1.91
6.0	1.0	4.0	1.97
6.0	1.0	5.0	1.94
6.0	1.0	6.0	1.87

Table 4.8 : Pseudo-first order rate constants for the redox reaction of Fe_2O^{4+} – EH_2 in aqueous HCl medium, λ_{max} = 520nm, I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}] = 2 \times 10^{-4}$ mol dm^{-3} , T = 26.0 ±1.0°C

$10^3[EH_2]$ (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})
4.0	1.0	3.0	1.51
6.0	1.0	3.0	1.57
8.0	1.0	3.0	1.58
10.0	1.0	3.0	1.58
12.0	1.0	3.0	1.60
14.0	1.0	3.0	1.60
16.0	1.0	3.0	1.60
6.0	0.4	3.0	1.41
6.0	0.6	3.0	1.34
6.0	0.8	3.0	1.34
6.0	1.0	3.0	1.38
6.0	1.2	3.0	1.21
6.0	1.4	3.0	1.30
6.0	1.0	1.0	1.56
6.0	1.0	2.0	1.56
6.0	1.0	3.0	1.56
6.0	1.0	4.0	1.50
6.0	1.0	5.0	1.53
6.0	1.0	6.0	1.53

Table 4.9: Pseudo-first order rate constants for the redox reaction of Fe_2O^{4+} – DH_2 in aqueous HCl medium, λ_{max} = 520nm, , I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}] = 5 \times 10^{-5}$ mol dm^{-3}, T = 26.0 ±1.0°C

$10^4[DH_2]$ (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^3k_{obs} (s^{-1})
4.0	1.0	3.0	1.35
6.0	1.0	3.0	1.38
8.0	1.0	3.0	1.28
10.0	1.0	3.0	1.41
12.0	1.0	3.0	1.30
14.0	1.0	3.0	1.30
16.0	1.0	3.0	1.40
6.0	0.4	3.0	1.41
6.0	0.6	3.0	1.34
6.0	0.8	3.0	1.34
6.0	1.0	3.0	1.38
6.0	1.2	3.0	1.21
6.0	1.4	3.0	1.30
6.0	1.0	1.0	1.30
6.0	1.0	2.0	1.40
6.0	1.0	3.0	1.29
6.0	1.0	4.0	1.30
6.0	1.0	5.0	1.37
6.0	1.0	6.0	1.29

Table 4.10: Pseudo-first order rate constants for the redox reaction of Fe_2O^{4+} – GSH in aqueous HCl medium, λ_{max} = 520nm, I = 0.30 mol dm^{-3} (NaCl), $[Fe_2O^{4+}] = 5 \times 10^{-5}$ mol dm^{-3} , T = 26.0 ±1.0°C

10^3[GSH] (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	10 [I] (mol dm^{-3})	10^3 k_{obs} (s^{-1})
2.0	1.0	3.0	4.32
4.0	1.0	3.0	3.92
6.0	1.0	3.0	4.10
8.0	1.0	3.0	4.08
12.0	1.0	3.0	4.01
14.0	1.0	3.0	4.01
16.0	1.0	3.0	3.89
6.0	0.4	3.0	4.13
6.0	0.6	3.0	4.36
6.0	0.8	3.0	4.24
6.0	1.0	3.0	4.40
6.0	1.2	3.0	3.87
6.0	1.4	3.0	4.23
6.0	1.0	1.0	3.60
6.0	1.0	2.0	4.12
6.0	1.0	3.0	4.10
6.0	1.0	4.0	3.70
6.0	1.0	5.0	3.70
6.0	1.0	6.0	4.01

concentrations constant and the temperature range $25.0^0C \leq T \leq 31.0^0C$. The reactions of Fe_2O^{4+} with all the reductants were found to be independent of $[H^+]$ as shown in the Tables 4.1- 4.10.

4.5 Effect of Changes of Ionic Strength of Reaction Medium

4.5.1 Fe_2O^{4+} reaction with thiourea and thiourea derivatives (TU, MTU, ATU DMTU and DETU), $S_2O_4^{2-}$, $S_2O_6^{2-}$, EH_2, DH_2 and GSH

Within the range of ionic strength of the media $0.1 \leq I \leq 0.6$ mol dm^{-3} (NaCl), effect of changes in I on the reaction rates was investigated for the reaction of Fe_2O^{4+} with thiourea (TU) and some of its derivatives (MTU, ATU, DMTU and DETU). At $25.0^0C \leq T \leq 31.0^0C$, $[H^+] = 1 \times 10^{-3}$ mol dm^{-3} and maintaining $[Fe_2O^{4+}]$ and [reductant] constant, the rate of reaction was not markedly affected by changes in ionic strength. Pseudo-first order, k_{obs}, and second order rate constants, k_2, remained fairly constant and the results are presented in Tables 4.1 – 4.5 for the reactions of the oxidant and thioureas. Also within the same range of ionic strength as mentioned above, keeping other conditions constant, the pseudo- first order rate constant, k_{obs}, were fairly constant in the reactions of Fe_2O^{4+} with $S_2O_4^{2-}$,$S_2O_6^{2-}$, EH_2, DH_2 and GSH and results are presented in Table 4.6 – 4.10.

4.6 Effect of Changes in Dielectric Constant of Reaction Medium on Rate

4.6.1 Fe_2O^{4+} reaction with the thioureas, $S_2O_4^{2-}$, $S_2O_6^{2-}$, EH_2, DH_2 and GSH

The effect of changes in the dielectric constant (D) of the reaction medium on the rates of the reactions of Fe_2O^{4+} and the reductants above was investigated at constant [oxidant], [reductant], $[H^+]$ and I of the medium and T of reaction but varying the dielectric constant of the medium using acetone-water mixture. Decreasing the dielectric constant of the reaction medium from

81 –58.74, using (CH_3COCH_3/H_2O) had no effect on the rate of reactions in all the systems investigated (Tables 4.11 – 4.20). The effect of dielectric constant (D) on the rate constant, k_2, for ion-ion interactions is given by equation 4.12.

4.7Effect of Added Ions on Reaction Rates

4.7.1 Fe_2O^{4+} reaction with the thioureas, $S_2O_4^{2-}$, $S_2O_6^{2-}$, EH_2, DH_2 and GSH

At constant concentrations of all other reactants, the effect of added ions on the rates of the reaction was investigated by varying the concentrations of X, where X represents either nitrate ion (NO_3^-), acetate ion (CH_3COO^-), formate ion ($HCOO^-$), sulphate ion (SO_4^{2-}), magnesium ion (Mg^{2+}) or potassium ion (K^+). For the reactions of Fe_2O^{4+} with thiourea (TU), *N*,-methylthiourea (MTU), *N*-allylthiourea (ATU),*N,N'*-dimethylthiourea (DMTU) and diethyl thiourea (DETU), the rate constants were found to be unaffected by the addition of cations but there was inhibition of the rate of reaction when anions were added as shown in Tables 4.21 – 4.30.The plots of the ion dependent second order rate constant, $k_2(X)$, versus concentrations of the ions, [X] are presented as Figures 4.42 – 4.51. The relationship between the ion-dependent second order rate constant, $k_2(X)$, and the concentrations of the ions for the Fe_2O^{4+}/ thioureas is given by equation 4.13

where X = CH_3COO^-, SO_4^{2-}, NO_3^- and $HCOO^-$

p = intercept and q = slope whose values for:

For Fe_2O^{4+}/ TU reaction:

where X = CH_3COO^-, ‘p’ = 2.56×10^{-2} $dm^3\ mol^{-1}\ s^{-1}$ and ‘q’ = -1.03×10^{-2} $dm^6\ mol^{-2}\ s^{-1}$

where X =SO_4^{2-}, ‘p’ = 2.62×10^{-2} $dm^3\ mol^{-1}\ s^{-1}$ and ‘q’ = -1.7×10^{-2} $dm^6\ mol^{-2}\ s^{-1}$

For Fe_2O^{4+}/ MTU**:**

Table 4.11: Dependence of rateof reaction on dielectric constant for[Fe_2O^{4+}]-[TU] system, at I= 0.3 mol dm^{-3}, [H^+] = 1.0 × 10^{-3} mol dm^{-3} , [Thiourea] = 5.0 × 10^{-2}mol dm^{-3}, [Fe_2O^{4+}] = 2.0 × 10^{-4} mol dm^{-3} , at λ_{max}= 520 nm, T = 27.0 ± 1.0°C

D	10^3k_{obs} (s^{-1})	k_2 ($dm^3mol^{-1}s^{-1}$)
81.00	13.00	2.60
77.57	13.30	2.66
75.86	13.40	2.68
72.43	13.10	2.60
70.71	12.70	2.54
69.00	12.60	2.52
67.29	13.30	2.66

Table 4.12: Dependence of rateof reactionon dielectric constant for[Fe_2O^{4+}]-[MTU] system, at I= 0.3 mol dm^{-3}, [H^+] = 1.0 × 10^{-3} mol dm^{-3} , [MTU] = 5.0 × 10^{-2}mol dm^{-3}, [Fe_2O^{4+}] = 2.0 × 10^{-4} mol dm^{-3} , at λ_{max}= 520 nm, T = 27.0 ± 1.0°C

D	10^3k_{obs} (s^{-1})	k_2 ($dm^3mol^{-1}s^{-1}$)
81.00	14.00	0.280
79.29	13.90	0.278
75.86	13.90	0.278
72.43	13.90	0.288
70.71	14.40	0.270
69.00	13.50	0.270
67.29	13.50	0.270

Table 4.13: Dependence of rate of reaction on dielectric constant for[Fe_2O^{4+}]-[ATU] system, at I= 0.3 mol dm^{-3}, [H^+] = 1.0 × 10^{-3} mol dm^{-3} , [ATU] = 5.0 × 10^{-2} mol dm^{-3} , [Fe_2O^{4+}] = 2.0 × 10^{-4} mol dm^{-3} , at λ_{max}= 520 nm, T = 27.0 ± 1.0°C

D	10^4k_{obs} (s^{-1})	10^2k_2 ($dm^3mol^{-1}s^{-1}$)
81.00	30.10	6.02
77.57	30.10	6.02
75.86	31.00	6.20
72.43	32.00	6.40
70.71	30.70	6.14
69.00	30.00	6.00
67.29	30.40	6.08

Table 4.14 : Dependence of rate of reaction on dielectric constant for[Fe_2O^{4+}]-[DMTU] system, at I= 0.3 mol dm^{-3}, [H^+] = 1.0 × 10^{-3} mol dm^{-3}, [DMTU] = 8.0 × 10^{-3} mol dm^{-3} , [Fe_2O^{4+}]= 2.0 × 10^{-4} mol dm^{-3}, at λ_{max} = 520 nm, T = 27.0 ± 1.0°C

D	$10^3 k_{obs}$ (s^{-1})	k_2 ($dm^3 mol^{-1} s^{-1}$)
81.00	29.10	0.364
78.60	29.00	0.362
76.20	29.30	0.366
73.80	28.80	0.360
71.40	29.00	0.362
69.00	28.80	0.360
66.66	29.20	0.365

Table 4.15 : Dependence of rate of reaction on dielectric constant for[Fe_2O^{4+}]-[DETU] system, at I= 0.3 mol dm^{-3}, [H^+] = 1.0 × 10^{-3} mol dm^{-3} , [DETU] = 8.0 × 10^{-2} mol dm^{-3} , [Fe_2O^{4+}] = 2.0 × 10^{-4} mol dm^{-3} , at λ_{max} = 520 nm, T = 30.0 ± 1.0°C

D	10^3k_{obs} (s^{-1})	10^2k_2 ($dm^3mol^{-1}s^{-1}$)
81.00	23.00	2.88
76.86	22.80	2.85
74.79	23.10	2.89
72.72	22.60	2.83
70.65	23.00	2.88
68.59	23.10	2.89
66.52	22.80	2.83

Table 4.16 : Dependence of rate of reaction on dielectric constant for $[Fe_2O^{4+}]$-$[S_2O_4^{2-}]$ system at I = 0.3 mol dm^{-3}, (NaCl), $[S_2O_4^{2-}] = 7.0 \times 10^{-3}$ mol dm^{-3}, $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$mol dm^{-3}, λ_{max} = 520nm, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, T = 26.0 ± 1.0°C

D	$10^3 k_{obs}$ (s^{-1})
81.00	3.04
79.06	3.10
77.13	3.17
75.19	3.17
73.26	3.04
71.32	3.00
69.39	3.00

Table 4.17 : Dependence of rate of reaction on dielectric constant for $[Fe_2O^{4+}]$- $[S_2O_6^{2-}]$ system at I = 0.3 mol dm^{-3} , (NaCl), $[S_2O_6^{2-}] = 6.0 \times 10^{-3}$ mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3},λ_{max}=520nm, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, T = 27.0 ± 1.0°C

D	$10^3 k_{obs}$ (s^{-1})
81.00	1.95
79.31	1.89
75.54	1.89
73.73	1.91
71.91	2.02
70.09	1.91
68.27	1.91

Table 4.18 : Dependence of rate of reaction on dielectric constant for $[Fe_2O^{4+}]$ - $[EH_2]$ system at I = 0.3 mol dm^{-3} , (NaCl), $[EH_2] = 6.0 \times 10^{-3}$ mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520nm, $[H^+] = 1.0 \times 10^{-3}$mol dm^{-3}, T = 27.0 ± 1.0°C

D	$10^3 k_{obs}$ (s^{-1})
81.00	1.39
79.31	1.30
75.54	1.30
73.73	1.32
71.91	1.22
70.09	1.22
68.27	1.20

Table 4.19 : Dependence of rate of reaction on dielectric constant for $[Fe_2O^{4+}]$ - $[DH_2]$ system at I = 0.3 mol dm^{-3} , (NaCl), T = 26.0 ± 1.0°C, $[DH_2]$ = 6.0 × 10^{-3}mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3}, λ_{max}= 520nm, $[H^+]$ = 1.0 × 10^{-3}mol dm^{-3}

D	$10^3 k_{obs}$ (s^{-1})
68.90	1.56
67.45	1.50
64.55	1.50
63.09	1.49
61.64	1.47
60.19	1.53
58.74	1.53

Table 4.20 : Dependence of rate of reaction on dielectric constant for[Fe_2O^{4+}] - [GSH] system at I = 0.3 mol dm^{-3} , (NaCl), T = 26.0 ± 1.0°C, [GSH] = 6.0 × 10^{-3} mol dm^{-3}, [Fe_2O^{4+}] = 2.0 × 10^{-4} mol dm^{-3}, λ_{max}= 520nm, [H^+] = 1.0 × 10^{-3}moldm^{-3}

D	10^3k_{obs} (s^{-1})
81.00	4.30
79.31	4.30
75.58	4.21
73.73	4.30
71.91	4.20
70.09	3.90
68.27	3.90

Table 4.21: Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$and [Thiourea] at I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C, [Thiourea] = 5.0 × 10^{-2} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3} , λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}

$10^3[K^+]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^2k_2 (dm^3 $mol^{-1}s^{-1}$)
00.0	13.10	2.62
10.0	13.00	2.60
25.0	13.00	2.60
50.0	12.95	2.59
75.0	12.43	2.49
100.0	12.75	2.55
125.0	12.65	2.53
10^3 $[Mg^{2+}]$ (mol dm^{-3})		
00.0	13.10	2.62
10.0	12.70	2.54
25.0	12.70	2.54
50.0	13.60	2.72
75.0	13.50	2.70
100.0	13.40	2.68
125.0	13.20	2.64

Table 4.22:Dependence of rate constant on addedanions for the redox reaction of $[Fe_2O^{4+}]$ and [TU] at I = 0.3 mol dm^{-3} (NaCl), [TU] = 5.0 × 10^{-2} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3} , λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}, T = 27.0 ± 1.0°C

$10^3[SO_4^{2-}]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^2k_2 (dm^3 $mol^{-1}s^{-1}$)
00.0	13.10	2.60
10.0	11.90	2.38
25.0	11.40	2.28
50.0	9.20	1.84
75.0	6.65	1.33
100.0	4.45	0.89
125.0	2.44	0.49
$10^3[CH_3OO^-]$(mol dm^{-3})		
00.0	13.10	2.62
10.0	12.15	2.43
25.0	11.55	2.31
50.0	9.80	1.96
75.0	8.90	1.78
100.0	7.80	1.56
125.0	6.40	1.28

Table 4.23: Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$and [MTU] at I = 0.3 mol dm^{-3} (NaCl), [MTU] = 5.0 × 10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3}, λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}, T = 27.0 ± 1.0°C

$10^3[K^+]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	k_2 (dm^3 $mol^{-1}s^{-1}$)
00.0	14.20	0.284
30.0	14.40	0.288
50.0	14.00	0.280
70.0	13.60	0.272
90.0	13.70	0.274
110.0	14.00	0.280
130.0	13.90	0.278
10^3 $[Mg^{2+}]$ (mol dm^{-3})		
00.0	14.00	0.280
30.0	14.10	0.282
50.0	13.50	0.272
70.0	13.30	0.266
90.0	13.00	0.260
110.0	14.20	0.284
130.0	13.70	0.274

Table 4.24: Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$ and [MTU] at I = 0.3 mol dm^{-3} (NaCl), [MTU] = 5.0×10^{-3} mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520 nm, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, T = 27.0 ± 1.0°C

$10^3[SO_4^{2-}]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	k_2 (dm^3 $mol^{-1}s^{-1}$)
00.0	14.40	0.288
30.0	11.80	0.236
50.0	9.80	0.196
70.0	8.30	0.166
90.0	6.84	0.137
110.0	5.95	0.119
130.0	4.92	0.098
$10^3[CH_3OO^-]$(mol dm^{-3})		
00.0	14.20	0.284
30.0	10.40	0.208
50.0	8.50	0.170
70.0	6.10	0.122
90.0	4.84	0.097
110.0	2.64	0.053
130.0	1.29	0.026

Table 4.25 :Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$and [ATU] at I = 0.3 mol dm^{-3} (NaCl), [ATU] = 5.0 × 10^{-2} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3} , λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3}, T = 27.0 ± 1.0°C

$10^3[K^+]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^2k_2 (dm^3 $mol^{-1}s^{-1}$)
00.0	30.00	6.00
10.0	30.10	6.02
25.0	29.80	5.96
50.0	29.20	5.84
75.0	30.40	6.08
100.0	30.20	6.04
120.0	30.50	6.10
10^3 $[Mg^{2+}]$ (mol dm^{-3})		
00.0	30.80	6.16
10.0	30.90	6.18
25.0	31.10	6.22
50.0	30.90	6.18
75.0	30.80	6.16
100.0	29.10	5.82
120.0	30.30	6.06

Table 4.26 :Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$ and [ATU] at I = 0.3 mol dm^{-3} (NaCl), [ATU] = 5.0×10^{-2} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0×10^{-4} mol dm^{-3}, λ_{max} = 520 nm, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, T = 27.0 ± 1.0°C

$10^3[SO_4^{2-}]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^2k_2 (dm^3 $mol^{-1}s^{-1}$)
00.0	30.10	6.02
10.0	26.20	5.24
25.0	25.30	5.06
50.0	21.20	4.24
75.0	19.00	3.80
100.0	18.05	3.60
120.0	16.00	3.20
$10^3[CH_3OO^-]$(mol dm^{-3})		
00.0	30.70	6.14
10.0	25.00	5.00
25.0	22.30	4.46
50.0	15.60	3.12
75.0	10.45	2.09
100.0	4.59	0.92
120.0	1.55	0.31

Table 4.27: Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$ and[DMTU] at I = 0.3 mol dm^{-3} (NaCl), [DMTU] = 8.0×10^{-3} mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520 nm, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, T = 27.0 ± 1.0°C

$10^3[K^+]$ (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})	k_2 (dm^3 $mol^{-1}s^{-1}$)
00.0	29.00	0.363
20.0	28.90	0.361
40.0	28.90	0.361
60.0	29.20	0.365
80.0	27.70	0.346
100.0	29.00	0.363
120.0	28.20	0.352
10^3 $[Mg^{2+}]$ (mol dm^{-3})		
00.0	29.00	0.363
20.0	28.60	0.358
40.0	28.80	0.360
60.0	28.20	0.353
80.0	28.20	0.353
100.0	29.10	0.364
120.0	28.80	0.360

Table 4.28:Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$ and [DMTU] at I = 0.3 mol dm^{-3} (NaCl), [DMTU] = 8.0 × 10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3} , λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3} , T = 27.0 ± 1.0°C

$10^3[NO_3^-]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	k_2 (dm^3 $mol^{-1}s^{-1}$)
00.0	29.00	0.363
20.0	25.80	0.323
40.0	20.80	0.260
60.0	18.00	0.225
80.0	14.64	0.183
100.0	12.00	0.150
120.0	9.68	0.121
$10^3[HCOO^-]$(mol dm^{-3})		
00.0	28.70	0.359
20.0	24.48	0.306
40.0	20.08	0.251
60.0	14.80	0.185
80.0	9.04	0.113
100.0	7.44	0.093
120.0	5.58	0.070

Table 4.29: Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$ and [DETU] at I = 0.3 mol dm^{-3} (NaCl), [DETU] = 8.0×10^{-2} mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, λ_{max} = 520 nm, T = 30.0 ± 1.0°C

$10^3[K^+]$ (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})	$10^2 k_2$ (dm^3 $mol^{-1}s^{-1}$)
00.0	22.80	2.85
30.0	23.00	2.88
50.0	22.40	2.80
70.0	22.50	2.81
90.0	23.10	2.89
110.0	22.90	2.86
130.0	22.50	2.81
10^3 $[Mg^{2+}]$ (mol dm^{-3})		
00.0	36.28	2.88
30.0	32.08	2.85
50.0	29.90	2.89
70.0	26.20	2.91
90.0	27.04	2.88
110.0	24.02	2.84
130.0	20.32	2.75

Table 4.30: Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$ and [DETU] at I = 0.3 mol dm^{-3} (NaCl), [DETU] = 8.0×10^{-2} mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, λ_{max} = 520 nm, T = 30.0 ± 1.0°C

$10^3[NO_3^-]$ (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^2k_2 (dm^3 mol^{-1} s^{-1})
00.0	23.20	2.90
30.0	21.68	2.71
50.0	19.69	2.46
70.0	16.70	2.09
90.0	15.10	1.89
110.0	13.00	1.63
130.0	11.20	1.40
$10^3[HCOO^-]$(mol dm^{-3})		
00.0	23.10	2.89
30.0	19.44	2.43
50.0	16.50	2.06
70.0	14.00	1.75
90.0	9.04	1.13
110.0	8.34	1.05
130.0	6.32	0.79

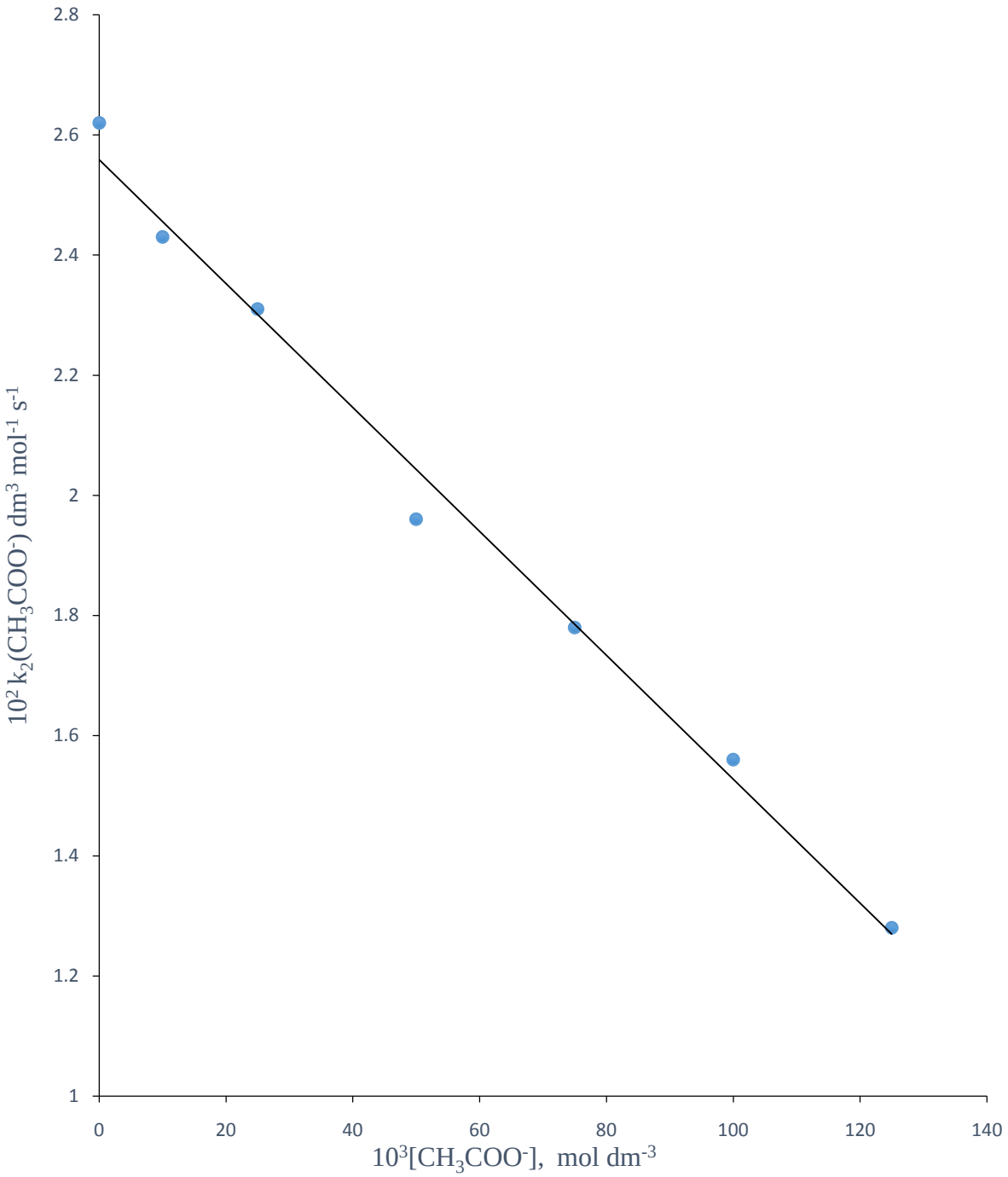


Figure 4.42: Plot of dependence of k_2 on $[CH_3COO^-]$ for the redox reaction of $Fe_2O^{4+}$and TU at **[**Fe_2O^{4+}] = 2.0 × 10^{-4}mol dm^{-3}, [TU] = 5.0 × 10^{-2}mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl),[H^+] = 1.0 × 10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 27.0 ± 1.0^{o}C

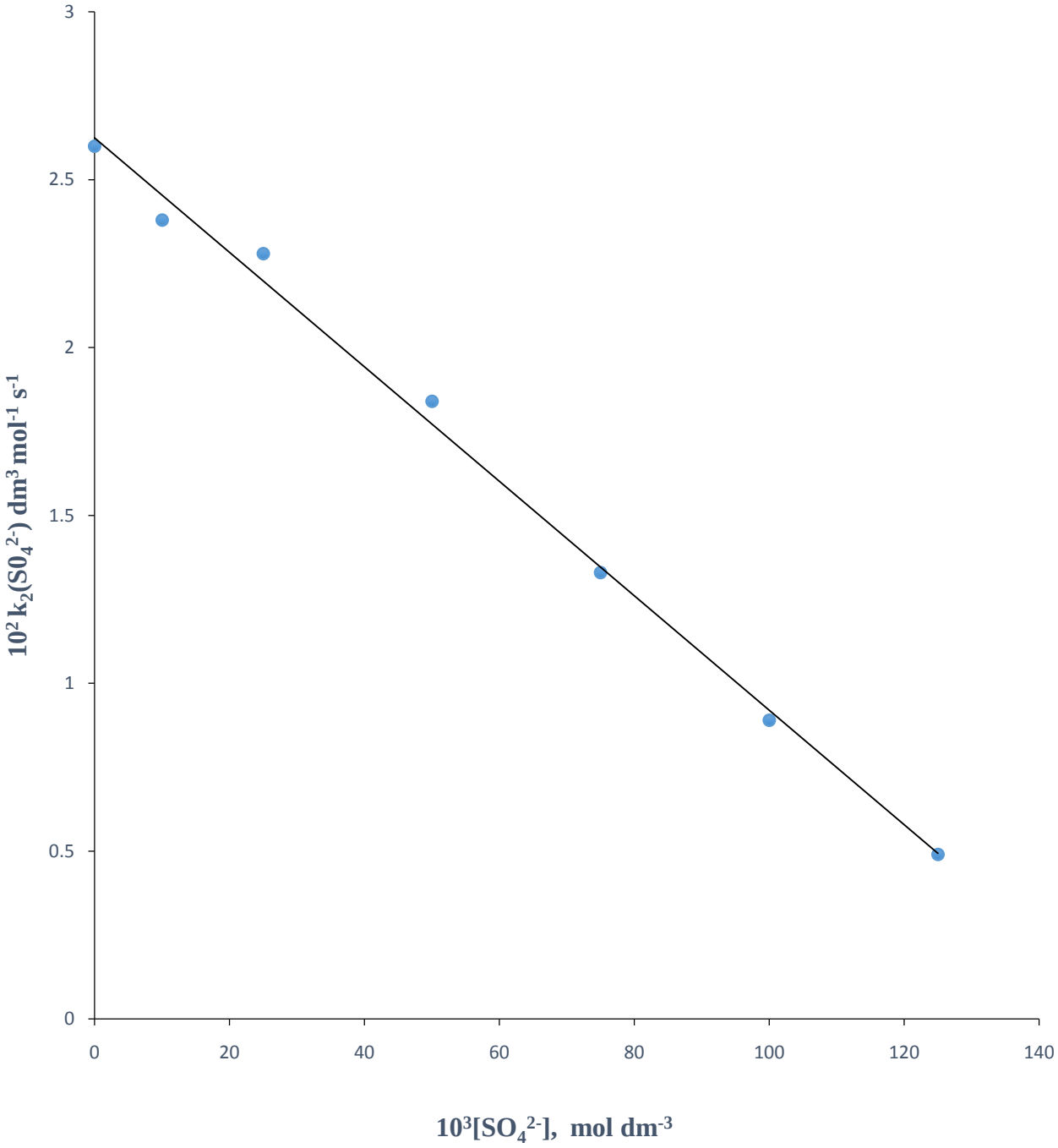


Figure 4.43: Plot of dependence of k_2 on $[SO_4^{2-}]$ for the redox reaction of $Fe_2O^{4+}$and TU at **[**Fe_2O^{4+}] = 2.0 × 10^{-4}mol dm^{-3}, [TU] = 5.0 × 10^{-2}mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl),[H^+] = 1.0 × 10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 27.0 ± 1.0^{o}C

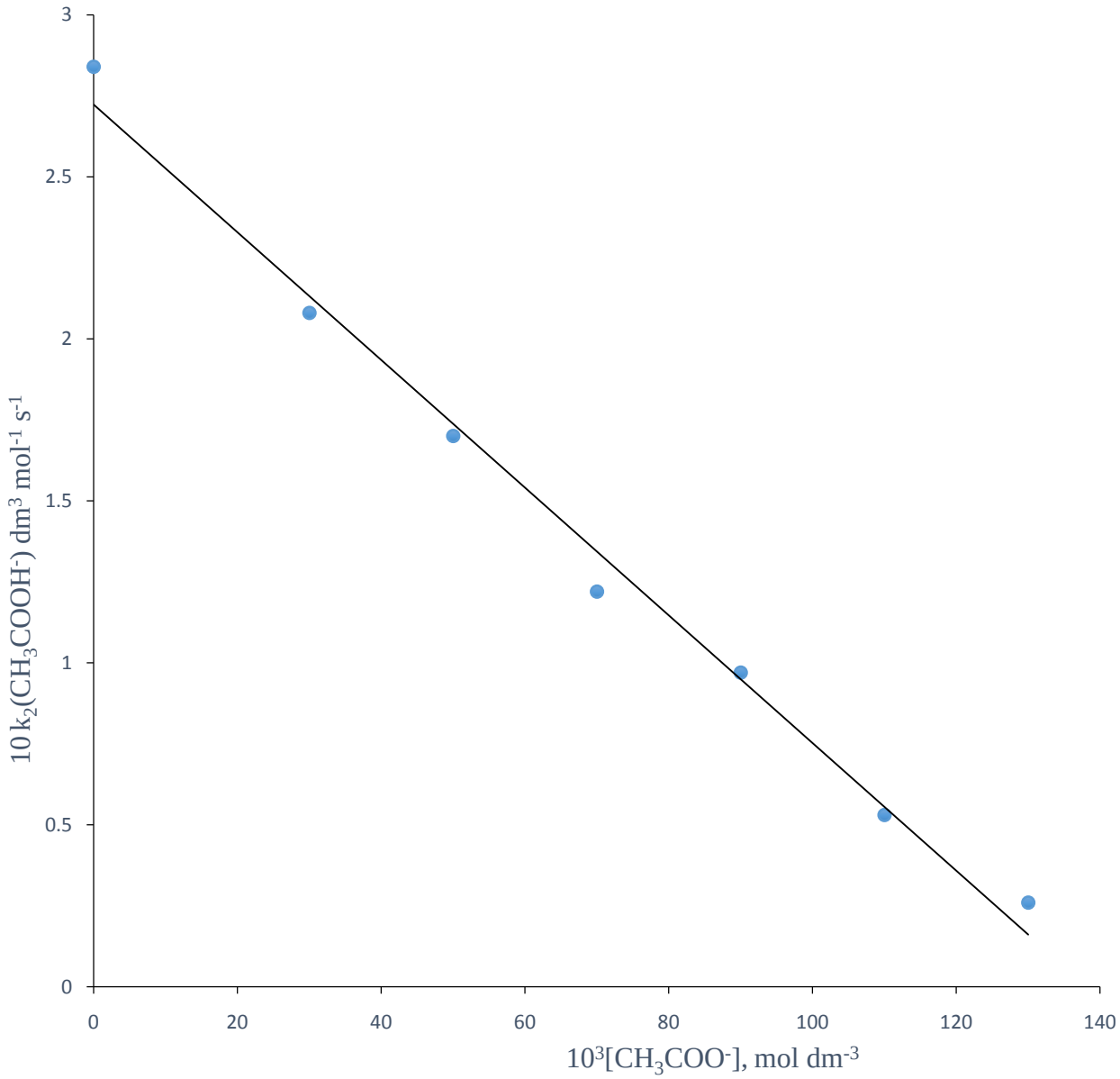


Figure 4.44: Plot of dependence of k_2 on $[CH_3COO^-]$ for the redox reaction of $Fe_2O^{4+}$and MTU at **[**Fe_2O^{4+}] = 2.0 × 10^{-4}mol dm^{-3}, [MTU] = 5.0 × 10^{-3}mol dm^{-3}, I = 0.30 mol dm^{-3}(NaCl),$[H^+]$ = 1.0 × 10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 27.0 ± 1.0^oC

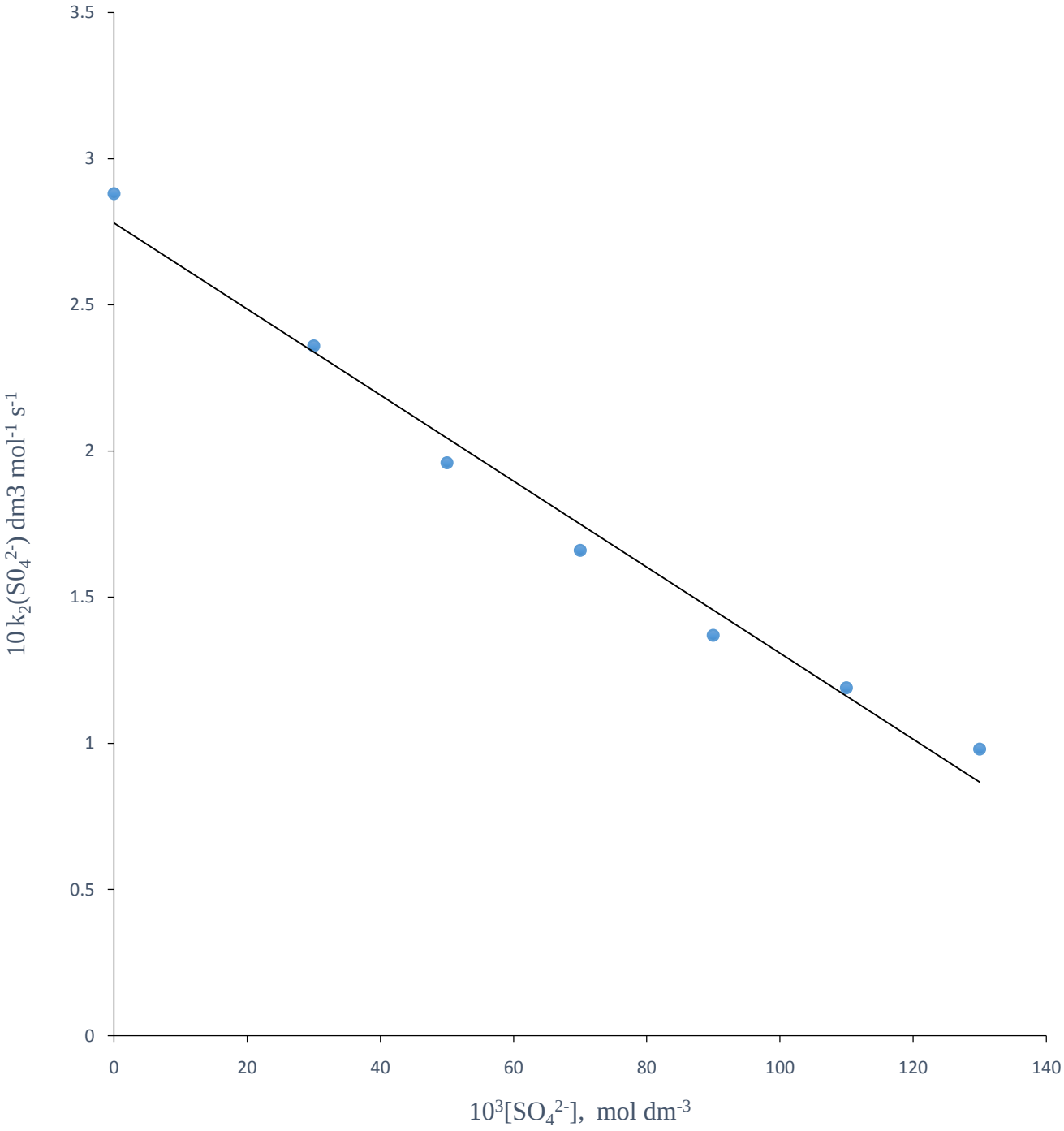


Figure 4.45: Plot of dependence of k_2 on $[SO_4^{2-}]$ for the redox reaction of $Fe_2O^{4+}$and MTU at **[**Fe_2O^{4+}] = 2.0 × 10^{-4}mol dm^{-3}, [MTU] = 5.0 × 10^{-3}mol dm^{-3}, I = 0.30 mol dm^{-3}(NaCl),[H^+] = 1.0 × 10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 27.0 ± 1.0^oC

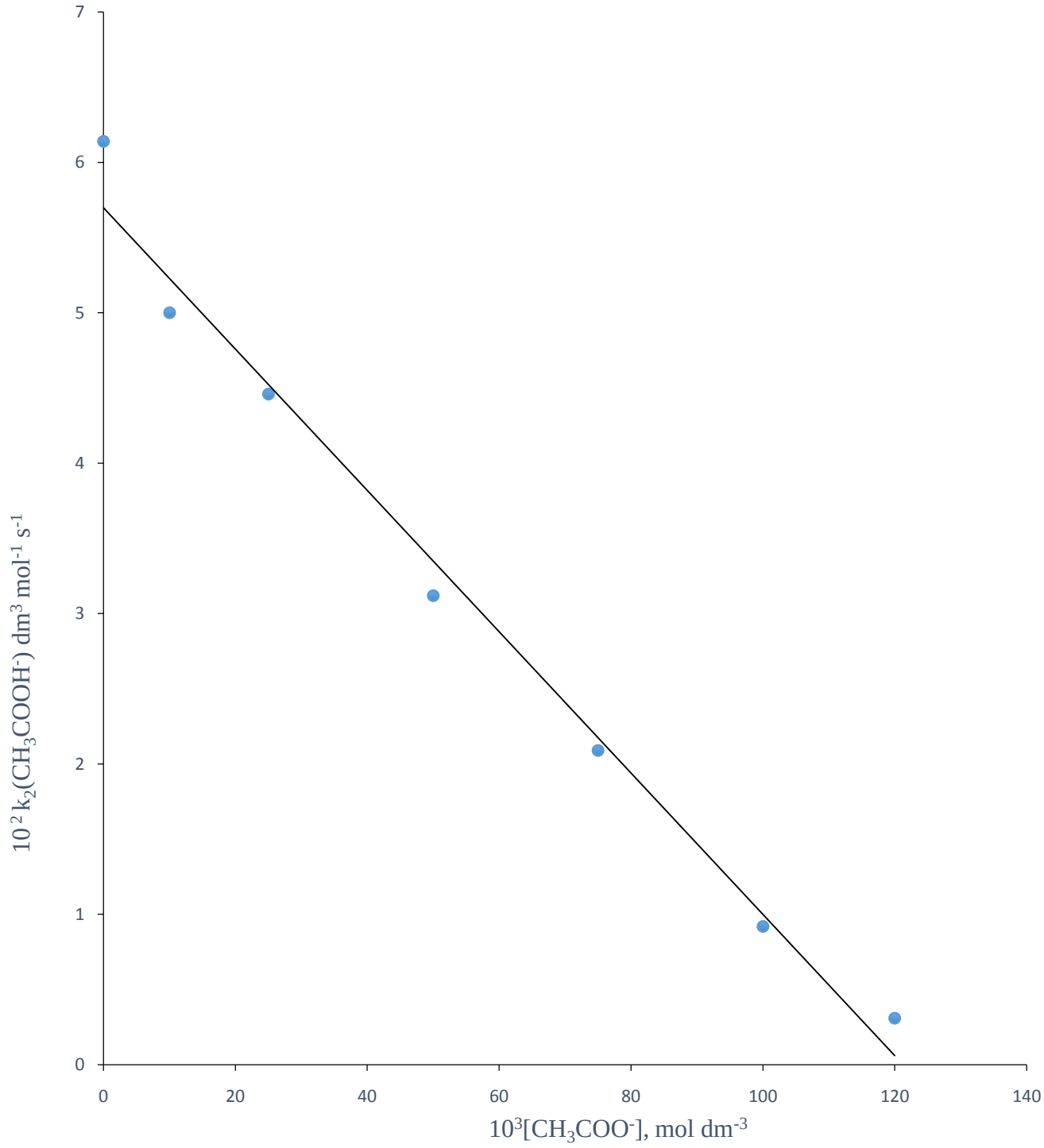


Figure 4.46: Plot of dependence of k_2 on $[CH_3COO^-]$ for the redox reaction of $Fe_2O^{4+}$and ATU at **[**Fe_2O^{4+}] = 2.0 × 10^{-4}mol dm^{-3}, [ATU] = 5.0 × 10^{-2}mol dm^{-3}, I = 0.30 mol dm^{-3}(NaCl),$[H^+]$ = 1.0 × 10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 27.0 ± 1.0^{o}C

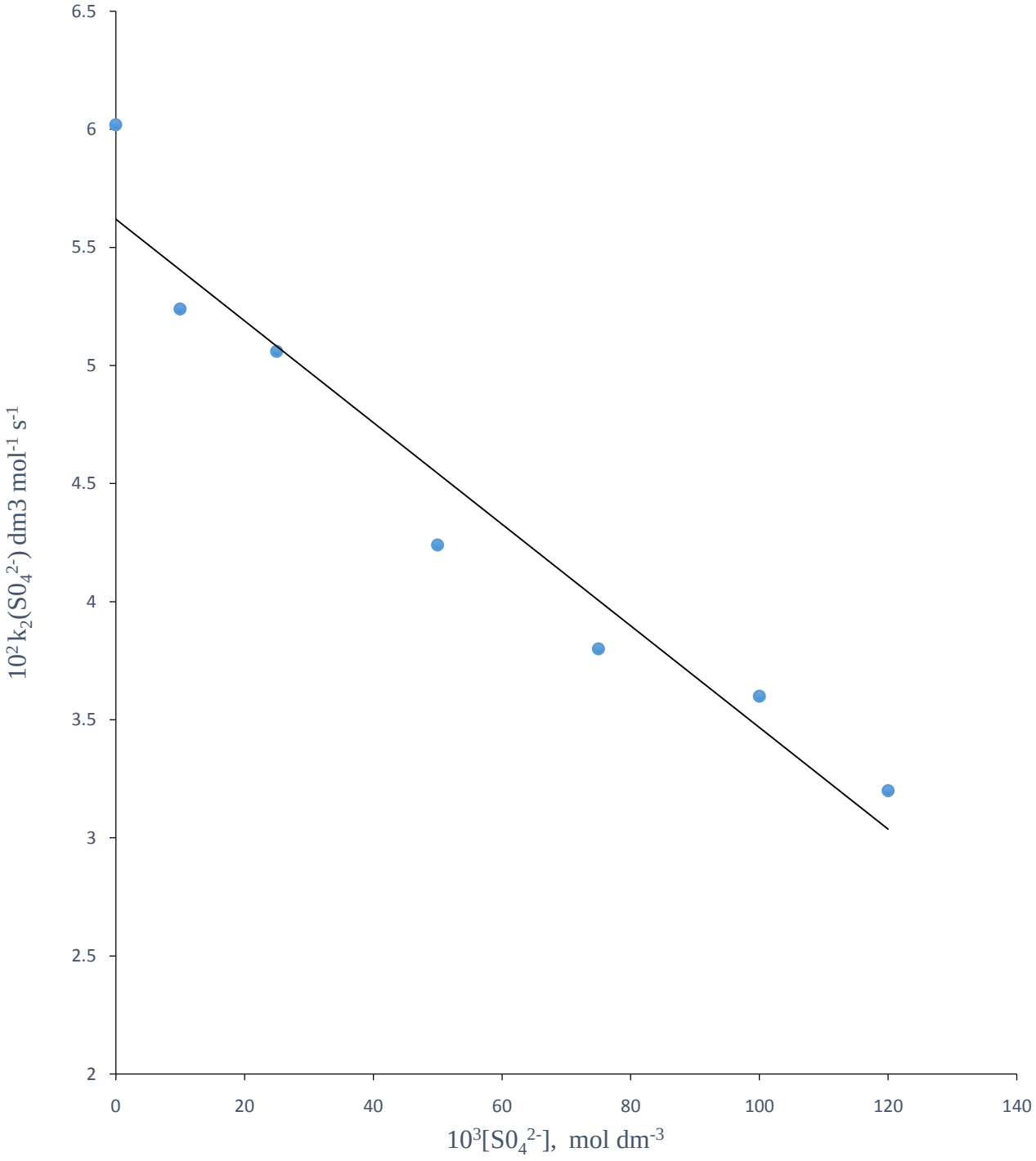


Figure 4.47: Plot of dependence of k_2 on $[SO_4^{2-}]$ for the redox reaction of $Fe_2O^{4+}$and ATU at **[**Fe_2O^{4+}] = 2.0 × 10^{-4}mol dm^{-3}, [ATU] = 5.0 × 10^{-2}mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl),[H^+] = 1.0 × 10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 27.0 ± 1.0^{o}C

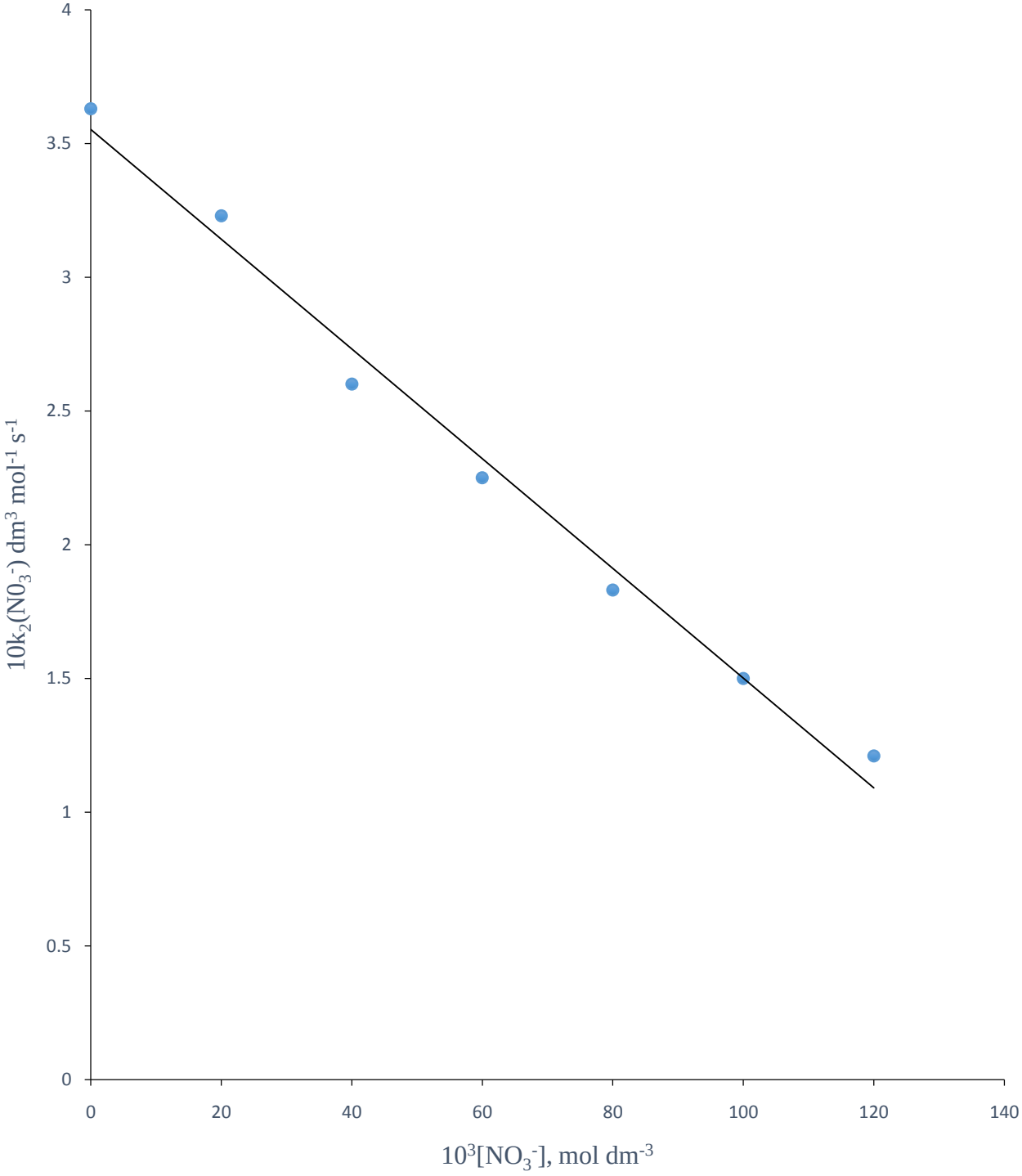


Figure 4.48: Plot of dependence of k_2 on $[NO_3^-]$ for the redox reaction of $Fe_2O^{4+}$and DMTU at **[**Fe_2O^{4+}] = 2.0×10^{-4}mol dm^{-3}, [DMTU] = 1.0×10^{-2}mol dm^{-3}, I = 0.30 mol dm^{-3}(NaCl),[H^+] = 1.0×10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 27.0 ± 1.0^{o}C

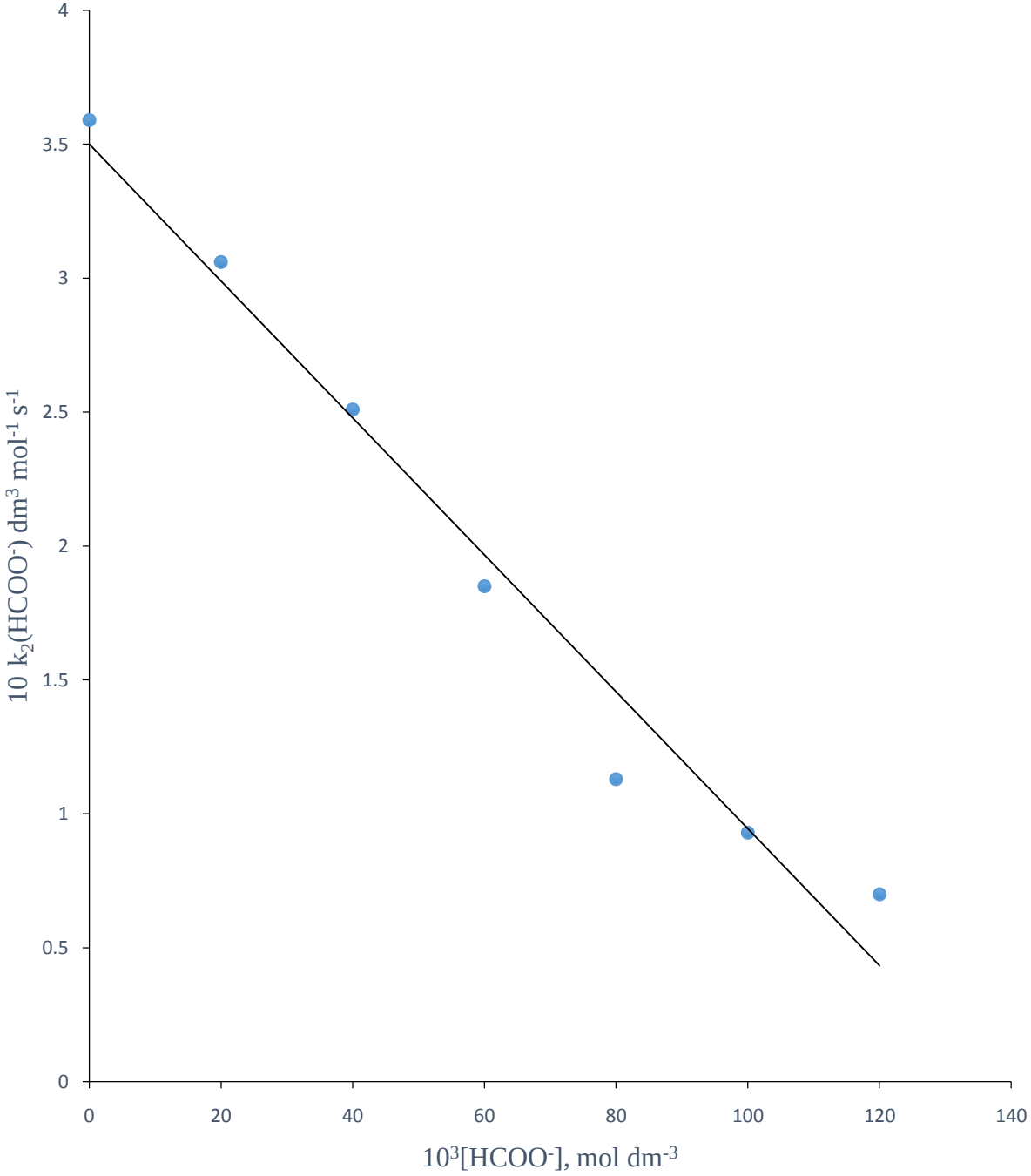


Figure 4.49: Plot of dependence of k_2 on $[HCOO^-]$ for the redox reaction of $Fe_2O^{4+}$and DMTU at **[**Fe_2O^{4+}] = 2.0×10^{-4}mol dm^{-3}, [DMTU] = 1.0×10^{-2}mol dm^{-3}, I = .0.30 mol dm^{-3}(NaCl),[H^+] = 1.0×10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 27.0 ± 1.0^{o}C

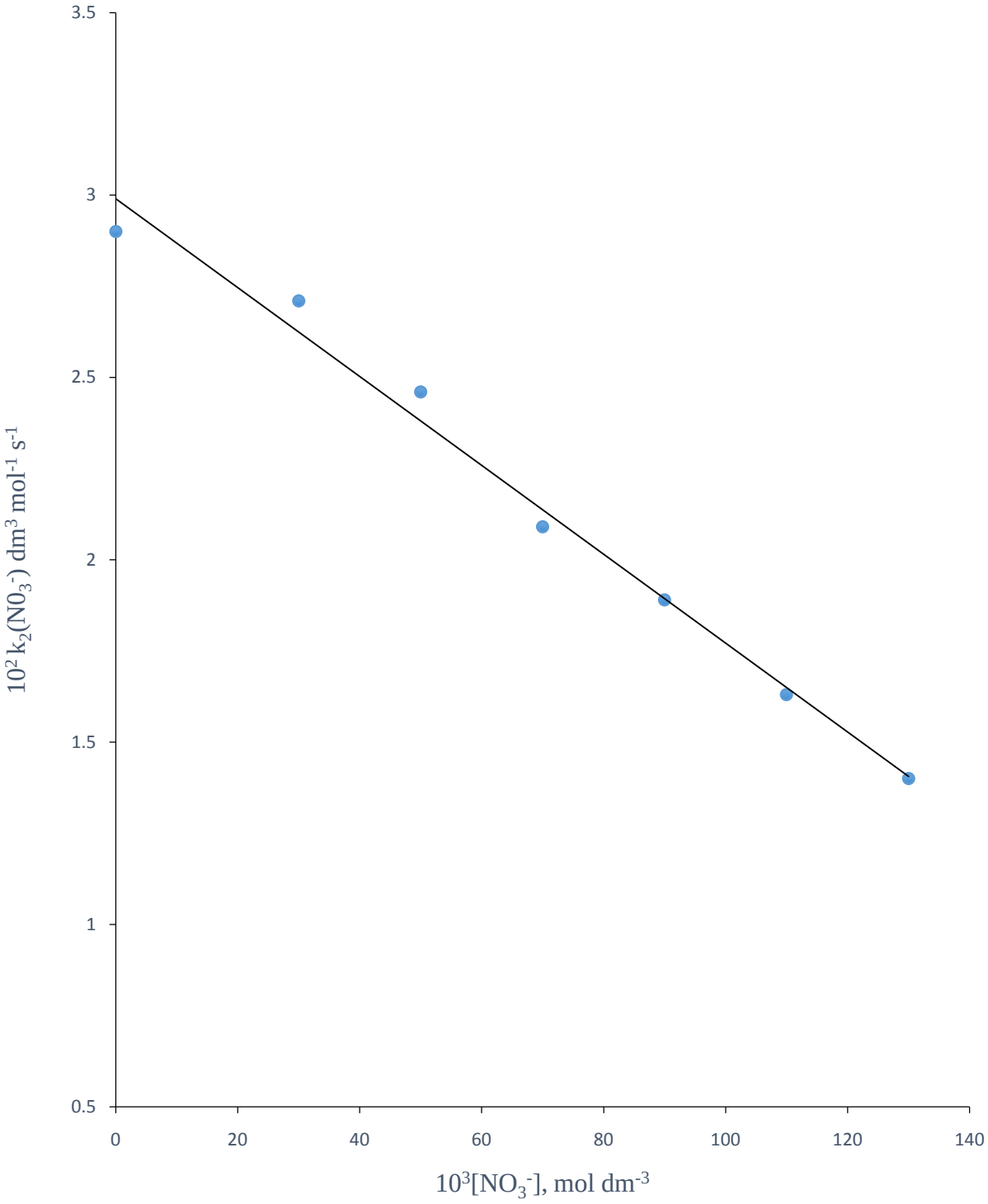


Figure 4.50: Plot of dependence of k_2 on $[NO_3^-]$ for the redox reaction of $Fe_2O^{4+}$and DETU at **[**Fe_2O^{4+}] = 2.0 × 10^{-4}mol dm^{-3}, [DETU] = 8.0 × 10^{-2}mol dm^{-3}, I = 0.30 mol dm^{-3}(NaCl),[H^+] = 1.0 × 10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 30.0 ± 1.0^{o}C

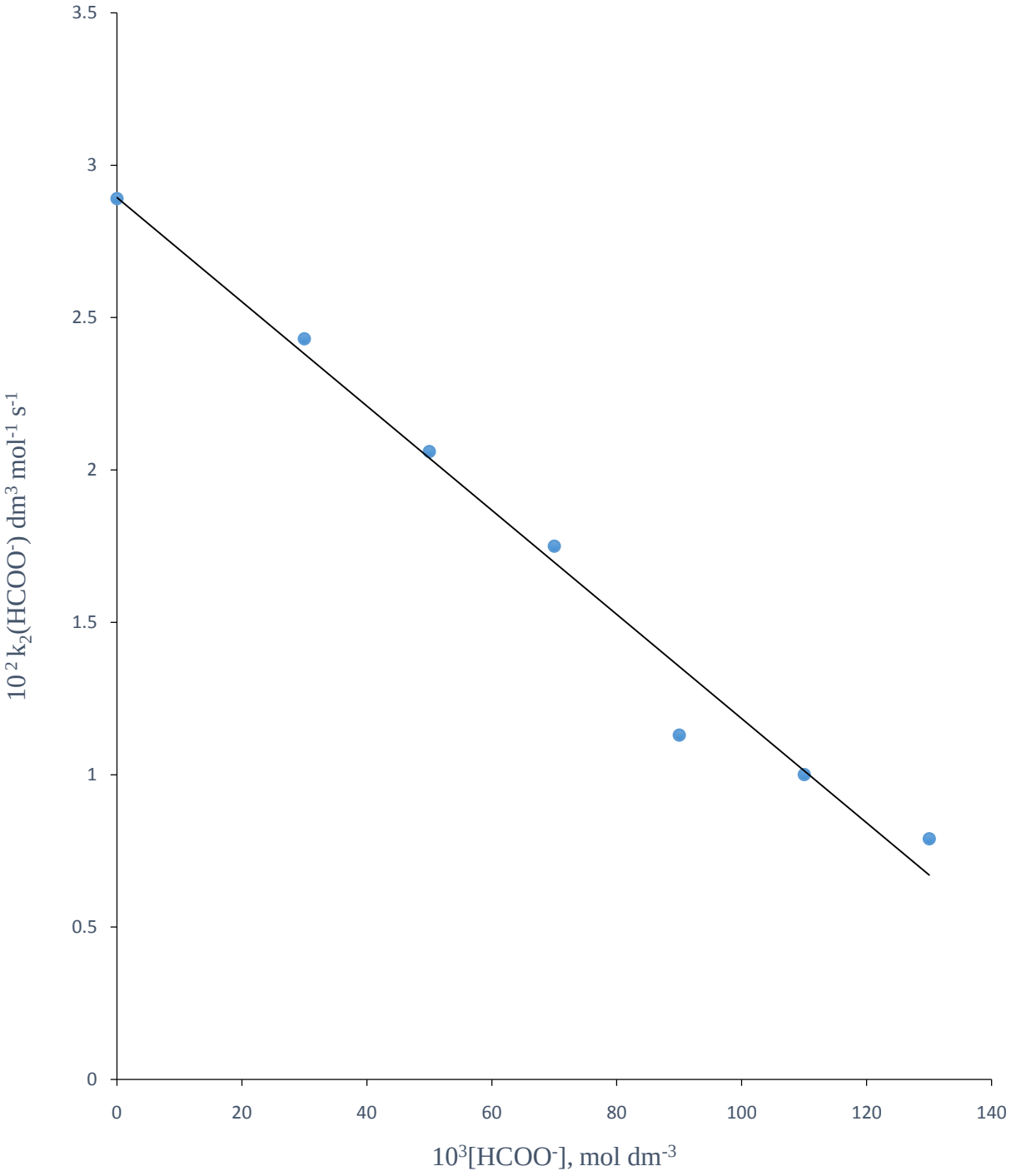


Figure 4.51: Plot of dependence of k_2 on $[HCOO^-]$ for the redox reaction of $Fe_2O^{4+}$and DETU at **[**Fe_2O^{4+}] = 2.0 × 10^{-4}mol dm^{-3}, [DETU] = 8.0 × 10^{-2}mol dm^{-3}, I = 0.30 mol dm^{-3} (NaCl),[H^+] = 1.0 × 10^{-3}mol dm^3, λ_{max} = 520 nm, and T = 30.0 ± 1.0^{o}C

where X = CH_3COO^-, 'p' = 2.72×10^{-1} dm^3 mol^{-1} s^{-1} and 'q' = -1.97 x 10^{-2} dm^6 mol^{-2} s^{-1}

where X =SO_4^{2-}, 'p' = 2.78×10^{-1} dm^3 mol^{-1} s^{-1} and 'q' = -1.47×10^{-2} dm^6 mol^{-2} s^{-1}

For Fe_2O^{4+}/ ATU**:**

where X = CH_3COO^-, 'p' = $5.70 \times 10^{-2} dm^3$ mol^{-1} s^{-1} and 'q' = -4.70×10^{-2} dm^6 mol^{-2} s^{-1}

where X =SO_4^{2-}, 'p' = 5.62×10^{-2} dm^3 mol^{-1} s^{-1} and 'q' = -2.15×10^{-2} dm^6 mol^{-2} s^{-1}

For Fe_2O^{4+}/ DMTU**:**

where X =NO_3^-, 'p' = 3.55×10^{-1} dm^3 mol^{-1} s^{-1} and 'q' = -2.05×10^{-2} dm^6 mol^{-2} s^{-1}

where X = $HCOO^-$, 'p' = 3.50×10^{-1} dm^3 mol^{-1} s^{-1} and 'q' = -2.56×10^{-2} dm^6 mol^{-2} s^{-1}

For Fe_2O^{4+}/ DETU**:**

where X =NO_3^-, 'p' = 2.99×10^{-2} dm^3 mol^{-1} s^{-1} and 'q' = -1.22×10^{-2} dm^6 mol^{-2} s^{-1}

where X = $HCOO^-$, 'p' = 2.89×10^{-1} dm^3 mol^{-1} s^{-1} and 'q' = -1.71×10^{-2} dm^6 mol^{-2} s^{-1}

For the reactions of Fe_2O^{4+} with $S_2O_4^{2-}$, $S_2O_6^{2-}$, EH_2, DH_2 and GSH the addition of cations and anions did not affect the rate of reaction, it therefore implies that the observed rate constants of the reaction remain fairly constant as shown in Tables 4.31- 40.

4.8 Test for the Formation of Intermediate Complex

4.8.1 Spectroscopic test

Spectroscopic tests were carried out to ascertain whether any spectroscopically determinable intermediate complex was formed from the reaction of the oxidant and the reductants. The electronic spectra of partially reacted and product were run between 400– 700nm for the Fe_2O^{4+} - reductant for all the systems. These studies showed that for all the systems under study, there was no shift in $\lambda_{max.}$

Table 4.31: Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$ and $[S_2O_4^{2-}]$ at I = 0.3 mol dm^{-3} (NaCl), $[S_2O_4^{2-}] = 7.0 \times 10^{-3}$ mol dm^{-3}, $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-2}, λ_{max} = 520 nm, T = 26.0 ± 1.0°C

$10^3[K^+]$,(moldm^{-3})	10^3k_{obs} (s^{-1})
00.0	3.15
10.0	3.08
25.0	3.05
50.0	3.04
75.0	3.01
100.0	3.05
125.0	3.01
10^3 $[Mg^{2+}]$ (mol dm^{-3})	
00.0	3.08
10.0	3.00
25.0	3.01
50.0	3.01
75.0	3.05
100.0	3.00
125.0	3.08

Table 4.32: Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$and $[S_2O_4^{2-}]$ at I = 0.3 mol dm^{-3} (NaCl), $[S_2O_4^{2-}] = 7.0 \times 10^{-3}$ mol dm^{-3}, $[Fe_2O^{4+}] = 1.0 \times 10^{-4}$ mol dm^{-3} , λ_{max} = 520 nm, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-2} , T = 26.0 ± 1.0°C

$10^3 [SO_4^{2-}]$ (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})
00.0	3.08
10.0	3.06
25.0	3.01
50.0	3.00
75.0	3.08
100.0	3.01
125.0	3.08
$10^3 [HCOO^-]$ (mol dm^{-3})	
00.0	3.04
10.0	3.10
25.0	3.00
50.0	3.07
75.0	3.10
100.0	3.00
125.0	3.01

Table 4.33: Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$ and $[S_2O_6^{2-}]$ at I = 0.3 mol dm^{-3} (NaCl), $[S_2O_6^{2-}] = 6.0 \times 10^{-3}$ mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, λ_{max} = 520 nm, T = 26.0 ± 1.0°C

$10^3[K^+]$	$10^2 k_{obs}$ (s^{-1})
00.0	1.93
20.0	1.91
40.0	1.95
60.0	1.88
80.0	1.88
100.0	1.93
120.0	1.95
10^3 $[Mg^{2+}]$ (mol dm^{-3})	
00.0	1.93
20.0	1.88
40.0	1.85
60.0	1.93
80.0	1.88
100.0	1.93
120.0	1.93

Table 4.34 : Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$ and $[S_2O_6^{2-}]$ at I = 0.3 mol dm^{-3} (NaCl), $[S_2O_6^{2-}] = 6.0 \times 10^{-3}$ mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520 nm, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, T = 26.0 ± 1.0°C

$10^3 [NO_3^-]$ (mol dm^{-3})	$10^2 k_{obs}$ (s^{-1})
00.0	1.92
20.0	1.88
40.0	1.92
60.0	1.97
80.0	1.92
100.0	1.92
120.0	1.94
$10^3 [HCOO^-]$ (mol dm^{-3})	
00.0	1.93
20.0	1.97
40.0	1.97
60.0	1.93
80.0	1.91
100.0	1.93
120.0	1.90

Table 4.35 : Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$ and $[EH_2]$ at I = 0.3 mol dm^{-3} (NaCl), $[EH_2]$ = 6.0 × 10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3} , λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3} ,T = 26.0 ± 1.0°C

$10^3[K^+]$	$10^2 k_{obs}$ (s^{-1})
00.0	1.36
20.0	1.30
40.0	1.37
60.0	1.31
80.0	1.38
100.0	1.35
120.0	1.37
10^3 $[Mg^{2+}]$ (mol dm^{-3})	
00.0	1.35
20.0	1.30
40.0	1.34
60.0	1.34
80.0	1.35
100.0	1.34
120.0	1.35

Table 4.36 : Dependence of rate constant on added anions for the redox reaction of the $[Fe_2O^{4+}]$and $[EH_2]$ at I = 0.3 mol dm^{-3} (NaCl), $[EH_2]$ = 6.0 × 10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3} , λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3} ,T = 26.0 ± 1.0°C

10^3 $[NO_3^-]$ (mol dm^{-3})	$10^2 k_{obs}$ (s^{-1})
00.0	1.38
20.0	1.38
40.0	1.20
60.0	1.31
80.0	1.26
100.0	1.20
120.0	1.34
10^3 $[HCOO^-]$ (mol dm^{-3})	
00.0	1.39
20.0	1.34
40.0	1.34
60.0	1.36
80.0	1.30
100.0	1.28
120.0	1.28

Table 4.37: Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$ and $[DH_2]$ at I = 0.3 mol dm^{-3} (NaCl), $[DH_2] = 6.0 \times 10^{-3}$ mol dm^{-3}, $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, λ_{max} = 520 nm, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, T = 26.0 ± 1.0°C

$10^3[K^+]$ (mol dm^{-3})	$10^2 k_{obs}$ (s^{-1})
00.0	1.56
20.0	1.52
40.0	1.52
60.0	1.52
80.0	1.50
100.0	1.53
120.0	1.53
$10^3[Mg^{2+}]$ (mol dm^{-3})	
00.0	1.58
20.0	1.54
40.0	1.58
60.0	1.54
80.0	1.51
100.0	1.57
120.0	1.48

Table 4.38: Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$and $[DH_2]$ at I = 0.3 mol dm^{-3} (NaCl), $[DH_2]$ = 6.0 × 10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3} , λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3} , T = 26.0 ± 1.0°C

10^3 $[SO_4^{2-}]$ (mol dm^{-3})	10^2 k_{obs} (s^{-1})
00.0	1.55
20.0	1.52
40.0	1.53
60.0	1.53
80.0	1.50
100.0	1.47
120.0	1.49
10^3 $[HCOO^-]$ (mol dm^{-3})	
00.0	1.55
20.0	1.52
40.0	1.50
60.0	1.48
80.0	1.50
100.0	1.50
120.0	1.48

Table 4.39: Dependence of rate constant on added cations for the redox reaction of $[Fe_2O^{4+}]$ and [GSH] at I = 0.3 mol dm^{-3} (NaCl), [GSH] = 6.0 × 10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0 × 10^{-4} mol dm^{-3} , λ_{max} = 520 nm, $[H^+]$ = 1.0 × 10^{-3} mol dm^{-3} , T = 26.0 ± 1.0°C

$10^3[K^+]$(moldm^{-3})	10^3 k_{obs} (s^{-1})
00.0	4.20
20.0	4.36
40.0	3.63
60.0	3.68
80.0	3.70
100.0	3.70
120.0	3.80
10^3 $[Mg^{2+}]$ (mol dm^{-3})	
00.0	4.32
20.0	4.30
40.0	4.30
60.0	4.20
80.0	4.21
100.0	4.30
120.0	4.21

Table 4.40: Dependence of rate constant on added anions for the redox reaction of $[Fe_2O^{4+}]$ and [GSH] at I = 0.3 mol dm^{-3} (NaCl), [GSH] = 6.0×10^{-3} mol dm^{-3}, $[Fe_2O^{4+}]$ = 2.0×10^{-4} mol dm^{-3}, λ_{max} = 520 nm, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, T = 26.0 ± 1.0°C

10^3 [$HCOO^-$] (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})
00.0	4.10
20.0	4.07
40.0	4.08
60.0	4.20
80.0	4.12
100.0	4.20
120.0	4.20
10^3 [SO_4^{2-}] (mol dm^{-3})	
00.0	4.20
20.0	4.00
40.0	3.90
60.0	3.90
80.0	3.76
100.0	3.82
120.0	4.00

4.8.2 Kinetic test (Michaelis-Menten type plots)

The least square fits for the Michaelis-Menten type plots of $^{1}/_{k_{obs}}$ versus $^{1}/_{[reductant]}$ were linear with zero intercept for the reactions of Fe_2O^{4+} and thioureas (TU, MTU, ATU, DMTU and DETU).The plots are presented in Figures 4.36 – 4.40. This is indicative of the probable absence of intermediates with appreciable equilibrium constant during the course of the electron transfer.

4.9 Free Radical Test

Addition of acrylamide to partially oxidised reaction mixtures of oxidants and reductants showed no gel formation in the presence of excess methanol for all systems studied. This is suggestive of absence of free radical formation during the electron transfer process.

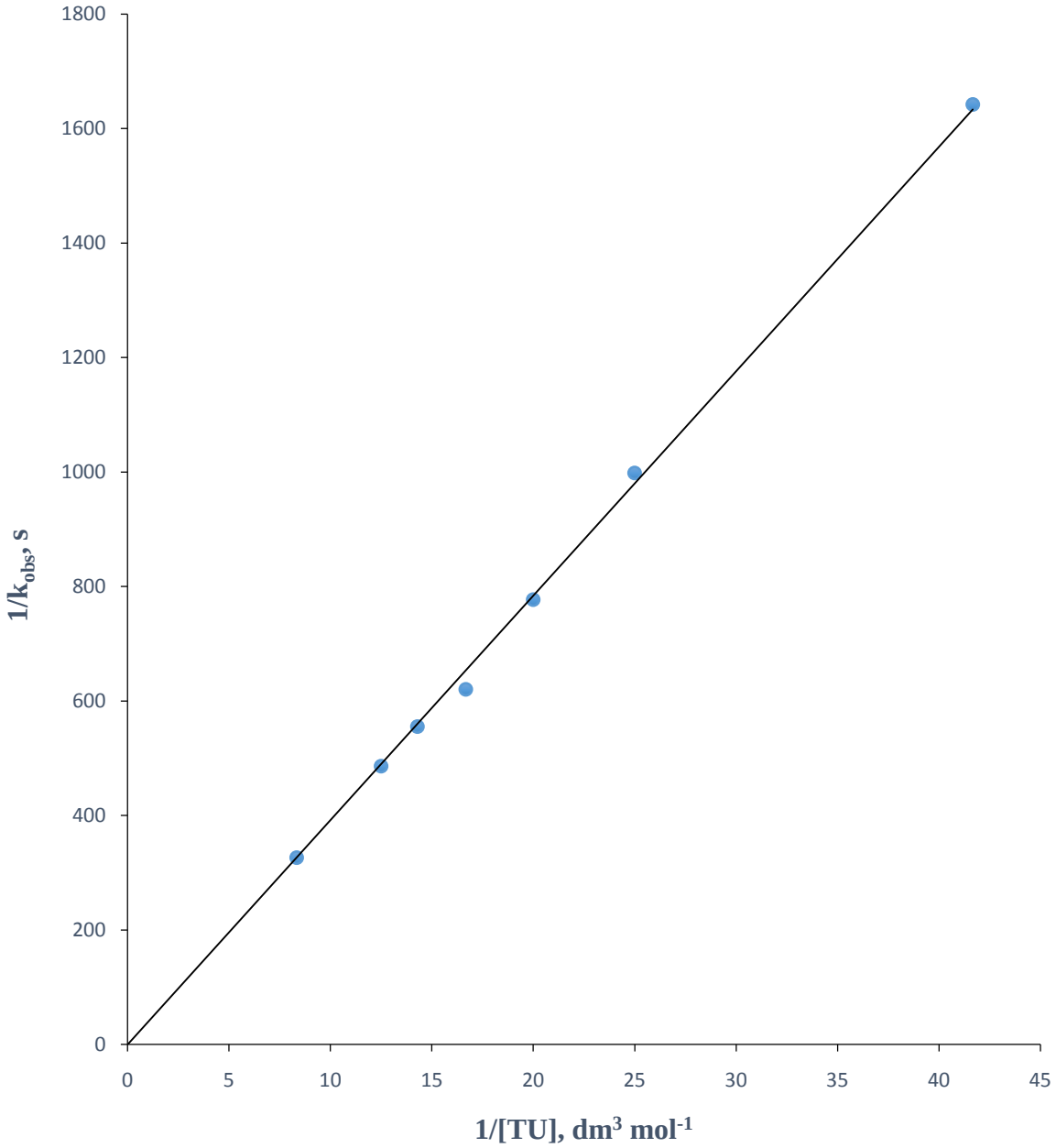


Figure 4.52: Michealis- Menten type plot of $1/k_{obs}$ versus 1/[TU] for the oxidation of TU by Fe_2O^{4+} at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$mol dm^{-3}, [TU] = (2.4 – 12.0) × 10^{-2}mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3mol dm^{-3} (NaCl), T = 27.0 ± 1.0^{o}C and λ_{max} = 520 nm

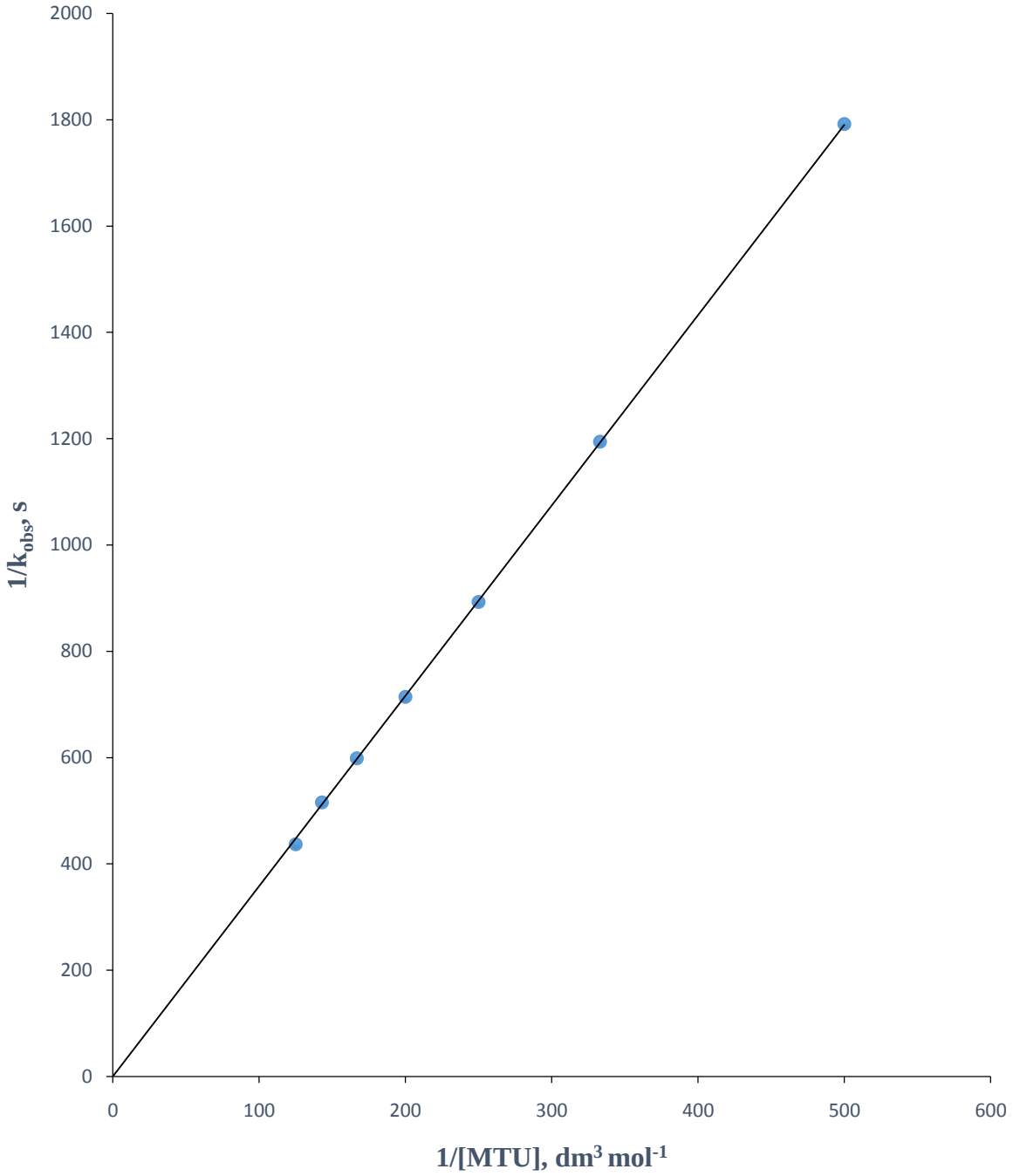


Figure 4.53: Michealis-Menten type plot of $1/k_{obs}$ versus 1/[MTU] for the oxidation of MTU by Fe_2O^{4+} at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$ mol dm^{-3}, [MTU] = (2.0 – 8.0) × 10^{-3} mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm

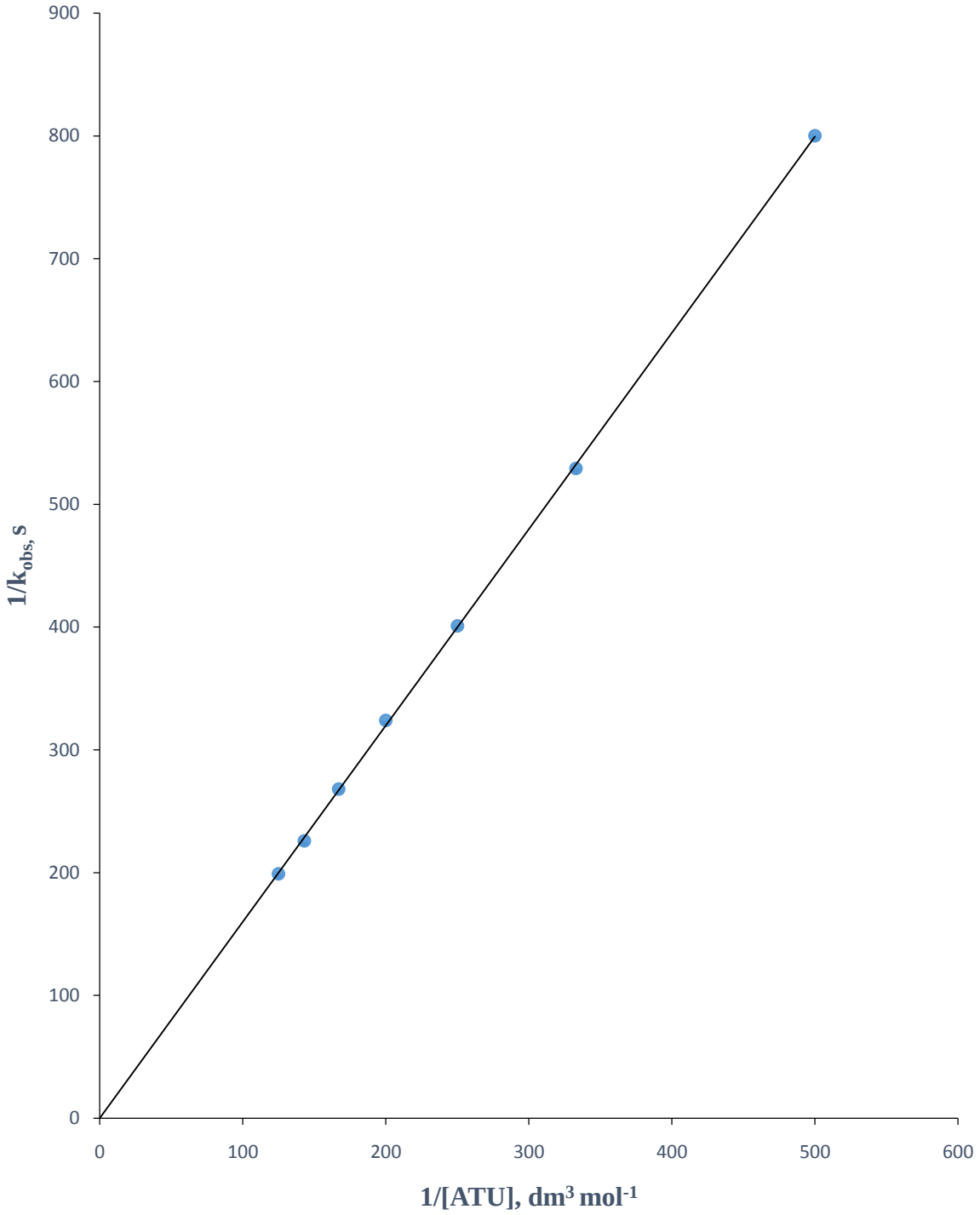


Figure 4.54:Michealis-Menten type plot of $1/k_{obs}$ versus 1/[ATU] for the oxidation of ATU by Fe_2O^{4+}at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$mol dm^{-3}, [ATU] = $(2.0 – 8.0) \times 10^{-2}$mol dm^{-3} $[H^+]$ = 10×10^{-3} mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0°C and λ_{max} = 520 nm

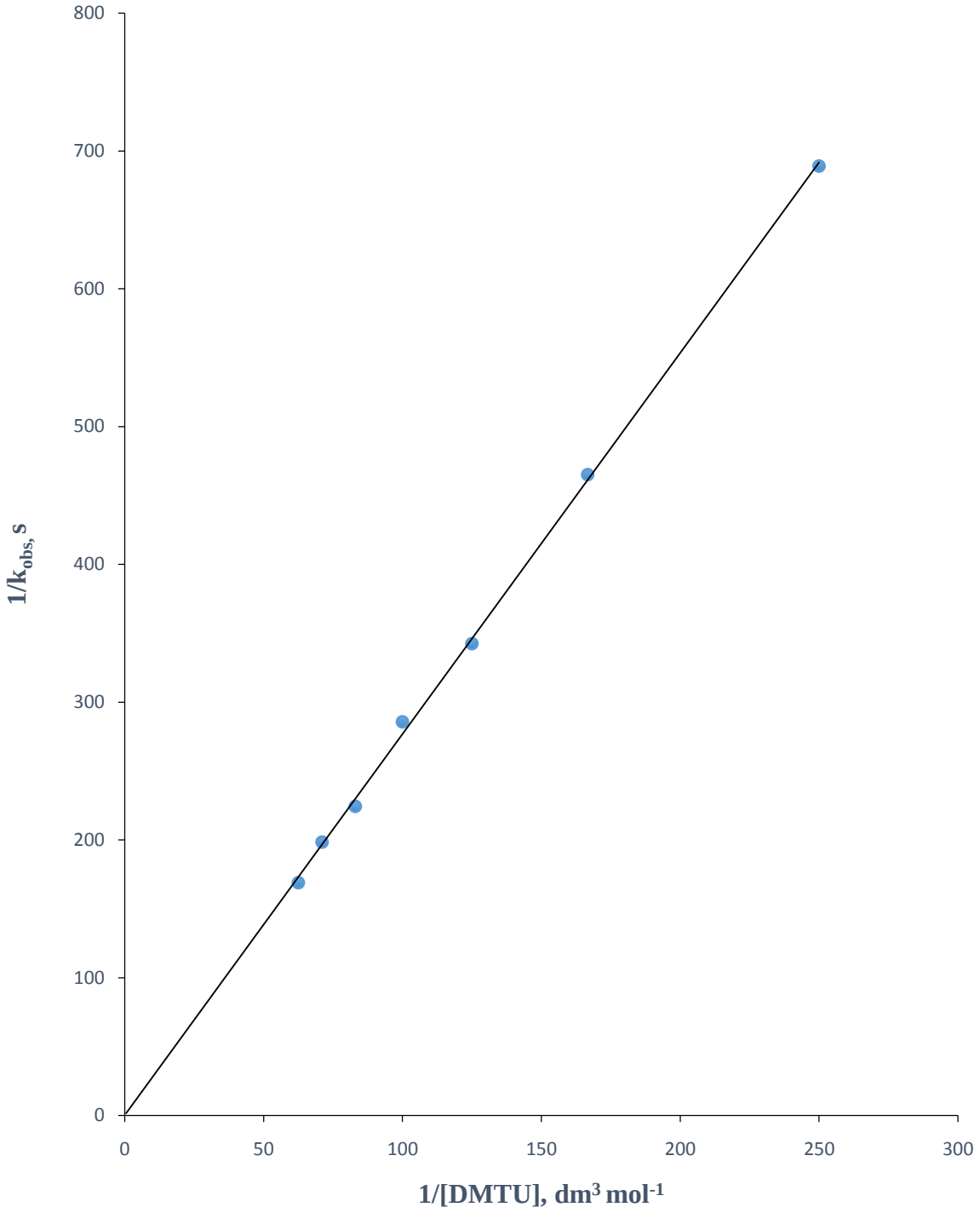


Figure 4.55: Michealis-Menten type plot of $1/k_{obs}$ versus 1/[DMTU] for the oxidation of DMTU by Fe_2O^{4+}at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$mol dm^{-3}, [DMTU] = (4.0 – 16.) × 10^{-3}mol dm^{-3} $[H^+] = 10 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 27.0 ± 1.0^{o}C and λ_{max} = 520 nm

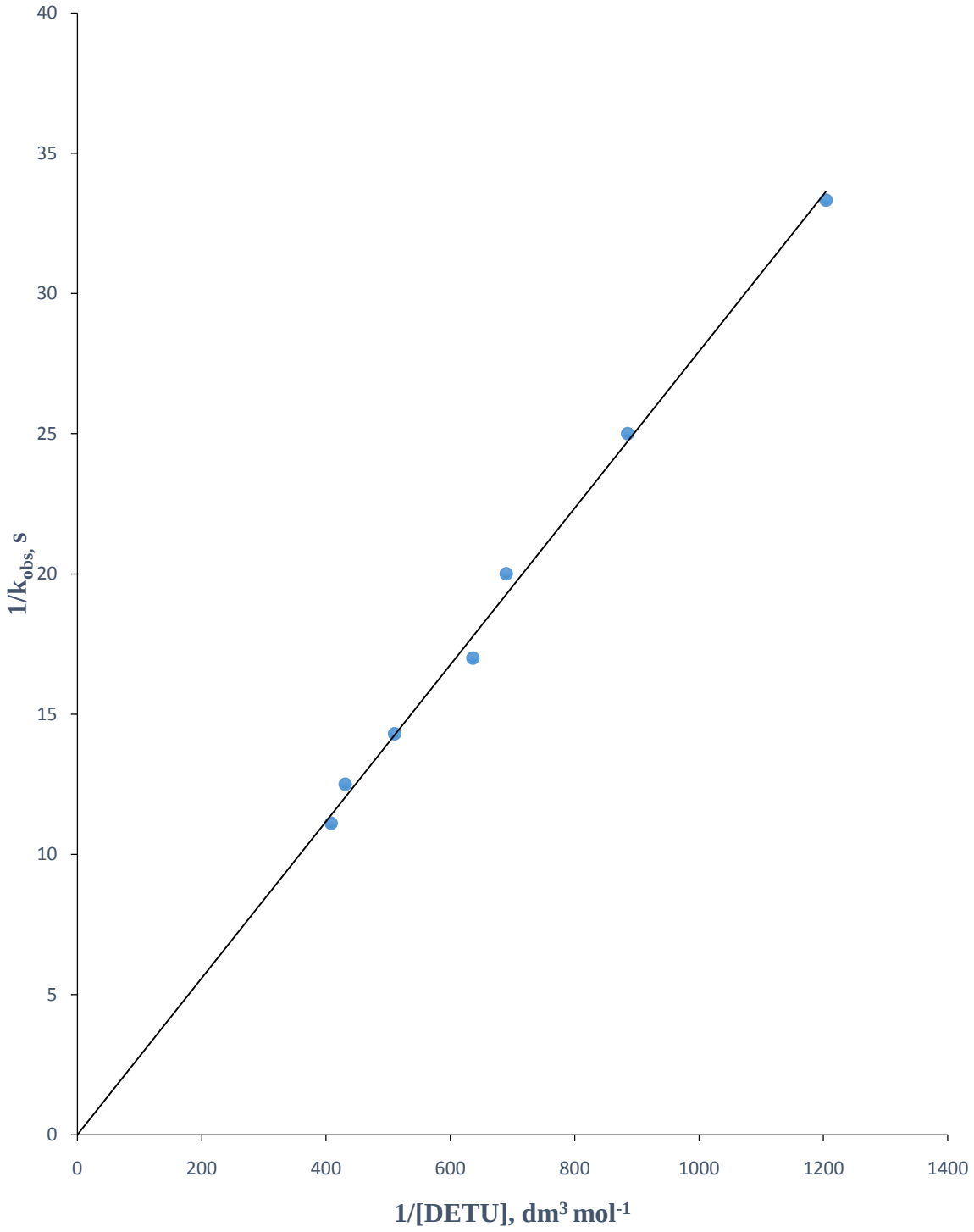


Figure 4.56: Michealis-Menten type plot of $1/k_{obs}$ versus 1/[DETU] for the oxidation of DETU by Fe_2O^{4+} at $[Fe_2O^{4+}] = 2.0 \times 10^{-4}$mol dm^{-3}, [DETU] = (30 - 90) × 10^{-3}mol dm^{-3} $[H^+] = 0.04$ mol dm^{-3}, I = 0.3 mol dm^{-3} (NaCl), T = 30.0 ± 1.0^{o}C and λ_{max} = 520 nm

CHAPTER FIVE

5.0 DISCUSSION

5.1 Fe_2O^{4+}-Reaction with Thiourea and its Derivatives

Stoichiometric studies by using the mole ratio method showed that for every mole of Fe_2O^{4+} consumed, one mole of thiourea (TU) and each of its derivatives (MTU, ATU, DMTU, and DETU) was oxidised. The plots of absorbance versus mole ratio (Fe_2O^{4+} : TU, MTU, ATU, DMTU and DETU) had sharp breaks at 1:1 (Figures 4.1- 4.5), this indicates that I mole of thiourea and each of its derivatives have been oxidised by 1mole of Fe_2O^{4+}. The stoichiometric equation can be represented as:

$$Fe_2O^{4+} + \quad TC{=}S \rightarrow \quad 2Fe^{2+} + \; TC{=}O \quad + \quad S \quad (5.1)$$

whereTC=S represents thioureas, equation 5.1 is similar to equations 4.1 – 4.5.

A similar stoichiometry has been reported for the electron transfer reactions of thiourea, 1,-methyl-2-thiourea, 1,3-dimethyl-2-thiourea, 1,1,3,3-tetramethyl-2- thiourea and 1-allyl-thiourea with µ-superoxobinuclear cobalt(III) complex (Osunlaja *et al*., 2013a, b ; Osunlaja, 2014), and reactions of 1,2 and 1,3 benzenediol with Fe_2O^{4+} (Idris *et al.*, 2004; Idris, 2005). Stoichiometries of 1:2 (Ru_2O^{4+}: reductant) were found for reaction of Ru_2O^{4+} (diaquotetrakis (2, 2□-bipyridine) – μ- oxodiruthenium(III) ion) with (thiourea, methylthiourea, allylthiourea and dimethyl thiourea) (Mohammed *et al*., 2014a, b; Mohammed, 2015). Reactions of ATU with chlorite and chlorine dioxide occurred following 1:2 stoichiometry and resulted into complete desulphurisation of the ATU thiocarbamide to produce the corresponding urea product (Olagunju*et al*., 2006). Similar resultwasobtained in the oxidation of I-phenylthiourea by chlorite (Chigwada *et al*., 2005). The stoichiometry reported in this research is in accordance with thioureas undergoing step-wise two electron oxidation to give the products. The comparison of

reactants and products spectra (Figures 4.11-4.20) supports the formation of new functional group identified as $v(\mathrm{C=O})$ of urea at $1644 \pm 30 cm^{-1}$ (Al-majthouls and Salman, 2012; Osunlaja *et al.,* 2013a, b, c; Osunlaja, 2014) as against $700 \pm 50 cm^{-1}$ of $v(\mathrm{C=S})$ of thiourea and its derivatives (Belgum *et al.,* 2009).

The appearance of an absorption maximum at 520nm in all Fe_2O^{4+} reactions in this study confirmed the formation of Fe^{2+} (Hazra and Lahiri, 1975; Ceulmans and Vanquickenborne, 1981;Ayoko *et al.,* 1993a, b, 1994, 1999, Iyun, *et al.,* 1996; Yusuf *et al.,* 2004; Iyun, 2004; Idris *et al.,* 2004; Idris, 2005). Besides, the absence of absorption peak at 620nm negates the presence of mononuclear complex of iron(III) in the reaction medium.When some portion of the products of reactions of Fe_2O^{4+} with thioureas were reacted with sodium nitroprusside on a tile violet colour was obtained, thus confirming the presence of sulphur (Murugan, 2013), as one of the products as seen in stoichiometric equations. Similar result was obtained in the reaction of thiourea with chlorite ion in acidic medium (Alamgir and Epstein, 1985).

From kinetic studies, the reaction between Fe_2O^{4+} and thioureas has been shown to have first order dependence on each of the reductant concentrations. Pseudo-first order plots of $\log(A_\infty - A_t)$ versus time (Figures 4.27- 4.31) were linear for greater than 80% extent of the reaction indicating first order with respect to$[Fe_2O^{4+}]$. Also plots of $\log k_{obs}$ versus log[TU] (Figure 4.32), log[MTU] (Figure 4.33), log [ATU] Figure (4.34), log [DMTU] (Figure 4.35) and log[DETU] (Figure 4.36) were linear with slopes approximately equal to one, suggesting that reactions are approximately first order in reductant concentrations. The kinetic studies of the oxidation of TU, MTU, ATU, DMTU and DETU with Fe_2O^{4+} hence indicated a second order overall. Similar second order kinetics have been reported for the oxidation of TU, MTU, ATU, DMTU and

TMTU by CoO_2Co^{5+} and methylene blue (Osunlaja *et al.*,2012; 2013a, b; Osunlaja, 2014) and in oxidation of TU, MTU, ATU and DMTU by Ru_2O^{4+} (Mohammed *et al.*, 2014 a, b; Mohammed, 2015).

Thus, these reactions fit into equation 5.2

$$\frac{-d}{dt}[Fe_2O^{4+}] = k_2[Fe_2O^{4+}][\text{thioureas}] \qquad (5.2)$$

The values of k_2 for the five systems at $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, I = 0.3 mol dm^{-3} , T = 27 ± 3^oC and $\lambda_{max} = 520$ nm are as follows:

Fe_2O^{4+}-TU system = (2.58 ± 0.02) ×10^{-2}dm^{3}mol^{-1} s^{-1} with [Fe^2O^{4+}] = 2.0×10^{-4}mol dm^{-3}

Fe_2O^{4+}- MTU system = (27.99 ± 0.03) ×10^{-2} dm^{3}mol^{-1} s^{-1} with [Fe^2O^{4+}] = 2.0×10^{-4}mol dm^{-3}

Fe_2O^{4+}- ATU system = (6.25 ± 0.02) ×10^{-2} dm^{3}mol^{-1} s^{-1} with [Fe^2O^{4+}] = 2.0×10^{-4}mol dm^{-3}

Fe_2O^{4+}- DMTU system = (36.3 ± 0.03) ×10^{-2} dm^{3}mol^{-1} s^{-1} with [Fe^2O^{4+}] =2.0×10^{-4}mol dm^{-3}

Fe_2O^{4+}-DETU system = (2.76 ± 0.05) ×10^{-2} dm^{3}mol^{-1} s^{-1} with [Fe^2O^{4+}]= 2.0×10^{-4}mol dm^{-3}

Within the acid $[H^+]$ range of 4.0×10^{-4} to 1.4×10^{-3}mol dm^{-3}, the rate constants were unaffected by change in hydrogen ion concentration (Tables 4.1 – 4.5).This observed acid independence is in accordance with the result obtained by Osunlaja (2014), in the oxidation reaction of TU, MTU, ATU, DMTU and TMTU by $CoCo_2O^{5+}$. Thus suggested a mechanism in which the hydrogen ion were being taken up by the superoxo complex to form the peroxo complex before it was reduced to the Co^{2+} ion by the C=S moiety.

Varying the ionic strength of the reaction media between 0.1 – 0.6 mol dm^{-3} (NaCl), had no effect on the rates of reaction as shown in Tables 4.1 – 4.5. For reactions of ions in aqueous

media, according to Atkins (1979), the rate of reaction is directly dependent on the square root of the ionic strength of the reaction medium according to equation 5.3.

$\log k_2 = \log k_1 + \beta Z_A Z_B I^{1/2}$ (5.3)

where k_2 = second order rate constant for the reaction, k_1 = hypothetical rate constant in a medium of infinite dielectric constant, Z_A and Z_B = charges on reactants A and B respectively, I = ionic strength of the medium and β = 0.5 at 25 ^{0}C.

If ionic strength is varied, the various values of the second order rate constans, k_2, obtained can be plotted as log k_2 against $\sqrt{I}$. The magnitude of the slope of the plot gives an idea of the product of the charges on the species' reacting in the rate determinig step (Bronsted, 1922). Non-dependence of rate of reaction on ionic strength will likely be due to no charge on one or both of the reactants. Similar observation of ionic strength on the rate of reaction have been noticed in the reactions of Fe_2O^{4+} with mercaptoacetic acid, L-cysteine, 1, 2-benzenediol, 1,3-benzendiol, $S_2O_3^{2-}$ and $S_2O_5^{2-}$ (Idris, 2005; Idris *et al.*, 2004). And in the reaction of Ru_2O^{4+} with TU, MTU, ATU and DMTU (Mohammed *et al.*, 2014a, b; Mohammed, 2015). By using water-acetone mixture at various proportions, the dielectric constant of the reaction medium was varied between 81 – 66.52. Moreover, changes in D had no effect on the reaction rates(Tables 4.11 – 4.15). This suggests that the reaction occurred between cation and neutral molecule.

Added anions inhibited the rate of reaction whereas added cations did not have any effect on the rate of chemical reaction (Table 4.21-4.30). Inhibition of the reaction rate by the added anions shows that the added ions have hindered the approach of reactant species in a simple collision process. The observed inhibition in reaction rate by the added anions in effect suggests that the reactant species are not linked together in the activated complex (Onu, 2010). Test for free

radicals using acrylamide in excess methanol for the five reactions system gave no gel formation confirming non-participation of free radicals in the reactions.

In ascertaining the presence or absence of the formation of interrmediate complexes in the course of the reactions of Fe_2O^{4+} and the thioureas, Michaelis-Menten plots of $1/ k_{obs}$ versus $1/$ [reductant] were made, as applied by Kumar *et al* (1991). All the plots were linear with negligible intercepts, indicating that the intermediates participating in these reactions have no appreciable equilibrium constants thereby ruling out the formation of intermediate complexes in the reactions. For an enzymatic action, under certain assumptions, such as the enzyme concentration being much less than the substrate concentration, the rate of product formation is given by equation 5.4.

$$\frac{d[\text{product}]}{dt} = k_{obs}[E_0] \qquad (5.4)$$

$$k_{obs} = \frac{V_{max}[S]}{k_m + [S]} \qquad (5.5)$$

where k_{obs} is the rate constant for the overall reaction, E_0 is total enzyme concentration, V_{max} represents the rate constant for the break-up of an active intermediate into products and k_m is the Michaelis-Menten rate constant representing the substrate concentration at which the reaction rate is half of V_{max}.. Leonor Michaelis and Maud Menten in 1913 (Johnson and Goody, 2011) observed that by taking the reciprocal of equation 5.5 and rearranging, it becomes equation 5.6.

$$\frac{1}{k_{obs}} = \frac{1}{V_{max}} + \left(\frac{k_m}{V_{max}}\right)[S]^{-1} \qquad (5.6)$$

where for a normal redox reaction, S represents the reductant.

According to equation 5.6, a plot of $1/k_{obs}$ versus $1/[S]$ gives $1/V_{max}$ as intercept. However, if, a linear plot which passes through the origin is obtained, it shows that the intercept is zero and $1/V_{max}$ is zero. This means that V_{max} or the equilibrium constant for the active intermediates is zero (Ukoha, 1999).

Within the limit of experimental condition employed in this research, the following results were relevant for proposing a mechanism: (a) 1 mole of Fe_2O^{4+} reacts with 1 mole each of thioureas; (b) chemical species (Fe_2O^{4+} and thioureas) involve in the reaction remained separate and intact before, during, and after the electron transfer event; (c) and the only activity in terms of oxidation (electron transfer and/or hydrolysis) is occurring at the sulphur centre of the thioureas ; (d) there is successive transfer of electron from the sulphur centre of thioureas to the oxobridge centre of binuclear complex of iron(III), (e) in the process oxygen dislodged sulphur from thiourea, thereby forming urea, the replacement of sulphur with oxygen is probably due to the fact that the electronegativity of oxygen is higher than that of sulphur. Moreover, based on these experimental results, the following mechanistic scheme is proposed:

Rate = $k_4[Fe^{2+}\text{-O- C =S}]$ (5.12)

Application of steady state hypothesis to $[Fe^{2+}\text{-O- C =S}]$ gives:

$k_3[Fe^{2+}\text{-O}][\text{-C=S}]\text{-}k_{-3}[Fe^{2+}\text{-O- C =S}]\text{-}k_4[Fe^{2+}\text{-O- C =S}] = 0$ (5.13)

$[Fe^{2+}\text{-O- C =S}] = \frac{k_3[Fe^{2+}-O][-C=S]}{k_{-3}+k_4}$ (5.14)

Rate = $\frac{k_4k_3[Fe^{2+}-O][-C=S]}{k_{-3}+k_4}$ (5.15)

If $\frac{k_3[Fe^{2+}-O]}{k_{-3}+k_4} \approx [Fe^{2+}\text{-O- }Fe^{2+}]$

Rate = $k_4[Fe^{2+}\text{-O- }Fe^{2+}][\text{-C =S}]$ (5.16)

With recourse to the above mechanism, there is transfer of electron from the C=S moiety of thiourea to the oxobridge and Fe^{3+}centre, leading to the formation of urea (C=O), methyl thiourea, allyl thiourea, dimethyl thiourea and diethyl thiourea follow similar route.

The basis for proposing the above mechanistic scheme is as follows:

(a) Absence of spectroscopic evidence suggests that a precursor complex is probably not formed prior to the act of electron transfer and that the electron transfer may occur by the outer-sphere path.

(b) Michaelis-Menten's plots of $1/k_{obs}$ versus 1/[thioureas] was found to be linear without positive intercept suggesting the absence of a pre-association step. This also favours the outer-sphere mechanism.

(c) The negative result of polymerization test suggests the absence of free radical intermediate in the reaction or the equilibrium constant for the formation of such radicals can be assumed to be negligible (Idris, 2005).

(d) A general inhibition of the rate of reaction by anions also point to the outer-sphere pathway in the electron transfer processes for these reactions. Such rationalization for anions effect on reaction rate havebeen reported for different redox systems(Iyun, 1990; Lohdip, 1999; Idris *et al.*, 2004).

Based on the issues raised in (a) – (d)an outer-sphere mechanistic pathway is proposed for these reactions.

5.2 Fe_2O^{4+} Reaction with $S_2O_4^{2-}$ and $S_2O_6^{2-}$

Stoichiometric investigation by the use of spectrophotometric titration showed that one mole of $S_2O_4^{2-}$ or $S_2O_6^{2-}$ is oxidised per mole of Fe_2O^{4+}(Figures 4.6- 4.7) and are shown in equations 4.6-4.7. Similar stoichiometry was reported for the reactions of dithionite with dicyanoporphyrinato ferrate(III) complex (Worthington and Hambright, 1980), p-phenylazobenzene sulphonic acid(Washmuth *et al*., 2008), monomethyl fuchsin (Onu and Iyun, 2000), potassium ferrate (Read *et al.,* 2001), toluidine blue (Hamza *et al*., 2012), malachite

green (Idris *et al*., 2015), adipato bridged iron(III)-salen complex (Ukoha *et al.*, 2015)and Ru_2O^{4+} (Mohammed, 2015). The stoichiometry of 1:1was also reported in the reaction of dithionate with toluidine blue (Babatunde and Ajaiyi, 2013), however in the reaction between $[FeSalen(H_2O)_2]^+$ and dithionate, two moles of the oxidant were consumed by one mole of dithionate (Ukoha *et al.*, 2010).

Kinetics studies of the reduction of Fe_2O^{4+} by $S_2O_4^{2-}$ and $S_2O_6^{2-}$ indicated first order dependence on the [oxidant]. Pseudo first order plots of log (A_∞ -A_t) versus time were linear (Figure 4.37 and 4.38) for about 75% of extent of reaction with respect to each reductant. The values of k_{obs}, evaluated from the slopes of the pseudo-first order plots were constant within the range of the concentrations of $S_2O_4^{2-}$ and $S_2O_6^{2-}$studied. This implies that variation in the concentration of the above reductants did not affect the rate of the reaction. In other word, the reaction waszero order on [$S_2O_4^{2-}$] and [$S_2O_6^{2-}$].The zero order dependence on the reductants ($S_2O_4^{2-}$ and $S_2O_6^{2-}$) is similar to the report given by Idris (2005), in the reaction of Fe_2O^{4+} with other sulphur oxyanions ($S_2O_3^{2-}$ and $S_2O_5^{2-}$). Nonetheless, first order with respect to oxidant and reductant was reported in the reaction of dithionite withmonomethyl fuchsin (Onu and Iyun, 2000), toluidine blue (Hamza *et al.*, 2012), malachite green (Idris *et al.*, 2015) andRu_2O^{4+} (Mohammed, 2015).

In the acid range of $(4.0 - 14) \times 10^{-4}$mol dm^{-3} the rate of reaction was independent of $[H^+]$ in the reaction of Fe_2O^{4+} with the two reductants. Similar observation has been reported by Idris (2005) in the reactions of Fe_2O^{4+} with $S_2O_3^{2-}$, $S_2O_5^{2-}$, mercaptoacetic acid, L-cysteine, 1,2-benzendiol and 1,3-benzenediol. The non-dependence nature of acid on the rate of the reactions of the two systems, underscore the relative non relevance of the process:

The instability of the Fe-O-Fe bridge in acid solutions has been reported (Schugar *et al.*, 1972; Rajeswari *et al.*, 1975; Baesi and Mesner, 1976; Ukoha, 1999; Idris, 2005). The presence of acid weakens Fe-O-Fe bond due to protonation at the bridged oxygen, thereby forming mononuclear species and this process is supposed to result in direct acid dependence. Nevertheless, the non-dependence of the rate on change in $[H^+]$ in these systems depicts the insignificant nature of the processas illustrated by equation 5.12 in the systems. It was also observed that at greater than 2.0 $\times 10^{-3}$ mol dm^{-3} of $[H^+]$, Fe-O-Fe was unstable and cleavage of the oxo-bridge resulted in change of colour of the complex from brown to deep red.

There was no significant change in the rate of reaction when the ionic strength of the reaction media was varied between 0.1 – 0.6 mol dm^{-3} (NaCl), as shown in Tables 4.6 – 4.7. Non-dependence of rate of reaction on ionic strength is a common feature of reaction occuring between ion and neutral species where the products of charges is zero at transition state (Atkins, 1979) and could also be due to ion-pair interaction at the activated complex. Since ion-pair complex does not possess a formal charge, the rate of reaction would also not be affected by changes in ionic strength if ion-pairs are involved in reactions with outersphere character (Iyun *et al*., 1992a,1995b). By using water-acetone mixture at various proportions, the dielectric constant of the reaction medium was varied between 81 – 69.39 and 81 – 68.27 for Fe_2O^{4+} - $S_2O_4^{2-}$ and Fe_2O^{4+} - $S_2O_4^{2-}$ systems respectively. The studies showed that changes in D had no effect on the reaction rates (Tables 4.16 – 4.17). This suggests that the reaction occurred between cation and neutral molecule or free radical. This is also consistent with a reaction involving ion-pairs with outersphere character (Iyun *et al*., 1992a,1995b)

Added anions and cations did not affect the reaction rates in the reactions between Fe_2O^{4+} and dithionite or dithionate ion (Tables 4.31 – 4.34). Absence of ion catalysis is in line with the formation of ion – pairs in the reaction prior to electron transfer. Since the ion-pair complex does not have a formal charge, interaction with added ions will not be possible suggesting that the reaction might have proceeded via the outersphere pathway. The non dependence of the added ions on the rate, however, further depict that the reactant ions are not linked together at the activated complex. Formation of ion-pair intermediates have been reported in the reaction of Ru_2O^{4+} with 2-mercaptoethanol, 2-mercaptoethylamine (Iyun *et al.*,1995b) and thioureas (TU, ATU, MTU and DMTU) (Mohammed *et al.,* 2014a,b; Mohammed, 2015), $[(FeHEDTA)_2O]^{2-}$ with mercaptoacetic acid (Ukoha, 1999) and Fe_2O^{4+} with $S_2O_3^{2-}$, $S_2O_5^{2-}$, mercaptoacetic acid, L-cysteine, 1,2-benzenediol and 1,3-benzenediol (Idris *et al.,* 2004; Idris, 2005). Spectroscopic studies of the reaction mixture did not implicate stable intermediate complexes as there was no shift in λ_{max} , but an isosbestic point was obtained at 520nm.The SO_4^{2-} was identified qualitatively by formation of white precipitate on addition of HCl and $BaCl_2$ solution to the reaction products in the reaction of Fe_2O^{4+} - $S_2O_4^{2-}$. Same observation was obtained for the Fe_2O^{4+} - $S_2O_6^{2-}$system, and the precipitate discolourized $KMnO_4$ solution, which ruled out the presence of SO_4^{2-} in the reaction product. With recourse to the experimental data schemes I and II are proposed as the mechanistic pathways for Fe_2O^{4+} - $S_2O_4^{2-}$ and Fe_2O^{4+} - $S_2O_6^{2-}$ systems respectively.

Scheme I

In view of the known equilibrium between dimer and monomer species of dithionite (Rinker *et al*., 1959; Burlamacchi, 1967, 1969; Srividya *et al.,* 1994), there exists two basic mechanisms for the reduction of oxidants by dithionite, one involves $S_2O_4^{2-}$, the other SO_2^- as the reducing species. With regard to the system under investigation the equilibrium that result in the formation of a dimeric species represented as

is unimportant, the only reacting specie is $S_2O_4^{2-}$. Moreover, the mechanistic route of scheme I is as:

Application of steady state hypothesis to $[Fe_2O^{3+}]$ gives:

$$k_2[Fe_2O^{4+},S_2O_4^{2-}]-k_{-2}[Fe_2O^{3+}][S_2O_4^-]-k_3[Fe_2O^{3+}] = 0 \qquad (5.25)$$

$$k_2[Fe_2O^{4+},S_2O_4^{2-}]-[Fe_2O^{3+}](k_{-2}[S_2O_4^-]+k_3) = 0 \qquad (5.26)$$

$$[Fe_2O^{3+}] = \frac{k_2[Fe_2O^{4+},\ S_2O_4^{2-}]}{k_{-2}[S_2O_4^-]+k_3} \qquad (5.27)$$

Substituting equation 5.27 into 5.24gives:

Rate = $\frac{k_3 k_2 [Fe_2O^{4+}, \ S_2O_4^{2-}]}{k_{-2}[S_2O_4^{-}] + k_3}$ (5.28)

If $k_3 \ll k_{-2}[S_2O_4^{-}]$ equation 5.28gives:

Rate = $\frac{k_3 k_2 [Fe_2O^{4+}, \ S_2O_4^{2-}]}{k_{-2}[S_2O_4^{-}]}$ (5.29)

From equation (5.19)

$[Fe_2O^{4+}, S_2O_4^{2-}] = \frac{k_1}{k_{-1}}[Fe_2O^{4+}][S_2O_4^{2-}]$ (5.30)

Substituting equation 5.30 into 5.29 gives :

Rate = $\frac{k_1 k_2 k_3}{k_{-1}} \frac{[Fe_2O^{4+}][S_2O_4^{2-}]}{k_{-2}[S_2O_4^{-}]}$ (5.31)

If $[S_2O_4^{2-}] \approx k_{-2}[S_2O_4^{-}]$ equation 5.31 reduces to:

Rate = $\frac{k_1 k_2 k_3}{k_{-1}}[Fe_2O^{4+}]$ (5.32)

where $\frac{k_1 k_2 k_3}{k_{-1}} = k_{obs}$ (5.33)

$\therefore$ rate = $k_{obs}[Fe_2O^{4+}]$ (5.34)

Equation 5.34 is analogous to equation 4.11

Scheme II

Application of steady state hypothesis for $[Fe_2O^{3+}]$ gives:

$$[Fe_2O^{3+}] = \frac{k_2[Fe_2O^{4+}, \ S_2O_6^{2-}]}{k_{-2}[S_2O_4^{-}] + k_3} \quad (5.40)$$

Substituting equation (5.35) into (5.34) givesn

$$\text{Rate} = \frac{k_3 k_2[Fe_2O^{4+}, \ S_2O_6^{2-}]}{k_{-2}[S_2O_6^{-}] + k_3} \quad (5.41)$$

If $k_3 \ll k_{-2}[S_2O_6^{-}]$Equation (5.36) gives

$$\text{Rate} = \frac{k_3 k_2[Fe_2O^{4+}, \ S_2O_6^{2-}]}{k_{-2}[S_2O_6^{-}]} \quad (5.42)$$

From equation 5.35

$$[Fe_2O^{4+}, S_2O_6^{2-}] = \frac{k_1}{k_{-1}}[Fe_2O^{4+}][S_2O_6^{2-}] \quad (5.43)$$

Substituting equation 5.43 into 5.42 gives:

$$\text{Rate} = \frac{k_1 k_2 k_3}{k_{-1}} \frac{[Fe_2O^{4+}][S_2O_6^{2-}]}{k_{-2}[S_2O_6^{-}]} \quad (5.44)$$

If $[S_2O_6^{2-}] \approx k_{-2}[S_2O_6^{-}]$ equation 5.44 reduces to:

$$\text{Rate} = \frac{k_1 k_2 k_3}{k_{-1}}[Fe_2O^{4+}] \quad (5.45)$$

Where $\frac{k_1 k_2 k_3}{k_{-1}} = k_{obs}$ (5.46)

$\therefore$ rate = $k_{obs}[Fe_2O^{4+}]$ (5.47)

Thus equation 5.47 is analogous to equation 4.11.

With respect to the proposed mechanisms, since Fe_2O^{4+} is coordinatively saturated, there would be substitution inertness thereby the ease of a ligand – bridged intermediate of inner-sphere character is remote. This rationalization is further buttressed by (i) absence of spectrophotometric evidence for precursor complex as scanning the reaction mixture as the reaction progressed did not show any shift in wavelength of maximum absorption. (ii) The negative result of polymerization test suggests the absence of free radical intermediate in the reaction or the equilibrium constant for the formation of such radicals can be assumed to be negligible (Idris, 2005). (iii) the above views are reinforced by the lack of anions and cations catalysis which might be due to the fact that, the rate determining steps in these reactions involved dissociation of the oxidant intermediates. These species are likely to exhibit little or no interaction with the added ions. Therefore the above mechanistic schemes followed outer-sphere with ion-pair character.

5.3 Fe_2O^{4+} Reaction with Carbazides (Semicarbazide and Diphenylcarbazide)

Spectrophotometric titration following the mole ratio method indicated that for every one mole of Fe_2O^{4+} one mole each of semicarbazide and diphenyl carbazide is oxidised (Figures4.8- 4.9). The stoichiometry of 1:1 (Fe_2O^{4+}: carbazides) obtained in the reactions is analogous to the result obtained for the reduction of $Fe_2(bipy)_4O^{4+}$ by catechol (Idris *et al*., 2004) and for the reduction of $[(FeHEDTA)_2O]^{2-}$ by ascorbic acid (Ukoha, 1999).

Kinetic studies show that the reaction is first order in $[Fe_2O^{4+}]$ owing to the fact that, the plots of log $(A_\infty - A_t)$versus time using the equation:

$$\log(A_\infty - A_t) = \frac{k_1 t}{2.303} + \log(A_t - A_\infty) (5.48)$$

was linear for about 75% of the reaction time (Figures 4.39-4.40).

From the slope of the plots, k_{obs} was obtained while the order in [carbazides] for $[Fe_2O^{4+}]$ - [carbazides] was zero because the k_{obs} was constant within the range of the concentrations of carbazides studied. Also using the Van't Hoff differential equation

$$R = k[A]^n \quad (5.49)$$

where $[A]$ is the concentration of the reactant. The values of the slopes were zero for the two carbazides.

Fourier Transform Infrared spectroscopy technique was used to test for the organic products of the reaction involving carbazides(i.e semicarbazide and diphenylcarbazide) and Fe_2O^{4+}. The spectra of the two reductants and the products of the reactions of the two systems were respectively taken (Figures 4.23 - 4.26). From the spectrum of semicarbazide, the absorption bands at 3252.09cm^{-1} and 3430.51cm^{-1} are due to symmetrical and asymmetrical stretching of NH_2 (Binil *et al.,* 2013; Janarthanan *et al.,* 2012). The band at 1687.77cm^{-1}, comes from ν(C=O) stretching of the molecule. From the diphenylcarbazide spectrum, the band at 756.6cm^{-1} is assigned to the stretching of the phenyl group of the molecule, ν(C=O) stretching of the molecule is assigned 1651cm^{-1}. Moreover, considering the products spectra of the two systems respectively, it is obvious that the C=O bond present in the two reductants are still present in the products: in Fe_2O^{4+} - EH_2 product,1644.37cm^{-1} comes from ν(C=O) stretching. Similarly in the Fe_2O^{4+} - DH_2 product, 1666.1cm^{-1} band is assigned to ν(C=O). Also in the Fe_2O^{4+} - DH_2 product

spectrum, the peak at 749.2cm^{-1} is the stretching of the phenyl group. On the basis of FTIR, it is highly apparent that the organic products formed from the two systems contained C=O functional group, and the phenyl group in the DH_2 is also present in the product of the reaction between the complex and DH_2. Perhaps, it can be asserted that the only different between the reductants of the two systems and their organic products is difference in the number of hydrogen. The number of hydrogen in the organic products of the two systems would be less than those of the reductants prior to the reactions.

Within the acid concentration range of $4.0 \times 10^{-4} - 1.4.0 \times 10^{-3}$ mol dm^{-3}, the rate of reaction was independent of change in [H^+] (Tables 4.8 - 4.9). Though, there is no literature evidence to account for the effect of acid on the rate of reaction that involved carbazides and any given oxidant. One would have expected the deprotonation of two moles of protons from each reductant in the course of the reaction. The two moles of protons then combined with O^{2-} (oxo), after the rupture of oxobridge of the binuclear complex to form water as seen in the stoichiometric equation.Added anions did not have any effect on reaction rates in the reactions between Fe_2O^{4+} and carbazides (Tables 4.35 – 4.38). Absence of ion catalysis is in line with the formation of ion – pairs in the reaction prior to electron transfer. Since the ion – pair complex does not have a formal charge, interaction with added ions will not be possible suggesting that the reaction might have proceeded through the outersphere pathway. Iyun *et al* (1995c) have reported formation of ion-pair intermediates in the reaction of Ru_2O^{4+} with 2-mercaptoethanol and 2-mercaptoethylamine.

On addition of acrylamide to the reaction mixtures for the two systems followed by excess methanol, there was no gelatinous precipitate formation, suggesting that polymerisation has not occurred. This confirms the absence of free radicals during the reactions. The rate of reaction was observed to be independent of variation in concentration of ionic strength. Non-dependence of rate of reaction on ionic strength could likely be due to no charge on one or both of the reactants. Since ion-pair complex does not possess a formal charge, the rate of reaction would also not be affected by changes in ionic strength if ion-pairs are involved in reactions with outersphere character (Iyun *et al*., 1992a,1995c).

By using water-acetone mixture at various proportions, the dielectric constant of the reaction medium was varied between 81 – 68.27 and 68.90 - 58.74 for Fe_2O^{4+}/EH_2 and Fe_2O^{4+}/DH_2 respectively. Our studies showed that changes in D had no effect on the reaction rates. (Tables 4.18 – 4.19). This suggests that the reaction occurred between cation and neutral molecule or free radical. This is also consistent with a reaction involving ion-pairs with outersphere character (Iyun *et al*., 1992a,1995c).

Spectral scanning during the reactions gave clear isosbestic points at 520 nm, indicating absence of significant amounts of reaction intermediates. This suggests that an intermediate complex is most likely not formed between the reactant ions, suggesting the reaction might occur by the outer-sphere mechanism (Iyun *et al.*, 1992c).

Based on the above findings, the mechanism of reaction has been rationalized on the basis of outer-sphere pathway, and the following mechanism is proposed

Application of steady state hypothesis for $[Fe_2OH^{5+}, R^{2-}]$ gives:

$$k_3[Fe_2OH^{5+}][RH^-] - k_{-3}[Fe_2OH^{5+}, R^{2-}][H^+] - k_4[Fe_2OH^{5+}, R^{2-}] = 0 \qquad (5.57)$$

$$[Fe_2OH^{5+}, R^{2-}] = \frac{k_3[Fe_2OH^{5+}][RH^-]}{k_{-3}[H^+] + k_4} \qquad (5.58)$$

Application of steady state hypothesis for $[Fe_2OH^{5+}]$ gives:

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2O^{4+}][H^+]}{k_{-2} + k_3[RH^-]} \qquad (5.59)$$

If $k_{-3}[H^+] \gg k_4$ equation 5.58 reduces to

$$[Fe_2OH^{5+}, R^{2-}] = \frac{k_3[Fe_2OH^{5+}][RH^-]}{k_{-3}[H^+]} \qquad (5.60)$$

From equation 5.59, if $k_{-2} \gg k_3[RH^-]$ then the equation reduces to

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2O^{4+}][H^+]}{k_3[RH^-]} \qquad (5.61)$$

Substituting equation 5.61 into 5.60 gives:

$$[Fe_2OH^{5+}, R^{2-}] = \frac{k_2 k_3 [Fe_2O^{4+}][H^+][RH^-]}{k_{-3}[H^+]k_3[RH^-]} \quad (5.62)$$

$$[Fe_2OH^{5+}, R^{2-}] = \frac{k_2}{k_{-3}}[Fe_2O^{4+}] \quad (5.63)$$

Substituting equation 5.63 into 5.56gives :

$$\text{Rate} = \frac{k_2}{k_{-3}}[Fe_2O^{4+}] \quad (5.64)$$

Where $\frac{k_2}{k_{-3}} = k_{obs}$ (5.65)

$\therefore$ rate = $k_{obs}[Fe_2O^{4+}]$(5.66)

Thus equation 5.66 is similar to equation 4.11

On the basis of above findings, the mechanism of reaction is proposed to follow outersphere withion-pairs character .

5.4 Fe_2O^{4+} Reaction with Glutathione (GSH)

Stoichiometric studies showed that one mole of Fe_2O^{4+} is reduced per two moles of GSH oxidised. The overall reactions can be represented in equation 4.9. The stoichiometry of 1:2 (oxidant: reductant) is in agreement with the literature report given as follows: Ru_2O^{4+} with glutathione (Ayoko *et al*., 1993b), Iron(III)-2,2□-bipydridyl withmethionine (Tiruveedhula *et al*., 1995),Ru_2O^{4+} with L-cysteine (Iyun *et al*., 1996), $[(FeHEDTA)_2O]^{2-}$ with mercaptoacetic acid, mercaptoethylamine and mercaptoethanol (Ukoha, 1999; Ukoha and Iyun, 2001). However, this mole ratio is not analogous to 1:1 (oxidant: reductant) reported foroxidation ofmercaptoacetic acid by 12-tungstocobaltate(III) (Ayoko, 1981; Ayoko and Olatunji, 1983), tris (polypyridyl) iron(III) complex with glutathione (Ayoko *et al.,* 1993a), reaction

oftrisoxalatocobaltate(III) iron with mercaptoacetic acid (Lawal *et al.,* 1994),Ru_2O^{4+} with mercaptoethylamine and mercaptoethanol (Iyun *et al.,* 1995c), Ru_2O^{4+} with mercaptoacetic acid (Musa *et a.,l* 1998), oxidation of mercaptoacetic acid and L-cysteine by Fe_2O^{4+} (Idris *et al.,* 2004; Idris,2005).

Tiruveedhula *et al.,* (1995) reported that the oxidation of many thiols can give rise to many products depending on the nature of the oxidant. Methionine and mercaptobenzoic acid were oxidised to sulphoxide by oxidants such as chloroauric acid, Cr(IV), hexachloroiridate sulphite, iron (III) -2, 2'-bipyridyl and $Mn^{II}O_2M^{IV}$ (Yan, 1970;Natile *et al.,* 1976; Goswami *et al.,* 1981; Olatunji and Ayoko, 1988; Ayoko *et al.,* 1992 ; Tiruveedhula *et al.,* 1995; Lohdip and Iyun, 1998; Lohdip, 1999). In the reaction of Fe_2O^{4+} with mercaptoacetic acid and L-cysteine, derivative of sulphonic acid was obtained as the organic product (Idris *et al.,* 2004:Idris2005). However disulphide (GSSG) was formed as the only organic product in the reactions and this was confirmed using the method of McAuley and Gowack (1968 and 1969) as reported earlier. Subsequently the crystals obtained from the above method was subjected to FTIR in order to authenticate the formation of disulphide (GSSG). The weak absorption at $\nu(542)cm^{-1}$ confirmed the formation of disulhpide (GSSG). Disulphide formation has been observed in the reactions of $Ru_2O^{4+}$with L-cysteine (Iyun *et al.,* 1996), and mercaptoacetic acid (Musa *et al.,* 1998) and $[(FeHEDTA)_2O]^{2-}$

with mercaptoacetic acid, mercaptoethanol and mercaptoethylamine (Ukoha 1999; Ukoha and Iyun, 2001),

Kinetic studies of the reduction of Fe_2O^{4+} by GSH indicated first order dependence on the $[Fe_2O^{4+}]$. Pseudo-first order plots of $\log(A_\infty - A_t)$ versus time were linear (Figure 4.41) for about 85% extent of reaction. The invariance of k_{obs} in Table 4.10 indicated zero order dependence on the [GSH]. The rate of redox process can therefore be represented as;

$$\frac{1}{2}\frac{d[Fe^{2+}]}{dt} = k_{obs}[Fe_2O^{4+}] \qquad (5.67)$$

The zeroth order with respect to [GSH] is similar to what was obtained in the reduction of Fe_2O^{4+} by mercaptoacetic acid and L-cysteine (Idris, 2005). However, this result does not conform to the result from earlier researchers. For instance, first order dependence were observed on both [reducant] and [oxidant] in the oxidation of mercaptoethanol, mercaptoethylamine and mercaptoacetic acid by Ru_2O^{4+} (Iyun *et al.*, 1995c; Musa *et al.*, 1998) and $[(FeHEDTA)_2O]^{2-}$ (Ukoha, 1999; Ukoha and Iyun, 2001), in the reactions of Cr(VI) with L-cysteine (Iyun and Tinounye, 1998), mercaptoacetic acid by IO_3^- (Ukoha and Ibrahim, 2004) and mononuclear Fe(III) with thiols (Wiberg *et al.*, 1968).

Within the acid range of $(4.0 - 14) \times 10^{-4}$mol dm^{-3} the rate of reaction displayed non-dependence on $[H^+]$ in the reaction ofFe_2O^{4+} and GSH. Similar report has been posited in the reaction of the oxidant (Fe_2O^{4+})with mercaoptacetic acid and L-cysteine (Idris, 2005).On the other hand, increased in reaction rate with increase in $[H^+]$ has been reported in the reaction of thiols with trisoxalatocobaltate(III) ion (Lawal *et al.*, 1994) and trispolypyridyl iron(III) complexes (Ekubo, 1992; Ayoko *et al.*, 1993a, b), also inverse acid dependence in thiols reaction with Ru_2O^{4+}(Ayoko *et al.*, 1993c; Iyun *et al.*, 1995c, 1996; Musa *et al.*,1998),iron(III)-2,2□-bipyridyl (Tiruveedhula *et al.*, 1995),Cr(VI) (Iyun and Tinouye 1998), and $[(FeHEDTA)_2O]^{2-}$

(Ukoha, 1999; Ukoha and Iyun, 2001) have been reported. Varying the ionic strength of the reaction media between 0.1 – 0.6 mol dm^{-3} (NaCl), had no effect on the rates of reaction as shown in Tables 4.10. Change in the dielectric constant of the medium did not affect the rate of the reaction as well. Similar observation with respect tothe effect of ionic strength and dielectric constant on the reaction rate have been noticed in the reaction of $[(FeHEDTA)_2O]^{2-}$ with mercaptoethylamine and mercaptoethanol (Ukoha and Iyun, 2001) and $Fe_2O^{4+}$with mercaptoacetic acid and L-cysteine (Idris, 2005). Nonetheless reactions of mercarptoacetic acid and L- cysteine with Ru_2O^{4+}(Iyun *et al.,* 1996; Musa *et al.,* 1998) decreased with increase in ionic strength. Also there was a marked enhancement of the rate of these reactions as a function of 1/D, both of these features posited that, the rate determining step involved oppositely charged redox species.

Free radical test was carried out by addition of acrylamide to the reaction mixtures, followed by excess methanol, there was no gel formation, suggesting that polymerisation has not occurred. Lack of polymerization from this reaction suggests probable absence of free radical formation during the electron transfer. On the other hand, free radical could have been formed but reacts so quickly that this method could not detect it (Iyun *et al.,* 1995c). The rate of reaction was not affected by added cations and anions, this observation is in consonant with what has been reported earlier in this research in the reaction of Fe_2O^{4+} with $S_2O_4^{2-}$, $S_2O_6^{2-}$, EH_2 and DH_2. Absence of spectroscopic evidence for the formation of intermediate during the reaction suggests that a precursor complex is probably not formed prior to the act of electron transfer and that the electron transfer may occur by the outer-sphere path. With recourse to the empirical kinetic data, the mechanism of this reaction is proposed as follows:

Application of steady state hypothesis for [Fe_2OH^{5+}, $GSGS^{2-}$] gives:

$$[Fe_2OH^{5+}, GSGS^{2-}] = \frac{k_3[Fe_2OH^{5+}][GSH.GS^-]}{k_{-3}[H^+] + k_4} \qquad (5.75)$$

If $k_{-3}[H^+] \gg k_4$ equation 5.75 reduces to

$$[Fe_2OH^{5+}, GSGS^{2-}] = \frac{k_3[Fe_2OH^{5+}][GSH.GS^-]}{k_{-3}[H^+]} \qquad (5.76)$$

Application of steady state hypothesis for [Fe_2OH^{5+}] gives:

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2O^{4+}][H^+]}{k_{-2} + k_3[GSH.GS^-]} \qquad (5.77)$$

From equation 5.77, if $k_{-2} \ll k_3[GSH.GS^-]$, then the equation reduces to:

$$[Fe_2OH^{5+}] = \frac{k_2[Fe_2O^{4+}][H^+]}{k_3[GSH.GS^-]} \quad (5.78)$$

Substituting equation 5.78 into 5.76 gives:

$$[Fe_2OH^{5+},GSGS^{2-}] = \frac{k_3 k_2[Fe_2O^{4+}][H^+][GSH.GS^-]}{k_{-3}[H^+]\, k_3[GSH.GS^-]} \quad (5.79)$$

$$[Fe_2OH^{5+},GSGS^{2-}] = \frac{k_2}{k_{-3}}[Fe_2O^{4+}] \quad (5.80)$$

Substituting equation 5.80 into 5.74 gives:

$$\text{Rate} = \frac{k_4 k_2}{k_{-3}}[Fe_2O^{4+}] \quad (5.81)$$

$$\text{Thus} \frac{k_4 k_2}{k_{-3}} = k_{obs} \quad (5.82)$$

Based on the above findings, the mechanism of reaction has been rationalized on the basis of ion-pairs with outersphere character .

5.5 Comparison of Fe_2O^{4+} – Thioureas Systems

The oxidation of reductants (TU, MTU, ATU, DMTU and DETU) followed the order k_2(TU) < k_2(DETU) < k_2(ATU) < k_2(MTU) < k_2(DMTU). The structure of the reductants can be used as a basis of comparison of their degree of reactivity since they possess the same functional group i.e. the C=S moiety is present in all the compounds used. This conclusion is in accordance with earlier assertion that changing the substituents on the nitrogen may affect the rate of reaction but not the mechanism, since the major reaction is taking place at the sulphur centre (Jonnalagadda *et al.,* 1996). The organic productscomprises urea/urea derivatives whereas the inorganic products were iron(II) and sulphur in each system. Change in the hydrogen ions, ionic strength,

dielectric constant, and added cations and anions did not affect the rate of reactions in all the systems. Reactions in all the systems were rationalized in favour of outer- sphere mechanism.

5.6 Comparison of Fe_2O^{4+} – Sulphur oxyanions

The two sulphur oxyanions used in the research are dithionite ion ($S_2O_4^{2-}$) and dithionate ion ($S_2O_6^{2-}$). The stoichiometries of the reaction in the two systems were 1:1. Change in the hydrogen ions, ionic strength, dielectric constant, and added cations and anions did not affect the rate of reactions in the two systems. Reactions involving dithionite ion was faster than dithionate ion, the difference in their reactivity could be due to the differences in their structure and geometry. From their structures, dithionite has two double bonds whereas dithionate has four double bonds, which therefore implies that the steric energy in dithionate is higher than dithionite, hence dithionite react faster than dithionate. Reactions in the two systems were rationalized in favour of outer- sphere mechanism with ion-pair character.

5.7 Comparison of Fe_2O^{4+} – Carbazides

The two carbazides used in the research are semicarbazide (EH_2) and diphenyl carbazide (DH_2). The stoichiometries of the reaction in the two systems were 1:1. Change in the hydrogen ions, ionic strength, dielectric constant, and added cations and anions did not affect the rate of reactions in all the systems. The trend in the rate constant is in the order k_{obs} (DH_2) □ k_{obs} (EH_2),

in the two systems, their C=O moiety in the two carbazides were found in their respective products, as shown in their FTIR spectra. Reactions in the two systems were rationalised in favour of outer- sphere mechanism with ion-pair character.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATIONS

6.1 Summary

The electron transfer reactions of tetrakis (2, 2- bipyridine)-μ-oxodiiron(III) (Fe_2O^{4+}) complex with thiourea (TU), *N*-methylthiourea (MTU), *N*–Allylthiourea (ATU), *N,N'*–dimethylthiourea (DMTU), *N,N'*-dimethylthiourea (DETU), dithionite ($S_2O_4^{2-}$) ion, dithionate ($S_2O_6^{2-}$) ion, semicarbazide (EH_2), diphenylcarbazide(DH_2) and glutathione (GSH) were studied in aqueous hydrochloric acid medium. The stoichiometries of the reactions were 1:1 (oxidants: reductants) in all the systems, except for Fe_2O^{4+}- GSH system which was 1:2 (oxidants: reductants). The reactions involving thioureas were first order in each of the reactant concentrations making it second order overall for each reaction system. However reactions of Fe_2O^{4+} with $S_2O_4^{2-}$, $S_2O_6^{2-}$, EH_2, DH_2 and GSH were zero order dependence in each of the reductants but first order in oxidant, hence making it first order overall. The rate of the reactions in all the systems

investigated were not affected by change in hydrogen ion concentration, variation in ionic strength, dielectric constant and added ions (cations and anions). Except for the reactions of thioureas in which there was inhibition of the rate of reaction when anions were added. Spectroscopic investigations for all the systems and Michaelis-Menten plots for the reactions involving thioureas showed that there is no intermediate complex formation for all the systems.

6.2 Conclusion

Based on the stoichiometries, order of reactions, rate constants, effect of changes of H^+ concentrations, effect of changes in ionic strength and dielectric constant of the reaction medium, effect of addition of ions to the reaction medium, polymerization test as well as the absence of kinetic and spectroscopic evidence for intermediate complex formation prior to electron transfer, the outersphere mechanism has been proposed for all of the reactions.

6.3 Recommendations

Based on these studies the following recommendations are made:

i. Temperature dependent studies should be carried out to determine thermodynamic parameters for the electron transfer reactions of the complex.
ii. This research should be carried out computationally, to test the reliability and validity of the results, thereby make certain comparison between the two methods.
iii. Concerted effort should be directed toward the electron transfer reactions of some binuclear complexes of iron(III) in micelle environment.

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