

**KINETICS AND MECHANISMS OF THE OXIDATION OF  
AMINOCARBOXYLATO-COBALT(II) COMPLEXES BY HYPOCHLORITE AND  
SILVER-CATALYSED PERSULPHATE IONS IN AQUEOUS ACIDIC MEDIUM**

**BY**

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**DEPARTMENT OF CHEMISTRY  
FACULTY OF PHYSICAL SCIENCES  
AHMADU BELLO UNIVERSITY, ZARIA  
NIGERIA.**

**FEBRUARY, 2018**



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**BY**

**Yusif AHMED, B. Sc. (Hon) Chemistry (ABU) 2014  
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**A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES,  
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MASTER OF SCIENCE DEGREE IN INORGANIC CHEMISTRY**

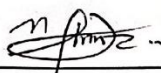
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FACULTY OF PHYSICAL SCIENCES  
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NIGERIA.**

**FEBRUARY, 2018**

### Declaration

I declare that the work in this Dissertation entitled “Kinetics and mechanisms of the oxidation of aminocarboxylatocobaltate(II) complexes by hypochlorite and silver-catalysed persulphate ions in aqueous acidic medium” has been carried out by me in the Department of Chemistry of Ahmadu Bello University, Zaria. The information derived from the 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.

Yusif AHMED



Signature

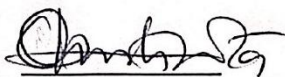
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### Certification

This dissertation entitled "KINETICS AND MECHANISMS OF THE OXIDATION OF AMINOCARBOXYLATOCOBALTATE(II) COMPLEXES BY HYPOCHLORITE AND SILVER-CATALYSED PERSULPHATE IONS IN AQUEOUS ACIDIC MEDIUM" by Yusif AHMED meets the regulations governing the award of the degree of Master of Science in Inorganic Chemistry of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Dr. A. D. Onu  
Chairman, Supervisory Committee

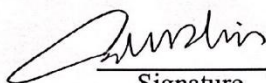


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## **Dedication**

This work is dedicated to my parents, Alh. Ahmadu Abdullahi and Umm-Salamah. May Allah (S.W.T.) forgive their shortcomings! Amen.

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All praise is to Almighty Allah, the Creator and Sustainer of the universe for sparing my life, guarding and guiding me throughout the course of my studies and research work in this great University. May His Peace and Blessings be onto His Noble Prophet (S. A. W), the Seal of prophets.

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## Abbreviations

Abbreviation	Name
BDH	British Drug House
D	Dielectric Constant
ATP	Adenosine triphosphate
EDTA	Ethylenediaminetetraacetate
IDA	Iminodiacetic acid
NTA	Nitrilotriacetic acid
HEDTA	n-(2-hydroxyethyl)ethylenediaminetetraacetate
I	Ionic Strength
In	Natural Logarithm
k	Rate Constant
K	Equilibrium Constant
M & B	May and Baker
obs	Observed
Redox	Reduction – Oxidation
t	Time
T	Temperature
TMDTA	trimethylenediaminetetraacetic acid
EGTA	ethyleneglycol bis(2 aminoethyl(ether)tetraacetic acid
UV – visible	Ultra Violet – visible
$\lambda_{\max}$	Wavelength of Maximum Absorption
PCBs	Polychlorinated biphenyls

## Abstract

The kinetics of the oxidation of aminocarboxylatocobaltate(II) complexes (hereafter,  $[\text{Co(II)EDTA}]^{2-}$  and  $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$ ) by hypochlorite ( $\text{ClO}^-$ ) and silver-catalysed persulphate ions ( $\text{S}_2\text{O}_8^{2-}$ ) at 300 K; 520 nm and 299 K; 525 nm (temperature and  $\lambda_{\text{max}}$ ) respectively was studied in aqueous acidic medium under pseudo-first order conditions. For the reaction of complexes with persulphate ion, the concentrations were:  $\text{I} = 0.5 \text{ mol dm}^{-3} (\text{NaNO}_3)$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3} (\text{HNO}_3)$  and  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3} (\text{AgNO}_3)$ . While  $\text{I} = 0.5 \text{ mol dm}^{-3}$  and  $0.2 \text{ mol dm}^{-3} (\text{NaNO}_3)$  and  $[\text{H}^+] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$  and  $1.0 \times 10^{-2} \text{ mol dm}^{-3} (\text{HNO}_3)$  are for the reaction of hypochlorite with  $[\text{Co(II)EDTA}]^{2-}$  and  $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$  complexes respectively. The stoichiometry obtained was 2:1 for the oxidation of complexes by persulphate ion and 1:1 for the reaction of complexes with hypochlorite ion. First order kinetics in the concentration of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{ClO}^-$  were observed for all the reactions except the reaction of  $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$  with persulphate ion, where zero order with respect to concentration of  $\text{S}_2\text{O}_8^{2-}$  was obtained. The reactions of complexes with  $\text{S}_2\text{O}_8^{2-}$  were independent of  $[\text{H}^+]$  but dependent on  $[\text{Ag}^+]$  while with  $\text{ClO}^-$  the reaction rates were inversely dependent on  $[\text{H}^+]$ . The reactions conform to the following rate equations:

$$\frac{d[\text{Co(III)EDTA}^-]}{dt} = a[\text{Ag}^+][\text{Co(II)EDTA}^{2-}][\text{S}_2\text{O}_8^{2-}]$$

$$\frac{d[\text{Co(III)HEDTA}]}{dt} = b[\text{Ag}^+][\text{Co(II)HEDTA}^-]$$

$$\frac{d[\text{Co(III)EDTA}^-]}{dt} = c[\text{H}^+]^{-1}[\text{Co(II)EDTA}^{2-}][\text{ClO}^-]$$

$$\frac{d[\text{Co(III)HEDTA}]}{dt} = d[\text{H}^+]^{-1}[\text{Co(II)HEDTA}^-][\text{ClO}^-]$$

where  $a = 5.90 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $b = 5.4 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $c = 1.23 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $d = 2.28 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Zero salt effects for the reaction of complexes with  $\text{S}_2\text{O}_8^{2-}$  and positive salt effects with  $\text{ClO}^-$  were observed. The thermodynamic parameters obtained from the temperature dependence studies showed that the activated complexes are ordered for the oxidation of  $[\text{Co(II)EDTA}]^{2-}$  ( $\Delta H^* = +28.67 \text{ kJ mol}^{-1}$ ,  $\Delta S^* = -170.72 \text{ JK}^{-1}\text{mol}^{-1}$ ) and  $[\text{Co(II)HEDTA(OH}_2)]^-$  ( $\Delta H^* = +53.12 \text{ kJmol}^{-1}$ ,  $\Delta S^* = -113.65 \text{ JK}^{-1}\text{mol}^{-1}$ ) by persulphate ion. The free radical species were detected only in the reaction of complexes with persulphate ion. Addition of ions affected the rates for all the reactions except for the reaction of  $[\text{Co(II)HEDTA(OH}_2)]^-$  with persulphate ion, where both added cations and anions had no effect on the reaction rate. Moreover, Michaelis – Menten plot of  $1/k_{\text{obs}}$  versus  $1/[\text{oxidant}]$  had zero intercept for all the reaction systems except for the oxidation of  $[\text{Co(II)HEDTA(OH}_2)]^-$  by persulphate ion. Based on the above observations, an outer-sphere mechanism is proposed as the plausible mechanism for all the reactions except for the reaction of  $[\text{Co(II)HEDTA(OH}_2)]^-$  with persulphate ion, where an inner-sphere mechanism is proposed.

## CHAPTER ONE

### 1.0 INTRODUCTION

Electron transfer (ET) reaction is simply the transfer of electrons between two species like ions, molecules, biological systems etc. The reaction usually involves rearrangement and transfer of outermost shell electrons of reacting species in order to gain stability. Thus, oxidation is the loss of electrons while reduction is the gain of electrons (Wong *et al.*, 2002). Many reactions in inorganic and biological systems involve transfer of electron, thus, electron transfer reaction plays a key role to various physical and biological systems (Onu *et al.*, 2008, 2009, 2015 and 2016; François and Jamal, 2016; Idris *et al.*, 2015; Ilbert and Bonnefoy, 2013; Xie *et al.*, 2012; Xiang-Rong and Xiang-Zhong 2010; Naik *et al.*, 2007 and 2010).

Both Adenosine triphosphate (ATP) and dioxygen radical/hydrogen peroxide ( $O_2^-$ / $H_2O_2$ ) are generated in living cell by electron transfer. ATP is the product of oxidative phosphorylation whereas  $O_2^-$  is generated by singlet electron reduction of dioxygen,  $O_2$  which is reduced by superoxide dismutase, SOD to  $H_2O_2$  (Mailloux, 2015). Importantly, the controlled production of  $O_2^-$ / $H_2O_2$  is required for intrinsic mitochondria signaling (e.g. Modulation of mitochondria processes) and communication with the rest of the cell. This can be checked by understanding the effect of various parameters on the reaction. Moreover, the damaging effect of oxygen towards anaerobic organism is associated with its free radical properties (Ilbert and Bonnefoy, 2013). One of the promising areas that explains the effect of various parameters on this electron transfer reaction is chemical kinetics.

Chemical kinetics also known as reaction kinetics is the area of Chemistry concerned with reaction rates, factors affecting the rates and sequence of steps (mechanistic pathways) by which reactions occur (McMurry and Fay, 2008). The two well established general mechanisms of electron transfer reactions are the outer-sphere and the inner-sphere mechanisms (Cox, 2004).

In the outer-sphere mechanism, no substitution of the ligands into the inner coordination spheres of either reactant is needed for electron transfer to take place (Housecroft and Sharpe, 2008). On the other hand, the inner-sphere mechanism involves distortion of the inner-coordination sphere of reactants with the formation of a bridged activated intermediate prior to electron transfer (Jagannadham, 2012).

### 1.1 Statement of Research Problem

Aminopolycarboxylic acids that have lost acidic protons form strong complexes with metal ions (Anderegg *et al.*, 2005) which makes them useful complexes in a wide variety of chemical, environmental and medical applications (Onu *et al.*, 2008, 2009, 2015 and 2016; Naik *et al.*, 2007 and 2010; Bugaje, 2006 and Mansour, 2003). Metal-aminocarboxylate complexes are used to study structure, stability, magnetic properties and non-covalent interactions, as well as play an important role in metalloenzyme catalysed reactions (Vuckovic *et al.*, 2011). Also, transition metal containing aminocarboxylate ligands are generally accepted as simple models for some biological systems involving transition metals (Swaroop *et al.*, 1991). Typical examples of these complexes are  $[Co(II)EDTA]^{2-}$  and  $[Co(II)HEDTA(OH)_2]^-$ . The biological importance of cobalt is well documented (Michihiko and Sakayu, 1999; David *et al.*, 1999 and Chang *et al.*, 2010). Cobalt is an active centre for co-enzymes called cobalamins (also known as vitamin B<sub>12</sub>). These are group of biologically active cobalt-containing compounds (corrinoids) (Miller *et al.*, 2005 and Arslan *et al.*, 2013). Cobalamin plays a specific role in amino acid metabolism, normal functioning of the brain and nervous system via the synthesis of myelin as well as an essential factor in DNA synthesis for chromosomal replication and division (Miller *et al.*, 2005; Schoonover *et al.*, 2004; Reynolds, 2006 and Arslan *et al.*, 2013). However, deficiency of cobalt in human leads to pernicious anemia and possible lethal disorder (Michihiko

and Sakayu, 1999). These can be treated by the use of synthesised cobalamins, hydroxocobalamin or cyano-cobalamin (Carmel, 2008 and Andres *et al.*, 2009 and 2010), hence, the need to study their reactions. Moreover, Despite the applications of these important complexes, there is a paucity of information on kinetics of electron transfer reaction of aminocarboxylatocobalt(II) with oxyanions such as persulphate ion,  $S_2O_8^{2-}$  and hypochlorite ion,  $ClO^-$  though, other researchers (Onu *et al.*, 2008, 2009, 2015 and 2016; Naik *et al.*, 2007 and 2010; Bugaje, 2006 and Mansour, 2003) have carried out the study using different oxidants. In fact  $S_2O_8^{2-}$  ion even though a good oxidant ( $E = +2.01$  V) but it is slow to reduction even in the presence of strongly reducing agents due to strong O-O bond which need to be broken in the redox process (Burgess, 1999). In addition, though  $ClO^-$  ion is the strongest oxidizing agent of the chlorine oxyanions (Mohammed *et al.*, 2010) but its reactions with these complexes have not been reported.

In view of the aforementioned important applications of cobalt-aminocarboxylate complexes coupled with desire to gain further insight into the reaction of the complexes with these oxyanions ( $S_2O_8^{2-}$  and  $ClO^-$ ), this study is therefore embarked upon to generate kinetic data for the reactions as well as to establish its mechanisms.

## 1.2 Justification of the Research

The study of oxidation of aminocarboxylate complexes by oxy-anions is of potential interest to understanding the mechanism of oxygen transport in biological systems (Onu, 2010). Interestingly, this study will be used as simple models to understanding or to mimic the biochemical pathways of some metabolic processes which involve the use of co-enzymes.

Moreover, the study will be significant to the inorganic mechanistic community as the kinetic data generated from this research will complement the much needed kinetic information that will deepen the ever growing field of inorganic reaction mechanism. Also, the research is

expected to contribute to knowledge particularly in the area of inorganic chemistry, biochemistry and science in general towards better understanding and more efficient utilization of the reactions of these complexes.

### **1.3 Aim and Objectives**

#### **1.3.1 Aim**

The aim of this work is to study the kinetics of oxidation of aminocarboxylatocobaltate(II) complexes (hereafter,  $[\text{Co(II)EDTA}]^{2-}$  and  $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$ ) each by persulphate and hypochlorite ions and establish the mechanism of the reactions.

#### **1.3.2 Objectives**

The aim will be achieved through the following objectives:

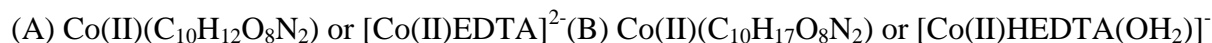
- a. preparation of the complexes
- b. determination of the stoichiometry of the reactions;
- c. determination of the kinetic and non-kinetic parameters for the reactions and
- d. generating the thermodynamic parameters for the reactions

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 Aminocarboxylatocobaltate(II) Complexes

An aminopolycarboxylic acid is a chemical compound containing one or more nitrogen atoms connected through carbon atoms to two or more carboxyl groups. The acid forms strong complexes with metal ions when it lost its protons (Andregget *al.*, 2005). This property makes it useful complexone in a wide variety of chemical, environmental and medical applications (Onu *et al.*, 2008, 2009, 2015 and 2016; Naik *et al.*, 2007 and 2010; Bugaje, 2006 and Mansour, 2003). The parent of this family of ligands is the amino acid glycine,  $\text{H}_2\text{NCH}_2\text{COOH}$  which is a bidentate ligand. Others are iminodiacetic acid, IDA (tridentate), nitrilotriacetic acid, NTA (tetradentate), ethylenediaminetetraacetic acid, EDTA (hexadentate) etc. The chemical structure of cobalt(II)-aminocarboxylate complexes are presented below:



A = ethylenediamine-N,N,N',N'-tetraacetatocobaltate(II)

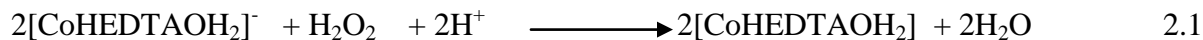
B = N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetatocobaltate(II)



Metal-aminocarboxylate complexes are used to study structure, stability, magnetic properties and non-covalent interactions, as well as play an important role in metalloenzyme catalyzed reactions (Vuckovic *et al.*, 2011). The pernicious anemia and possible lethal disorder in humans caused by a deficiency of cobalt (Michihiko and Sakayu, 1999) can be treated by the use of aqueous solution of cobalt complexes, hydroxocobalamin (Andres, *et al.*, 2010).

The preparation of Co(II) complex by direct synthesis using reactants  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , N,N',N'',N'''-terakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) and neutralized S-phenylalanine in molar ratio of 2:1:1 has been reported by Vuckovic *et al.* (2011). The wavelength of maximum absorption,  $\lambda_{\text{max}}$  of the complex,  $[\text{Co}_2(\text{S-phe})\text{tpmc}](\text{ClO}_4)_3$  was at 510 and 512 nm. Also the synthesis of aminocarboxylatocobaltate(II) complex,  $[\text{CoHEDTAOH}_2]^-$  using  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and N-(2-hydroxy-ethyl)ethylenediamine-N,N',N'-triacetic acid, HEDTA has been reported by Onu *et al.* (2015). Interestingly, slight excess of HEDTA was added for complete complexation and trapping of possible impurities. The synthesised complex was found to have wavelength of maximum absorption,  $\lambda_{\text{max}}$  at 510 nm.

Onu *et al.* (2015) studied the kinetics and stoichiometry of the reduction of hydrogen peroxide by an aminocarboxylatocobaltate(II) complex,  $[\text{CoHEDTAOH}_2]^-$  in aqueous acidic medium. The stoichiometry study shows that two moles of the complex was oxidised by one mole of peroxide which is in conformity with equation 2.1. In here, the peroxide forms an intermediate by accepting two electrons from the reductant and consequently water is formed.



The mechanistic pathway of this reaction was proposed to be outer sphere mechanism and the spectrum of the product formed had two maxima 380 and 536 nm which were attributed to Co(III) ion. Similarly, the kinetic studies of the oxidation of  $[\text{Co}^{\text{II}}\text{HDTA}]^{4-}$  (HDTA is

hexamethylenediaminetetraacetic acid) by periodate ion have been investigated by Naik *et al.*, (2010). Change in ionic strength of the reaction medium has no effect on the reaction rates and an inner-sphere has been proposed as a mechanistic pathways. This assertion is supported by the value of activation parametres ( $\Delta H^* = 28.69 \text{ kJ mol}^{-1}$  and  $\Delta S^* = -481.13 \text{ J K}^{-1} \text{ mol}^{-1}$ ) obtained from the temperature dependence study using Eyring's equation. Also, Onuet *al.* (2009) studied the kinetics of reduction of tetraoxoiodate(VII) by N-(2-hydroxyethyl)ethylenediamminetriacetatocobalt(II) ion in aqueous perchloric acid medium. The stoichiometry of the reaction was found to be 2:1 and the reaction was found to be second order overall. The rate equation conforms to equation 2.2.

$$\frac{d[\text{CoHEDTA}(\text{OH}_2)]}{dt} = (a + b[\text{H}]^{-1})[\text{CoHEDTA}(\text{OH}_2)][\text{IO}_4^-] \quad 2.2$$

Naik *et al.*, (2007) reported the rate law as shown in equation 2.3 in their work, the kinetics and mechanistic studies of oxidation of amine-N-polycarboxylate complexes,  $[\text{Co}(\text{II})\text{L}(\text{OH}_2)]^{2-n}$ , L is trimethylenediamnetetraacetic acid (TMDTA) and ethylene glycol bis(2-aminoethyl(ether) N,N,N',N'-tetraacetic acid (EGTA) by periodate ions in aqueous medium.

$$\text{Rate} = (k_2[\text{IO}_4^-] + k_3[\text{IO}_4^-]^2)[\text{Co}^{\text{II}}\text{L}(\text{OH}_2)]^{2-n} \quad 2.3$$

The reaction rate was found to be independent of the pH and the ionic strength of the medium for the  $[\text{Co}(\text{II})\text{TMDTA}(\text{OH}_2)]^{2-n}$  complex while positive salt effect was reported for the  $[\text{Co}(\text{II})\text{EGTA}(\text{OH}_2)]^{2-n}$  complex. The stiochiomery of 1:1 and outer-sphere mechanism for the oxidation of  $[\text{Co}(\text{II})\text{HEDTA}(\text{OH}_2)]^-$  by  $\text{NO}_2^-$  was reported by Onu *et al.* (2008) while Bugaje (2006) reported a stoichiometry of 6:1 for the oxidation of  $[\text{Co}(\text{II})\text{EDTA}]^{2-}$  by bromate ion. However, 2:1 stoichiometry for  $[\text{Co}(\text{II})\text{EDTA}^{2-}] : [\text{H}_2\text{O}_2]$ , inverse acid dependence and inner-sphere mechanism were established by Onu *et al.* (2016) in the oxidation of ethylenediaminetetaacetatocobaltate(II) complex by hydrogen peroxide. Furthermore, kinetics

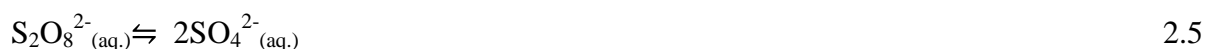
and mechanism of the oxidation of N-(2-hydroxy-ethyl)ethylenediamine-N,N',N'-triacetatecobalt(II) by vanadate ion in aqueous acidic medium have been investigated by Mansour (2003). The product of the reaction exhibits two maxima of absorption at 380 and 550 nm which were possibly due to formation of Co(III) ion in form of  $[\text{Co}^{\text{III}}\text{HEDTA}(\text{OH})_2]$ . The HEDTA in the product of this reaction was pentacoordinated to Co(III) in which the hydroxyethyl group is free. This was supported by another study which showed that the product of oxidation of  $\text{Co}^{\text{II}}\text{HEDTA}$  by hydrogen peroxide (Onu *et al.*, 2015) is not the hexadentate species,  $\text{Co}^{\text{III}}\text{HEDTA}$ , but rather pentadentate species  $\text{Co}^{\text{III}}\text{HEDTA}(\text{H}_2\text{O})$ .

## 2.2 Reactions of Persulphate Ion

Persulphate ion,  $\text{S}_2\text{O}_8^{2-}$  also known as peroxydisulphate ion is one of the strongest oxidants known in aqueous solution (Mcheik and Jamal, 2013). It is mainly used as a radical initiator for emulsion polymerisation reactions for styrene based polymers such as acrylonitrile butadiene styrene (Harald *et al.*, 2005). The polymerisation is initiated by the homolysis of the peroxydisulphate.



It is also used as bleach, as a detergent component, as a soil conditioner, modification of starch etc. The vast application of this ion may be attributed to its oxidising ability as can be depicted from its redox potential +2.01V for



The use of persulphate ions has gained considerable attention in environmental sector especially for soil organic pollutants removal. Application of iron-activated persulphate oxidation for the degradation of polychlorinated biphenyls (PCBs) in soil was studied by Tang *et*

*al.* (2015). The results indicated that  $\text{FeSO}_4$  had the best activation for sodium persulphate with highest PCBs degradation compared with other iron compounds ( $\text{Fe}_3\text{O}_4$ , iron powder,  $\text{FeCl}_3$ ).

Despite the redox potential of persulphate, little or no reaction occurs in the absence of catalyst for some of its redox reactions. Catalysts such as Ag(I) (Ayokoet *al.*, 1992; Gong and Lin, 2011), Fe(II) (Tang *et al.*, 2015) and Cu(II) (Grochala and Mazej, 2015) have been used in the redox reaction involving persulphate ions. The effectiveness of Ag(I) and Cu(II) as catalysts is due to their oxidation to Ag(II) or Ag(III) and Cu(III) states respectively (Grochala and Mazej, 2015). When different metal ions (Ag(I), Co(II), Fe(II), Mn(II) and Cu(II)) were used as catalysts to activate persulphate ion for the same reaction, Ag(I) was the most effective agent (Gong and Lin, 2011). The presence of either  $\text{Ag}^{2+}$  or  $\text{Ag}^{3+}$  (Khandual, 1991) have all been reported in the redox reactions of  $\text{S}_2\text{O}_8^{2-}$  catalysed by Ag(I). Some number of investigations have been reported in the oxidation of metal complexes (Rao *et al.*, 1987) and various organic compounds (Gong and Lin, 2011; Tang *et al.*, 2015) by  $\text{S}_2\text{O}_8^{2-}$  ion. The degradation of diphenylamine (Shen-Xin *et al.*, 2009), azo dye Orange G with ferrous ion (Xiang-Rong and Xiang-Zhong, 2010), aniline (Xie *et al.*, 2012), discoloration of Rhodamine B (Mcheik and Jamal, 2013) and degradation of polychlorinated biphenyls (PCBs) using iron (Tang *et al.*, 2015) by persulphate ion have been studied. Electron transfer reactions of persulphate ion are characterised by the presence of free radical sulphate ion as intermediate as the reaction progressed (Ayokoet *al.*, 1992). Also most of the electron transfer reactions of persulphate ion occur by the outer-sphere mechanism (Ayokoet *al.*, 1992). The electron transfer reaction of  $\text{S}_2\text{O}_8^{2-}$  was found to be independent of hydrogen ion concentration except, when the reducing agent can be affected by the presence of acid (Lawal, 1997).

### **2.3 Reactions of Hypochlorite Ion**

Hypochlorite,  $\text{ClO}^-$  is an ion composed of chlorine and oxygen. It is also known as chlorate(I) ion. It can combine with a number of counter ions to form hypochlorites, which may also be regarded as the salts of hypochlorous acid. Examples include sodium hypochlorite (household bleach) and calcium hypochlorite (bleaching powder or swimming pool "chlorine"). Hypochlorites are very strong oxidizing agents with low stability. They react with many organic and inorganic compounds. It is the strongest oxidizing agent of the chlorine oxyanions (Mohammed *et al.*, 2010). This oxidizing property makes the ions effective bleaching and stain removing agents (Warren and Stuart, 2012). Other primary applications are as disinfection and water treatment agents, used in chemistry for chlorination and oxidation reactions.

Recently, there is interest in the use of hypochlorite to remedy environmental pollution. The investigations of sodium hypochlorite oxidation of aliphatic petroleum contaminants in a calcareous soil have been reported by François and Jamal (2016). The decontamination objective was to lower the high concentration of  $\text{C}_{10}\text{--}\text{C}_{50}$  aliphatic hydrocarbons to 700 ppm under experimental conditions of 2 to 16 hours reaction time, at room temperature, with a 1 to 12.5 wt%  $\text{NaClO}$  oxidative solution and a fixed 2:1 solution-to-soil ratio.  $\text{CO}_2$  acidity was used to boost the  $\text{NaClO}$  oxidation yield and seems to have played a role in desorbing the natural organic matter and the research suggested that the strong chlorine smell remaining after the reaction was completed suggests that part of the  $\text{NaClO}$  requirement can be recycled.

Idris *et al.* (2015) investigated the kinetics of the redox reaction between malachite green,  $\text{MG}^+$ , and hypochlorite ion,  $\text{ClO}^-$  and the data indicated a first order dependence on both  $[\text{MG}^+]$  and  $[\text{ClO}^-]$  giving a second order overall. The second order rate law for the reaction conforms to the equation 2.6.

$$-d[MG^+]/dt = k_2[MG^+][ClO^-] \quad 2.6$$

$k_2 = 115.55 \pm 1.21 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , at  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\mu = 0.1 \text{ mol dm}^{-3}$  and

$T = 25 \pm 1^\circ\text{C}$ .

Similarly, the kinetics and mechanism of the reaction of azide with hypochlorite have been investigated by Betterton *et al.* (2010). The reaction stoichiometry was found to be 2:1 which is in conformity with equation (2.7) below:



The reaction was found to proceed by a key intermediate chlorine azide,  $ClN_3$ , which subsequently decomposes by reaction with a second azide molecule in the rate determining step:



Kinetic and spectroscopic studies of oxidation of azo dyes in surfactant solutions by hypochlorite have been carried out by Oakes *et al.* (2010) to examine the influence of cationic, anionic and nonionic surfactants upon the oxidation of an azo dye, II by hypochlorite showed that the oxidation rates were unaffected by the presence of anionic or nonionic surfactant either in micellar or submicellar regions. This indicates the absence of any specific dye-surfactant interactions. While specific interactions were observed with cationic surfactants, both in submicellar and micellar regions. The reaction is attributed with formation of a sparingly soluble 1:1 complex with the dye, via interactions with the sulphonate groups. Furthermore Jiann-Kuo, (1987) investigated the reduction of potassium hypochlorite using a rotating cylindrical platinum cathode. First order kinetic with respect to the activity of  $H^+$  and  $ClO^-$  was observed. The mechanism of reduction of  $ClO^-$  involved formation of  $HClO$  followed by the transfer of an electron to the acid as shown:





## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 Materials

All chemicals and reagents used were of analar grade and distilled water was used in preparing all the solutions. The chemicals used are: sodium nitrate; nitric acid; silver nitrate, cobaltous nitrate; EDTA; HEDTA; sodium persulphate; sodium hypochlorite; sodium acetate; lithium nitrate; potassium nitrate; sodium formate; acrylamide and acetone. The instruments are: Sherwood Colorimetre 254; Corning 252 colorimetre; Carey series 300 UV-Vis spectrophotometre and Mettler Toledo MS-TS analytical balance.

#### 3.2 Methods

##### 3.2.1 Preparation of [Co(II)EDTA]<sup>2-</sup> complex

The complex ion, [Co(II)EDTA]<sup>2-</sup> was prepared according to the method adopted by Onu *et al.* (2016). Concentration of 0.1 mol dm<sup>-3</sup> [Co(II)EDTA]<sup>2-</sup> solution was prepared by adding 0.11 mol dm<sup>-3</sup> Na<sub>2</sub>H<sub>2</sub>EDTA (M & B) to 0.1 mol dm<sup>-3</sup> of Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Sigma-Aldrich). Excess amount of EDTA was used to ensure complete complexation. The prepared complex gave λ<sub>max</sub> of 519 nm after characterization using Cary series 300 UV-Vis spectrophotometre in the wavelength range of 400 – 800 nm. Other researchers (Onu *et al.*, 2016 and Paraneewiswaran *et al.*, 2015) reported wavelength of 510 and 490 nm respectively using CoCl<sub>2</sub>.6H<sub>2</sub>O as a starting metal centre.

##### 3.2.2 Preparation of [Co(II)HEDTAOH<sub>2</sub>]<sup>-</sup> complex

The complex,  $[\text{Co(II)HEDTAOH}_2]^-$  was prepared according to the method of Mansour (2003). Concentration of  $0.1 \text{ mol dm}^{-3}$   $[\text{Co(II)HEDTAOH}_2]^-$  solution was prepared by keeping the mixed solution of  $0.1 \text{ mol dm}^{-3}$  of  $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich) with slight excess HEDTA (Sigma-Aldrich) solution for 24 hours for complete complex formation. The complex was characterised using Cary series 300 UV-Vis spectrophotometre in the wavelength range of 400 – 800 nm and gave  $\lambda_{\text{max}}$  of 526 nm. This differ with the one reported by Onu *et al.* (2016) which is 510 nm when  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was used as metal centre.

### 3.2.3 Preparation of stock solution of sodium nitrate

Stock solution of  $\text{NaNO}_3$  ( $2.0 \text{ moldm}^{-3}$ ) was prepared by dissolving 17.0 g of the salt with distilled water in a  $100 \text{ cm}^3$  volumetric flask and made up to the mark.

### 3.2.4 Preparation of standard sodium carbonate solution

Solution of  $\text{Na}_2\text{CO}_3$  ( $0.1 \text{ moldm}^{-3}$ ) was prepared by dissolving accurately weighed 0.5300 g of the salt with distilled water in a  $50 \text{ cm}^3$  volumetric flask and made up to the mark. The solution was used as a primary standard in the standardization of nitric acid.

### 3.2.5 Preparation of standard nitric acid solution

Stock solution of nitric acid ( $0.53 \text{ mol dm}^{-3}$ ) was prepared by transferring  $7.87 \text{ cm}^3$  of 70.5 %  $\text{HNO}_3$  solution (specific gravity 1.42) into a  $250 \text{ cm}^3$  volumetric flask and made up to the mark with distilled water. The acid was standardized volumetrically using  $\text{Na}_2\text{CO}_3$  and methyl orange as indicator and its concentration was calculated according to equation 3.1 (Vogel, 2000).



### 3.2.6 Preparation of silver nitrate solution



Concentration of  $0.5 \text{ mol dm}^{-3}$  stock solution of silver nitrate was prepared by dissolving a weighed quantity of the salt with distilled water in a  $50 \text{ cm}^3$  volumetric flask and made up to the mark.

### **3.2.7 Preparation of salts solutions**

The solutions of sodium acetate (M&B), sodium formate (M&B), potassium nitrate (M&B) and lithium nitrate (M&B) were all prepared by dissolving known weights of the respective salts with distilled water each in a  $100 \text{ cm}^3$  volumetric flask. These solutions were used to investigate the effect of added ions.

### **3.2.8 Preparation of sodium persulphate stock solution**

A stock solution of sodium persulphate ( $0.1 \text{ mol dm}^{-3}$ ) was prepared by dissolving an accurate weight (2.3803 g) of the salt with distilled water in a  $100 \text{ cm}^3$  volumetric flask and made up to the mark.

### **3.2.9 Preparation of sodium hypochlorite stock solution**

Stock solution of NaClO ( $1.0 \text{ mol dm}^{-3}$ ) was prepared by transferring  $25.85 \text{ cm}^3$  of 12 % NaClO (density  $1.2 \text{ g cm}^{-3}$ ) into a  $50 \text{ cm}^3$  volumetric flask and made up to the mark with distilled water.

### **3.2.10 Stoichiometry study**

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method (Ayoko *et al.*, 1991; Lohdip and Iyun, 1993 and Onu *et al.*, 2015). The concentration of  $[\text{Co(II)EDTA}]^{2-}$  and  $[\text{Co(II)HEDTAOH}_2]^-$  were kept constant at  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  while that of oxy-anions ( $\text{S}_2\text{O}_8^{2-}$  and  $\text{ClO}^-$ ) were varied four folds below and above the concentration of complexes. The reactions were allowed to go to completion at the various

conditions as presented in Table 3.1. This was ascertained by taking the absorbance of the mixtures at intervals. The reactions were taken to be completed when the absorbance remained constant after series of repeated readings and the stoichiometry (indicated by the point of inflexion) of each of the reaction was determined by a plot of absorbance against mole ratio of oxidant/reductant.

**Table 3.1: Conditions for the stoichiometry study**

S/No.	Systems	$10^3[\text{H}^+]$ , mol dm <sup>-3</sup>	$10^3[\text{Ag}^+]$ , mol dm <sup>-3</sup>	$10 \text{ I}$ , mol dm <sup>-3</sup>	T, K	$\lambda_{\text{max}}$ , Nm
1	[Co(II)EDTA] <sup>2-</sup> - S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	10	10	5.0	299	520
2	[Co(II)HEDTA] <sup>2-</sup> -S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	10	10	5.0	299	525
3	[Co(II)EDTA] <sup>2-</sup> - ClO <sup>-</sup>	40	0.0	1.0	300	520
4	[Co(II)EDTA] <sup>2-</sup> - ClO <sup>-</sup>	10	0.0	1.0	300	525

### 3.2.11 Kinetic measurement

The rates of the reactions were monitored by monitoring the rate of change in absorbance at  $\lambda_{\text{max}}$ , 520 and 525 nm on a Sherwood Colorimetre 254 and Corning 252 colorimetre. The kinetic study was carried out under pseudo-first order conditions with the concentration of [Co(II)EDTA]<sup>2-</sup> and [Co(II)HEDTAOH<sub>2</sub>]=  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup> and that of the oxidants in at least ten-folds excess over the [reductants] at temperature of 299K, ionic strength of 0.5 mol dm<sup>-3</sup> (NaNO<sub>3</sub>),  $[\text{H}^+] = 1.0 \times 10^{-2}$  mol dm<sup>-3</sup> (HNO<sub>3</sub>),  $[\text{Ag}^+] = 1.0 \times 10^{-2}$  mol dm<sup>-3</sup> (AgNO<sub>3</sub>) for [Co(II)EDTA]<sup>2-</sup>- S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system; temperature of 299K, ionic strength of 1.0 mol dm<sup>-3</sup> (NaNO<sub>3</sub>),

$[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  ( $\text{HNO}_3$ ),  $[Ag^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  ( $\text{AgNO}_3$ ) for  $[\text{Co(II)HEDTA}]^{2-}$ - $\text{S}_2\text{O}_8^{2-}$  system; temperature of 300K, ionic strength of  $0.5 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ),  $[H^+] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$  ( $\text{HNO}_3$ ) for  $[\text{Co(II)EDTA}]^{2-}$ - $\text{ClO}^-$  system and temperature of 300K, ionic strength of  $0.2 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ),  $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  ( $\text{HNO}_3$ ) for  $[\text{Co(II)HEDTA}]^{2-}$ - $\text{ClO}^-$  system.

Pseudo-first order rate constants ( $k_{\text{obs}}$ ) for the reactions were obtained from the slopes of the plots of  $\log (A_{\infty}-A_t)$  versus time (where  $A_{\infty}$  is the absorbance at infinity and  $A_t$  is the absorbance at time t). The order with respect to the oxidants concentration,  $[\text{S}_2\text{O}_8^{2-}]$  and  $[\text{ClO}^-]$  were determined from the slopes of the plots of  $\log k_{\text{obs}}$  versus  $\log [\text{S}_2\text{O}_8^{2-}]$  and  $\log [\text{ClO}^-]$  respectively.

### 3.2.12 Effect of acid and catalyst on the reaction rates

The effect of  $[H^+]$  was investigated by varying  $[H^+]$  in the range of  $(2.50-40.0) \times 10^{-3} \text{ mol dm}^{-3}$  at  $5.0 \times 10^{-2} \text{ mol dm}^{-3} [\text{S}_2\text{O}_8^{2-}]$  for  $[\text{Co(II)EDTA}]^{2-}$ - $\text{S}_2\text{O}_8^{2-}$  system,  $(6.25-400) \times 10^{-4} \text{ mol dm}^{-3}$  at  $16.0 \times 10^{-2} \text{ mol dm}^{-3} [\text{S}_2\text{O}_8^{2-}]$  for  $[\text{Co(II)HEDTAOH}_2]^-$ - $\text{S}_2\text{O}_8^{2-}$  system,  $(3.0-8.0) \times 10^{-2} \text{ mol dm}^{-3}$  at  $9.0 \times 10^{-2} \text{ mol dm}^{-3}$  for  $[\text{Co(II)EDTA}]^{2-}$ - $[\text{ClO}^-]$ ,  $(6.0-16.0) \times 10^{-3} \text{ mol dm}^{-3}$  at  $9.0 \times 10^{-2} \text{ mol dm}^{-3}$  for  $[\text{Co(II)HEDTAOH}_2]^-$ - $[\text{ClO}^-]$ .

The order with respect to  $[Ag^+]$  and its effect on the reaction rate was determined by varying  $[Ag^+]$  in the  $(2.50-40.0) \times 10^{-3} \text{ mol dm}^{-3}$  range, maintaining  $[\text{S}_2\text{O}_8^{2-}]$  at  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$  for  $[\text{Co(II)EDTA}]^{2-}$ - $\text{S}_2\text{O}_8^{2-}$  system. Similarly, variation of  $[Ag^+]$  in the  $(1.25-40.0) \times 10^{-3} \text{ mol dm}^{-3}$  range maintaining  $[\text{S}_2\text{O}_8^{2-}]$  at  $16.0 \times 10^{-2} \text{ mol dm}^{-3}$  for  $[\text{Co(II)HEDTAOH}_2]^-$ - $\text{S}_2\text{O}_8^{2-}$  system was used to determine its effect on the reaction rate, while all other conditions remain the same as stated in the kinetic measurements.

### 3.2.13 Effect of changes in ionic strength

The effect of ionic strength on the rate constants of the reactions were determined by keeping the concentration of reactants constant and varying the concentration of the inert electrolyte (NaNO<sub>3</sub>) from 0.3 – 0.7 mol dm<sup>-3</sup>, 0.6 – 1.2 mol dm<sup>-3</sup>, 0.2 – 0.8 mol dm<sup>-3</sup>, and 0.2 – 0.8 mol dm<sup>-3</sup> for [Co(II)EDTA]<sup>2-</sup> – S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, [Co(II)HEDTAOH<sub>2</sub>]<sup>-</sup> – S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, [Co(II)EDTA]<sup>2-</sup> – ClO<sup>-</sup> and [Co(II)HEDTAOH<sub>2</sub>]<sup>-</sup> – ClO<sup>-</sup> systems respectively. The relationship between the reaction rate with changes in ionic strength was determined by plotting log k<sub>2</sub> against √I.

### 3.2.14 Effect of change in dielectric constant on the reaction rates

The effect of dielectric constant (D) on the reaction rates was determined at different dielectric constants in the range 80.10 – 66.54, 80.10 – 58.73, 80.10 – 58.19 and 79.07 – 74.93 for [Co(II)EDTA]<sup>2-</sup> – S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, [Co(II)HEDTAOH<sub>2</sub>]<sup>-</sup> – S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, [Co(II)EDTA]<sup>2-</sup> – ClO<sup>-</sup> and [Co(II)HEDTAOH<sub>2</sub>]<sup>-</sup> – ClO<sup>-</sup> systems respectively using water-acetone mixture at constant [oxidants], [reductants], [H<sup>+</sup>] and [Ag<sup>+</sup>] (where applicable) (Onu *et al.*, 2016).

The dielectric constant for the reaction medium was calculated as:

$$D = \frac{D_{H_2O} \times V_{H_2O} + D_{acetone} \times V_{acetone}}{V_{H_2O} + V_{acetone}} \quad 3.2$$

### 3.2.15 Effect of temperature on the reaction rates

The influence of temperature has been studied in the temperature range of 309 – 329 and 303 – 323K for [Co(II)EDTA]<sup>2-</sup> – S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and [Co(II)HEDTAOH<sub>2</sub>]<sup>-</sup> – S<sub>2</sub>O<sub>8</sub><sup>2-</sup> systems respectively using thermostated water bath. The reactant solutions were equilibrated at the temperature of the water bath, mixed and quickly transferred into a colorimeter to measure the change in absorbance with time. The temperature of the reaction mixture before and at the end of

the reaction was found to be fairly the same. Activation parameters were calculated by plotting  $\ln\left(\frac{k_2}{T}\right)$  versus  $\left(\frac{1}{T}\right)$  using Eyring equation (3.3).

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{R}\left(\frac{1}{T}\right) \quad 3.3$$

where  $k$  = reaction rate constant,  $T$  = Kelvin temperature,  $k_B$  = Boltzmann's constant,  $h$  = Planck's constant,  $\Delta S^*$  = entropy of activation,  $\Delta H^*$  = enthalpy of activation and  $R$  = Molar Gas constant

### 3.2.16 Effect of added ions on the reaction rates

The effect of added ions on the reaction rate was studied by addition of  $(1.0 - 5.0) \times 10^{-2}$  and  $(1.0 - 5.0) \times 10^{-3}$  mol dm<sup>-3</sup> solutions of ions ( $K^+$ ,  $Li^+$ ,  $CH_3COO^-$ , and  $HCOO^-$ ), keeping [oxidants], [reductants],  $[Ag^+]$ ,  $[H^+]$  and ionic strength constant (Onu *et al.*, 2016).

### 3.2.17 Spectroscopic test for the presence of intermediate complex

Test for the presence of an intermediate formed during the course of the reactions were carried out spectrophotometrically. Electronic spectra of partially reacted mixtures were recorded at various time intervals using Corning 252 Colorimetre at wavelength range of 450 – 700 nm. This was carried out to determine whether there is a shift in  $\lambda_{max}$  as the reactions progressed for all the systems.

### 3.2.18 Free radical test

About 0.5 g of acrylamide was added to partially oxidized reactions mixture for all the systems. This was followed by a large excess of methanol. Formation of polyacrylamide evidenced by gel formation would provide information for the presence of free radicals in the reaction mixture (Onu *et al.*, 2016).

### **3.2.19 Products analysis**

UV-visible scanning of the solution of the products formed for all the systems were carried out at the wavelength range of 350 – 700 nm. Also confirmatory tests were carried out on the inorganic products of the reactions using qualitative analysis (Vogel, 1996). These tests were carried out on both reductants and oxidants before the start of the reaction (Onu *et al.*, 2016).

## **CHAPTER FOUR**

### **4.0 RESULTS**

#### **4.1 Stoichiometry Studies**

The curves of the spectrophotometric titration from which the stoichiometries of the reactions were determined, are presented in Figures 4.1 – 4.4 for all the reaction systems respectively.

#### **4.2 Order and Rate Constants of the Reactions**

The results of the kinetic study obtained by plotting  $\log(A_{\infty}-A_t)$  against time are shown in Figures 4.5 – 4.8 and pseudo-first order rate constants,  $k_{\text{obs}}$  obtained from these plots, are presented in Tables 4.1 – 4.4. The logarithmic plot of  $k_{\text{obs}}$  versus  $\log$  [oxidant] from which order of the reactions were determined, are presented in Figures 4.9 – 4.11. The values of second order

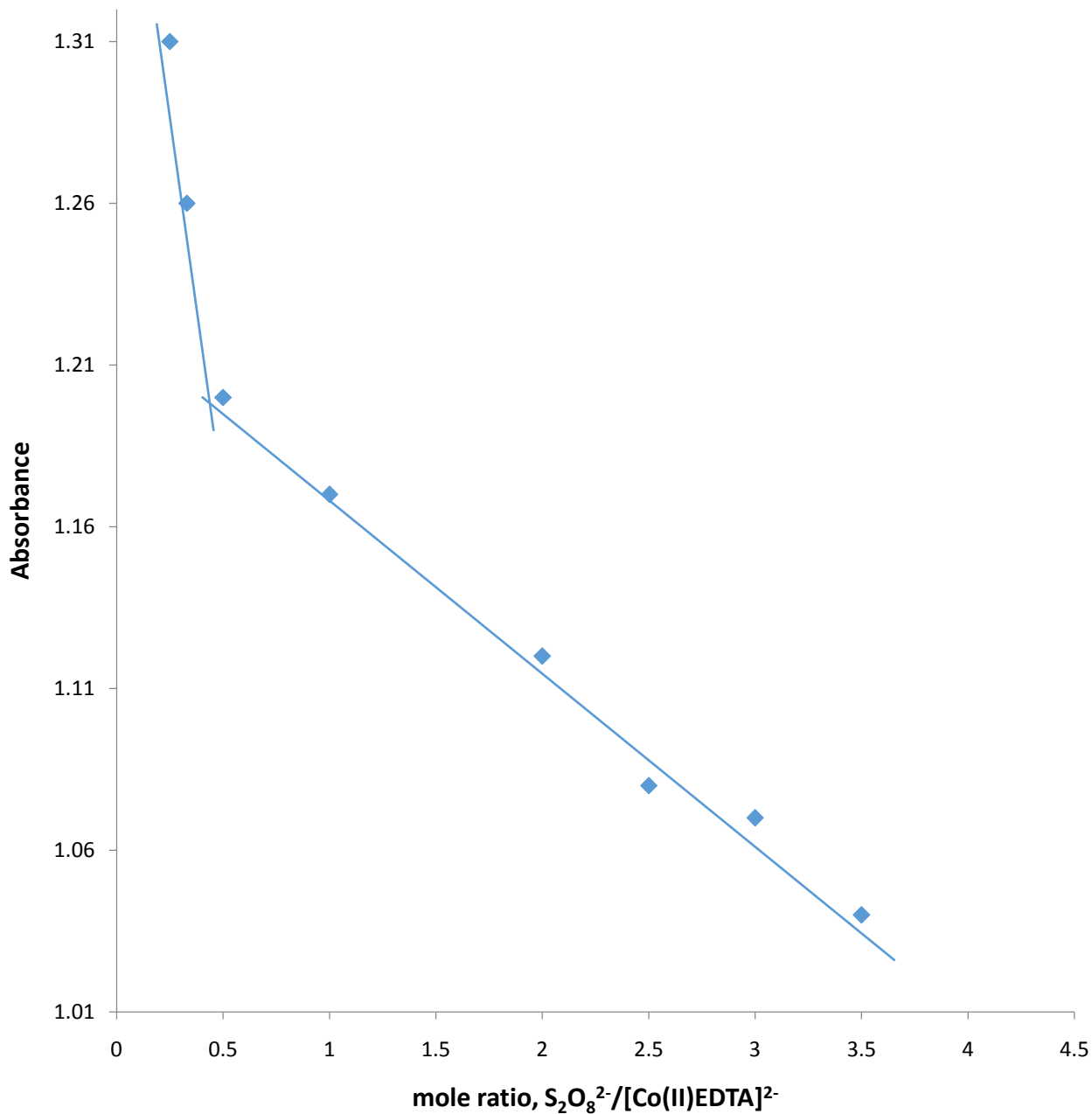
rate constants  $k_2$ , or  $k_1$  (for zero order reaction) determined as  $k_{\text{obs}}/[\text{oxidant}]$  for all the reactions were reported (Tables 4.1 – 4.4).

### 4.3 Effect of Acid and Catalyst on the Reaction Rates

The plots of  $k_2$  versus  $[H^+]^{-1}$  for  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{ClO}^-$  and  $[\text{Co(II)HEDTA}]^-$ -  $\text{ClO}^-$  systems are presented in Figures 4.12 - 4.13, while plots of  $k_2$  versus  $[\text{Ag}^+]$  for  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{S}_2\text{O}_8^{2-}$  and  $[\text{Co(II)HEDTA}]^-$ - $\text{S}_2\text{O}_8^{2-}$  systems are reported in Figures 4.14 - 4.15.

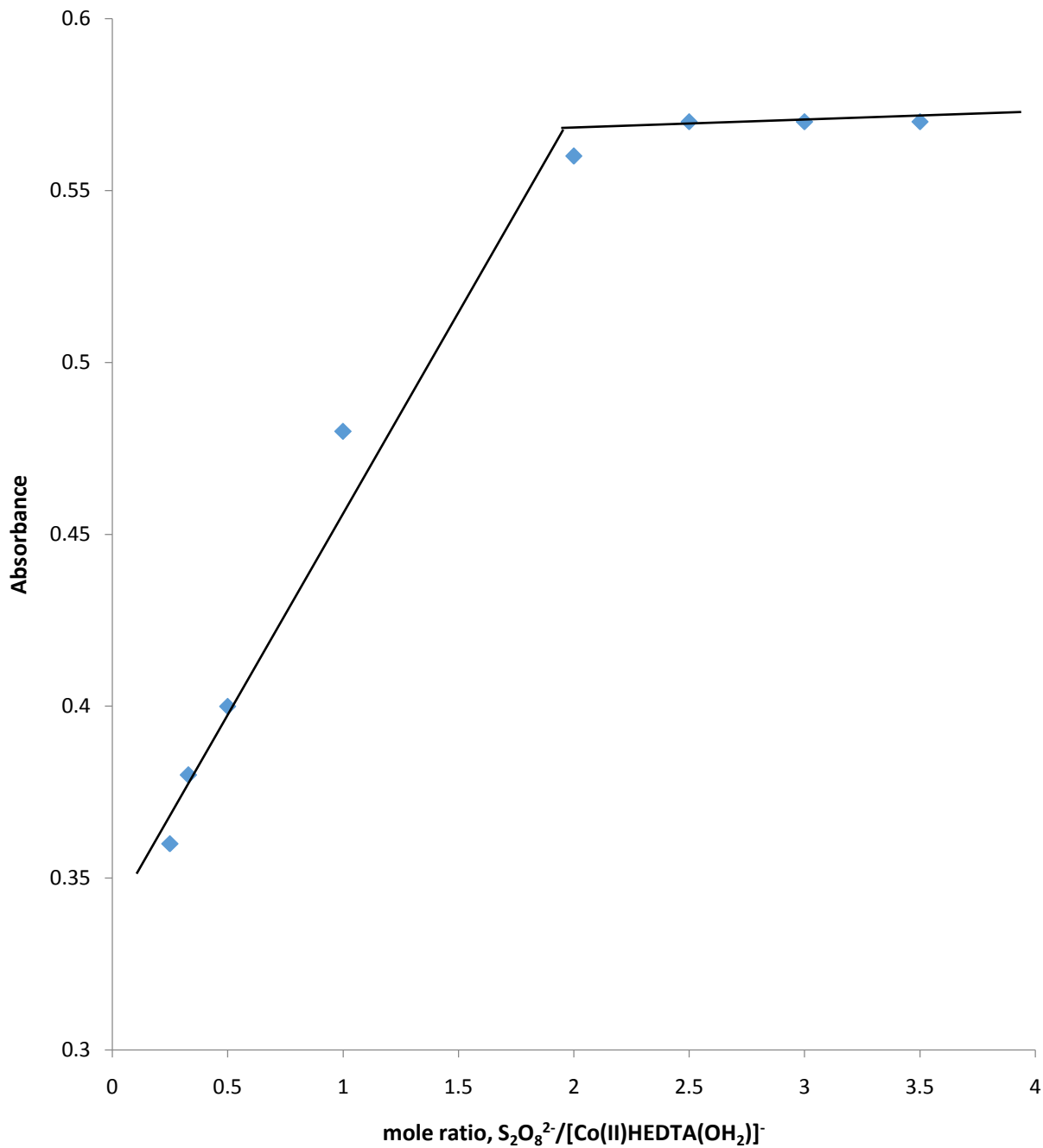
### 4.4 Effect of Changes in Ionic Strength and Dielectric Constant on the Reaction Rates

The results of the effect of changes in ionic strength on the reaction's medium are presented in Tables 4.1- 4.4. Plots of  $\log k_2$  versus  $I^{1/2}$  for  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{ClO}^-$  and  $[\text{Co(II)HEDTA}]^-$ -  $\text{ClO}^-$  systems are shown in Figures 4.16 – 4.17. Similarly, results of the effect of dielectric constants on the reaction's medium are presented in Tables 4.5 - 4.8 and plot of  $\log k_2$  versus  $1/D$  for  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{ClO}^-$  reaction is shown in Figure 4.18.

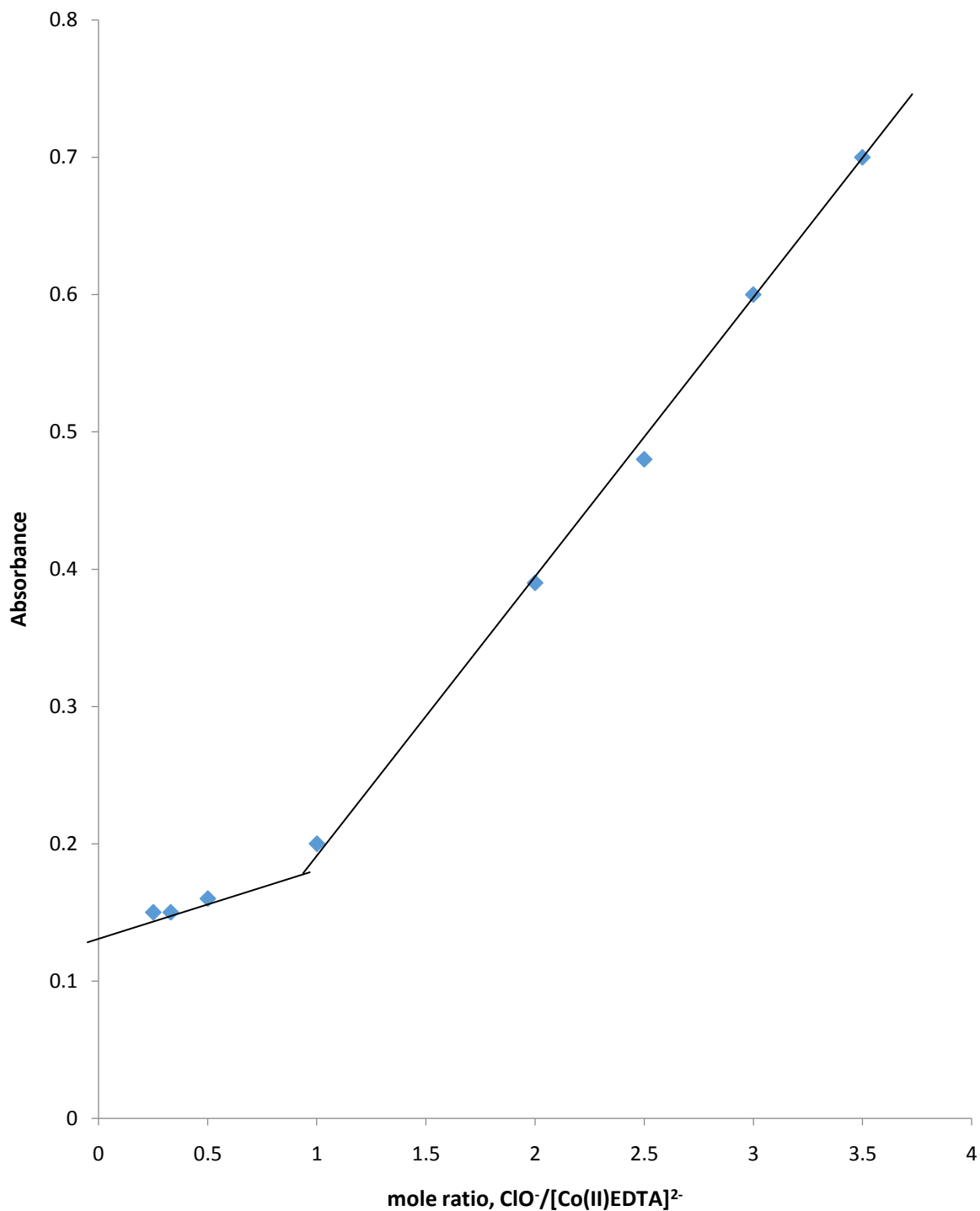


**Figure 4.1:** Plot of Absorbance versus mole ratio for the reaction of  $[Co^{II}EDTA]^{2-}$  with  $S_2O_8^{2-}$  at  $[Co^{II}EDTA^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[S_2O_8^{2-}] = (0.125 - 2.0) \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[Ag^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1 \text{ K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

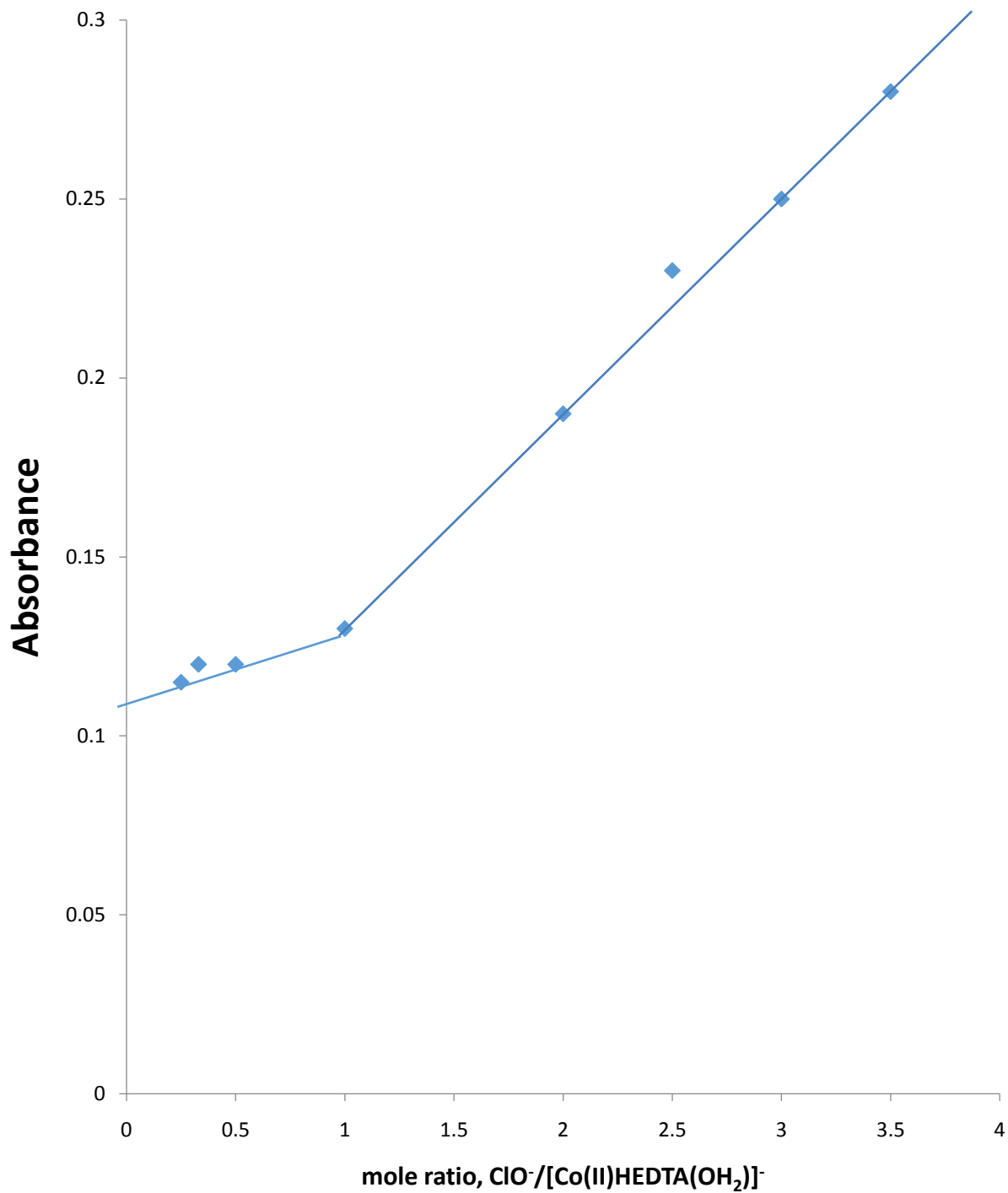




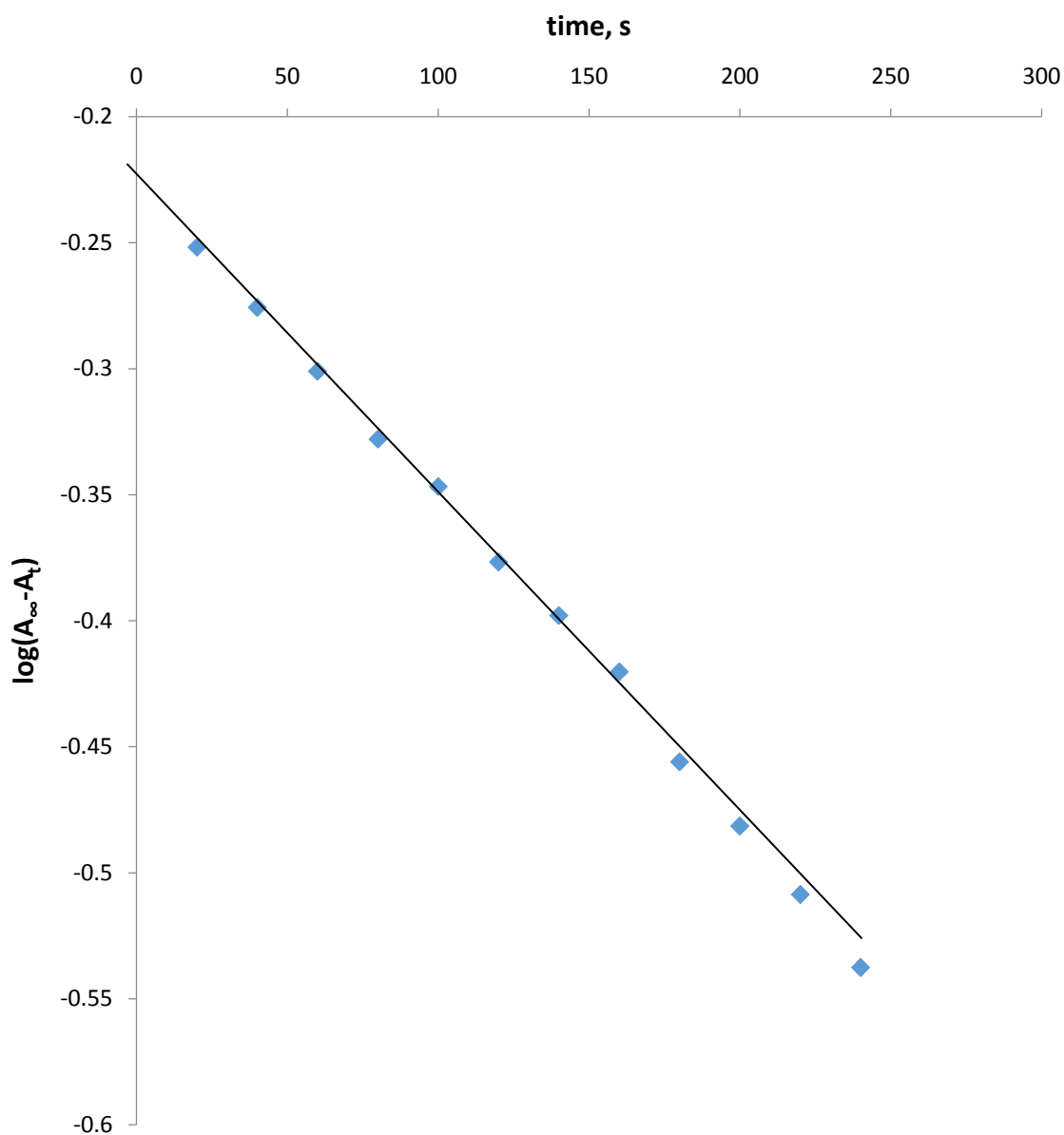
**Figure 4.2:** Plot of Absorbance versus mole ratio for the reaction of  $[Co(II)HEDTA(OH_2)]^-$  with  $S_2O_8^{2-}$  at  $[Co(II)HEDTA(OH_2)]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[S_2O_8^{2-}] = (1.25 - 17.50) \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[Ag^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1K$  and  $\lambda_{\text{max}} = 525 \text{ nm}$



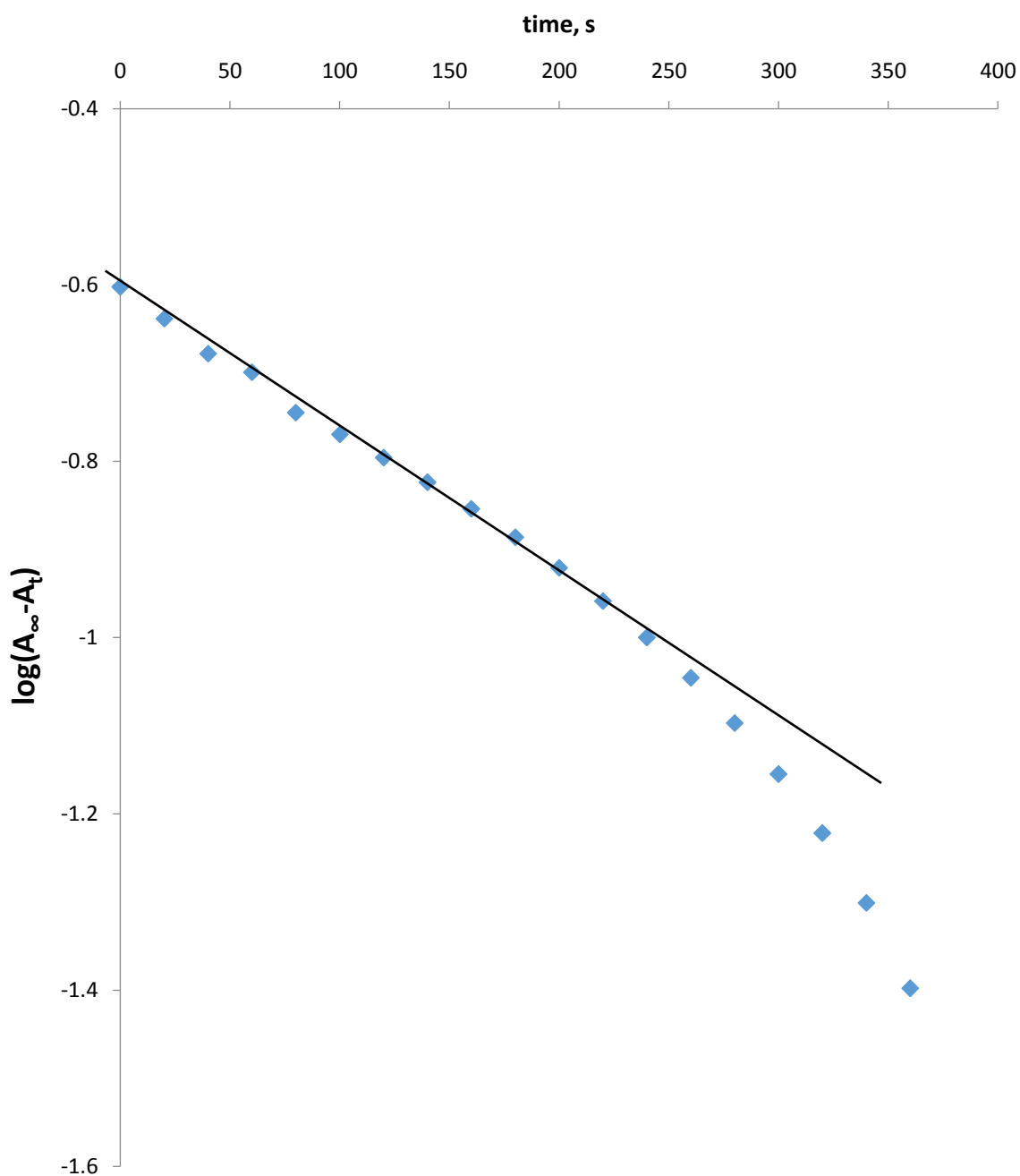
**Figure 4.3:** Plot of Absorbance versus mole ratio for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = (0.125 - 2.0) \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.1 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1 \text{ K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



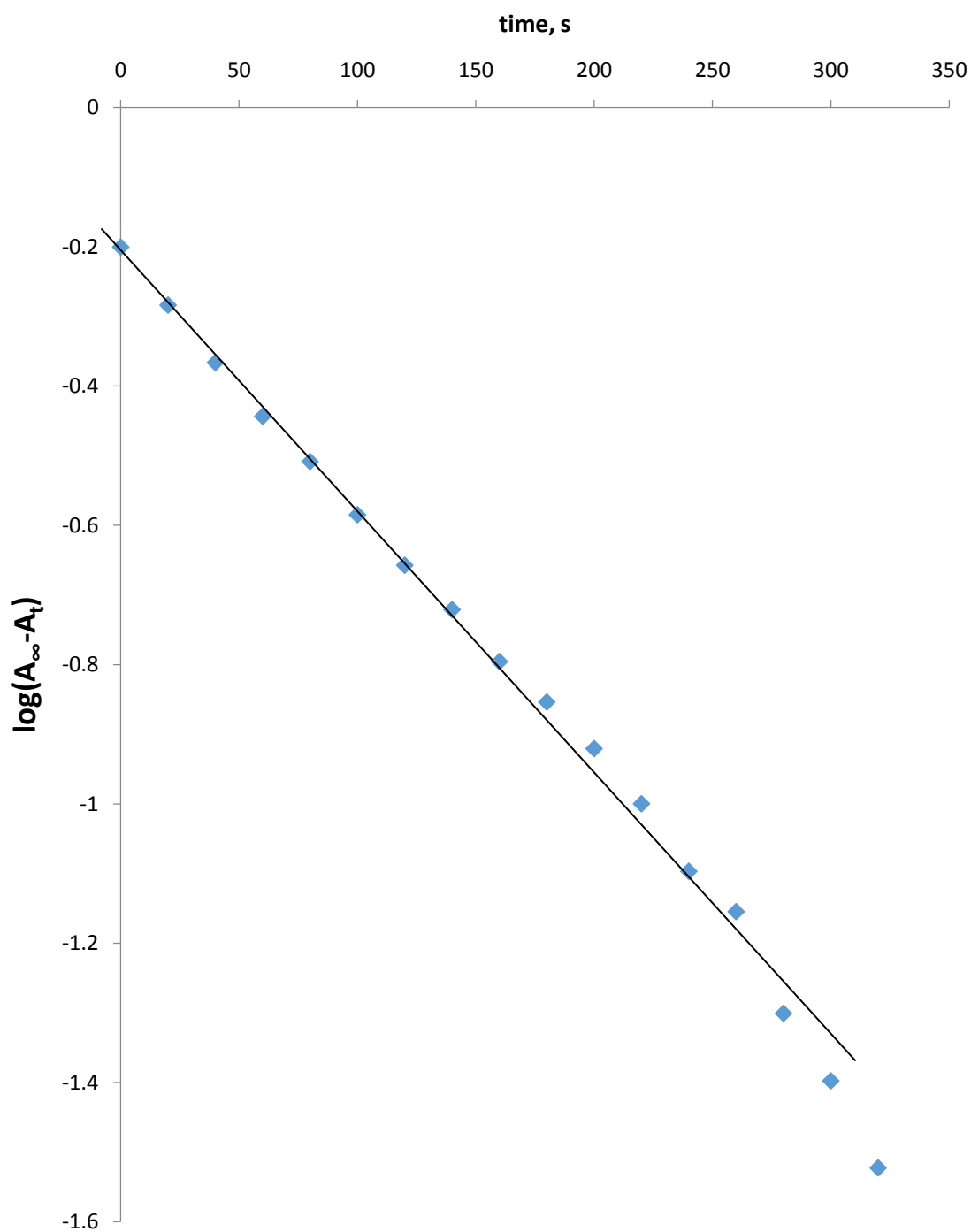
**Figure 4.4:** Plot of Absorbance versus mole ratio for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{HEDTA(OH}_2\text{)}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = (0.125 - 2.0) \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.1 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$



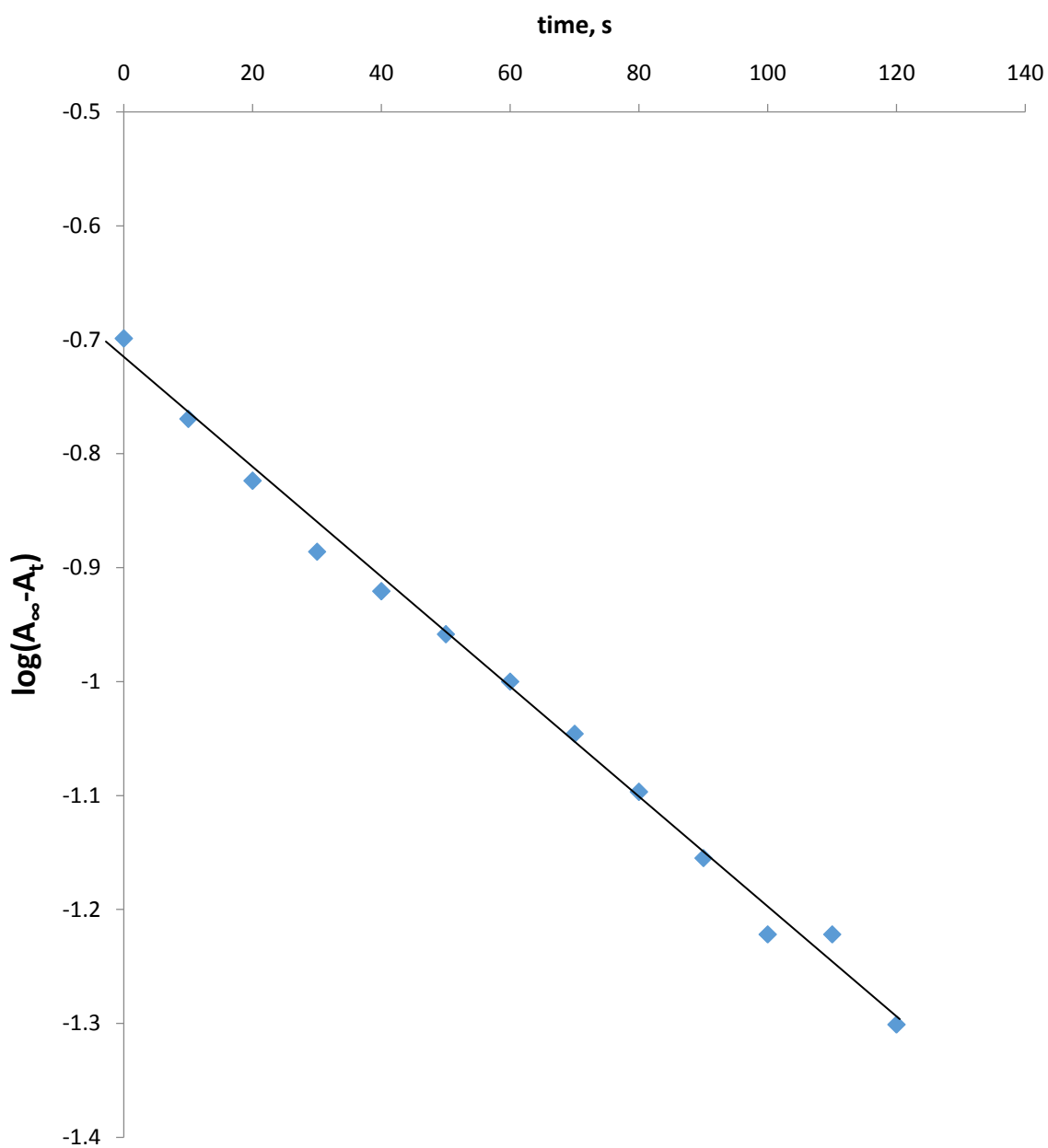
**Figure 4.5:** Typical pseudo-first order Plot for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



**Figure 4.6:** Typical pseudo-first order Plot for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)]^-$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 12.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$



**Figure 4.7:** Typical pseudo-first order plot for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{ClO}^- = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



**Figure 4.8:** Typical pseudo-first order plot for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)]^-$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{ClO}^- = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

**Table 4.1:** The pseudo-first order and second order rate constants for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  and  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

$10^3[\text{S}_2\text{O}_8^{2-}]$ , mol $\text{dm}^{-3}$	$10^3[\text{H}^+]$ , mol $\text{dm}^{-3}$	$10^3[\text{Ag}^+]$ , mol $\text{dm}^{-3}$	$10^2 I$ , mol $\text{dm}^{-3}$	$10^3 k_{\text{obs}}$ , $\text{s}^{-1}$	$10^2 k_2$ , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
30.0	10.0	10.0	50.0	2.9	9.7
35.0	10.0	10.0	50.0	3.5	9.9
40.0	10.0	10.0	50.0	3.9	9.8
45.0	10.0	10.0	50.0	4.4	9.7
50.0	10.0	10.0	50.0	4.8	9.7
55.0	10.0	10.0	50.0	5.3	9.7
60.0	10.0	10.0	50.0	5.8	9.6
65.0	10.0	10.0	50.0	6.3	9.7
70.0	10.0	10.0	50.0	6.7	9.5
50.0	10.0	2.5	50.0	1.4	2.8
50.0	10.0	5.0	50.0	2.8	5.5
50.0	10.0	10.0	50.0	4.8	9.7
50.0	10.0	20.0	50.0	10.1	20.3
50.0	10.0	40.0	50.0	17.9	35.8
50.0	2.5	10.0	50.0	4.5	9.1
50.0	5.0	10.0	50.0	4.8	9.6
50.0	10.0	10.0	50.0	4.8	9.6
50.0	20.0	10.0	50.0	4.5	9.1
50.0	40.0	10.0	50.0	4.5	9.1
50.0	10.0	10.0	30.0	4.6	9.2
50.0	10.0	10.0	40.0	4.8	9.7
50.0	10.0	10.0	50.0	4.8	9.7
50.0	10.0	10.0	60.0	4.8	9.7
50.0	10.0	10.0	70.0	4.6	9.2



**Table 4.2:** The pseudo-first order and reaction rate constants for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)]^-$  and  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

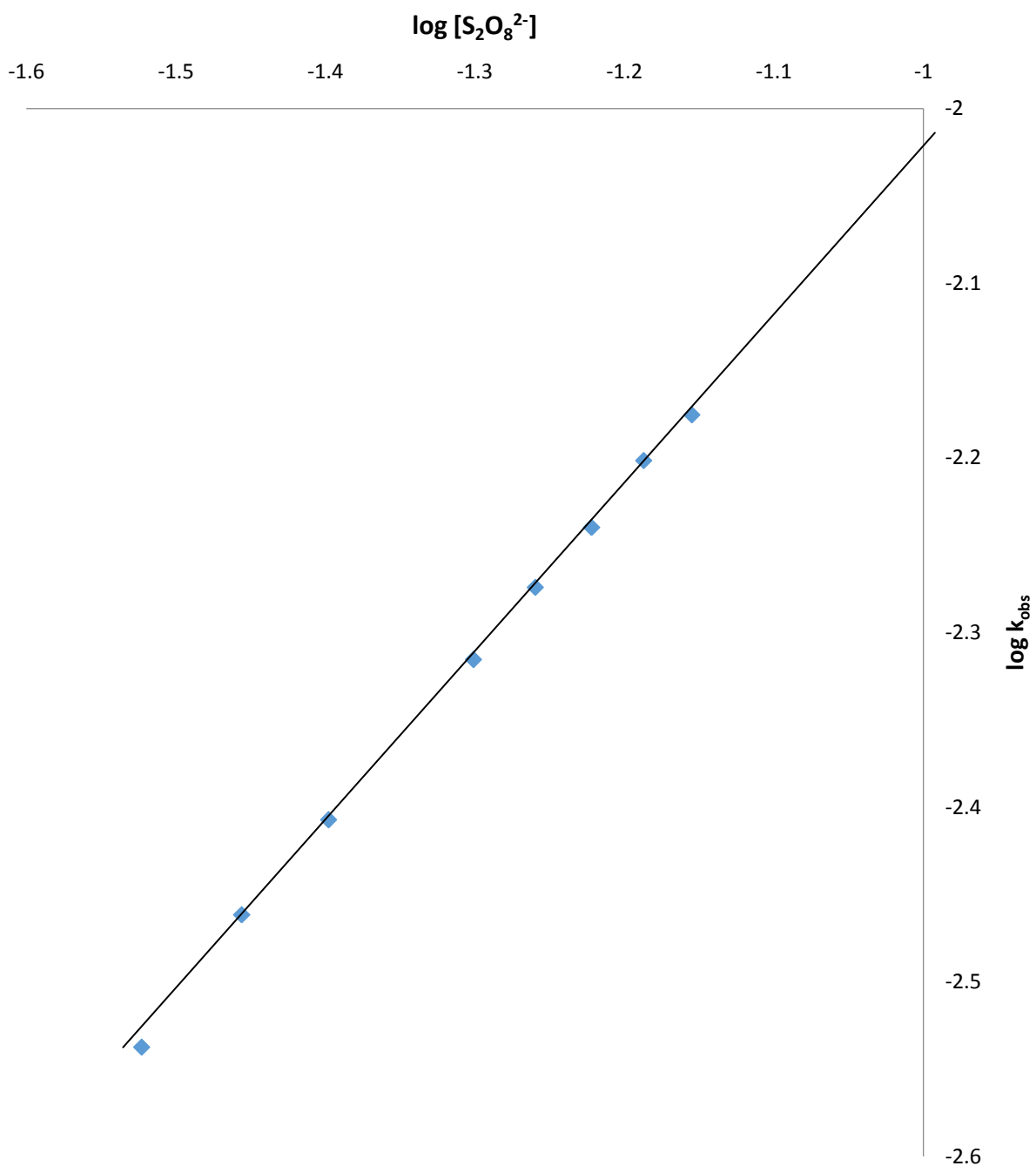
$10^2[\text{S}_2\text{O}_8^{2-}]$ , mol dm <sup>-3</sup>	$10^3[\text{H}^+]$ , mol dm <sup>-3</sup>	$10^3[\text{Ag}^+]$ , mol dm <sup>-3</sup>	$10^2 \text{ I}$ , mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	$10^3 k_1$ , s <sup>-1</sup>
8.0	10.0	10.0	50.0	5.8	5.8
10.0	10.0	10.0	50.0	6.0	6.0
12.0	10.0	10.0	50.0	6.2	6.2
14.0	10.0	10.0	50.0	6.0	6.0
16.0	10.0	10.0	50.0	6.0	6.0
18.0	10.0	10.0	50.0	6.0	6.0
20.0	10.0	10.0	50.0	6.0	6.0
22.0	10.0	10.0	50.0	6.0	6.0
16.0	0.6	10.0	50.0	6.0	6.0
16.0	1.3	10.0	50.0	6.2	6.2
16.0	2.5	10.0	50.0	6.0	6.0
16.0	5.0	10.0	50.0	6.0	6.0
16.0	10.0	10.0	50.0	6.0	6.0
16.0	20.0	10.0	50.0	6.2	6.2
16.0	40.0	10.0	50.0	6.2	6.2
16.0	10.0	1.3	50.0	1.6	1.6
16.0	10.0	2.5	50.0	2.8	2.8
16.0	10.0	5.0	50.0	4.8	4.8
16.0	10.0	10.0	50.0	6.0	6.0
16.0	10.0	20.0	50.0	12.6	12.6
16.0	10.0	40.0	50.0	22.8	22.8
16.0	10.0	10.0	50.0	6.0	6.0
16.0	10.0	10.0	60.0	6.2	6.2
16.0	10.0	10.0	70.0	6.0	6.0
16.0	10.0	10.0	80.0	6.0	6.0
16.0	10.0	10.0	90.0	6.0	6.0
16.0	10.0	10.0	100.0	6.2	6.2
16.0	10.0	10.0	110.0	6.2	6.2
16.0	10.0	10.0	120.0	6.0	6.0

**Table 4.3:** The pseudo-first order and second order rate constants for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  and  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-} = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

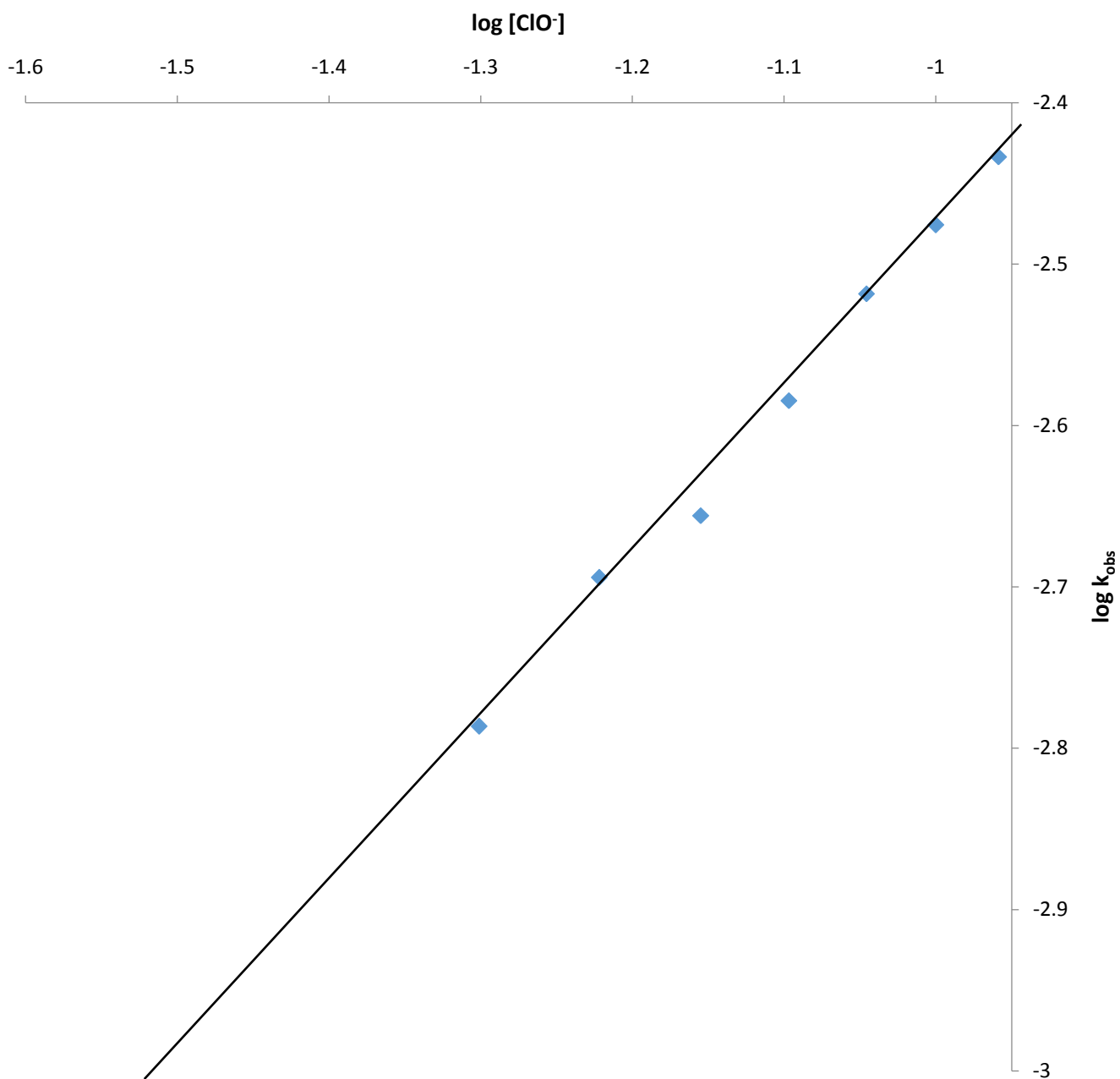
$10^3[\text{ClO}^-]$ , mol dm <sup>-3</sup>	$10^3[\text{H}^+]$ , mol dm <sup>-3</sup>	$10^2 I$ , mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	$10^2 k_2$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
50.0	40.0	50.0	1.5	3.3
60.0	40.0	50.0	1.8	3.4
70.0	40.0	50.0	2.2	3.2
80.0	40.0	50.0	2.6	3.3
90.0	40.0	50.0	3.0	3.4
100.0	40.0	50.0	3.3	3.3
110.0	40.0	50.0	3.7	3.3
90.0	40.0	20.0	2.0	2.2
90.0	40.0	30.0	2.4	2.6
90.0	40.0	40.0	2.9	3.2
90.0	40.0	50.0	3.2	3.5
90.0	40.0	60.0	4.1	4.5
90.0	40.0	70.0	4.4	4.9
90.0	40.0	80.0	4.9	5.5
90.0	30.0	50.0	3.8	4.2
90.0	40.0	50.0	3.0	3.4
90.0	50.0	50.0	2.5	2.8
90.0	60.0	50.0	2.2	2.4
90.0	70.0	50.0	1.7	1.9
90.0	80.0	50.0	1.5	1.6

**Table 4.4:** The pseudo-first order and reaction rate constants for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)]^-$  and  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

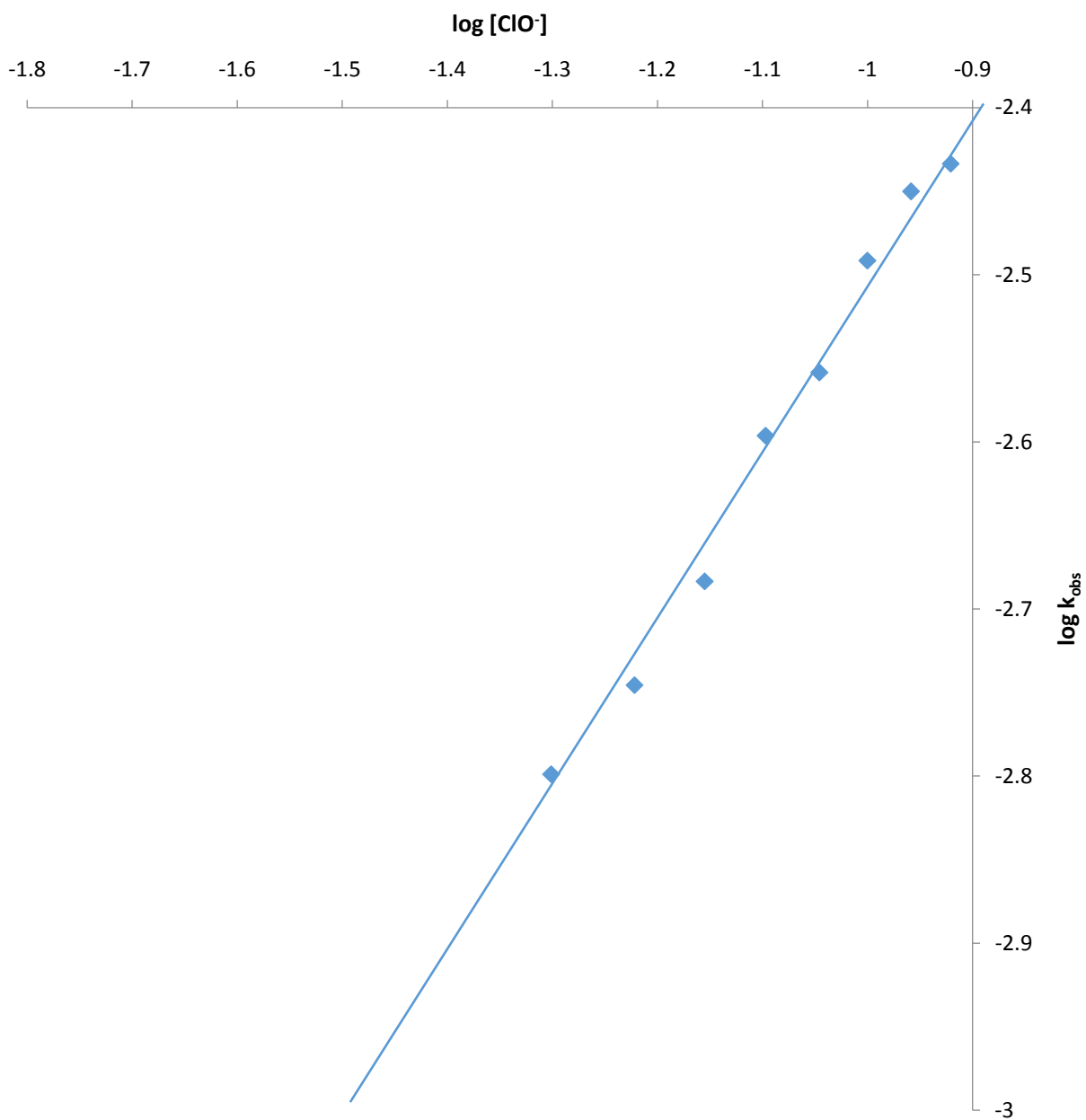
$10^3[\text{ClO}^-]$ , mol dm <sup>-3</sup>	$10^3[\text{H}^+]$ , mol dm <sup>-3</sup>	$10^2 I$ , mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	$10^2 k_2$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
50.0	10.0	20.0	1.6	3.2
60.0	10.0	20.0	1.8	3.0
70.0	10.0	20.0	2.1	3.0
80.0	10.0	20.0	2.5	3.2
90.0	10.0	20.0	2.8	3.1
100.0	10.0	20.0	3.2	3.2
110.0	10.0	20.0	3.5	3.2
120.0	10.0	20.0	3.7	3.1
90.0	10.0	20.0	2.9	3.2
90.0	10.0	30.0	3.2	3.6
90.0	10.0	40.0	3.8	4.2
90.0	10.0	50.0	3.9	4.4
90.0	10.0	60.0	4.0	4.5
90.0	10.0	70.0	4.3	4.8
90.0	10.0	80.0	4.8	5.3
90.0	06.0	20.0	4.0	4.4
90.0	08.0	20.0	3.4	3.8
90.0	10.0	20.0	2.7	3.0
90.0	12.0	20.0	2.4	2.6
90.0	14.0	20.0	2.1	2.4
90.0	16.0	20.0	1.8	2.0



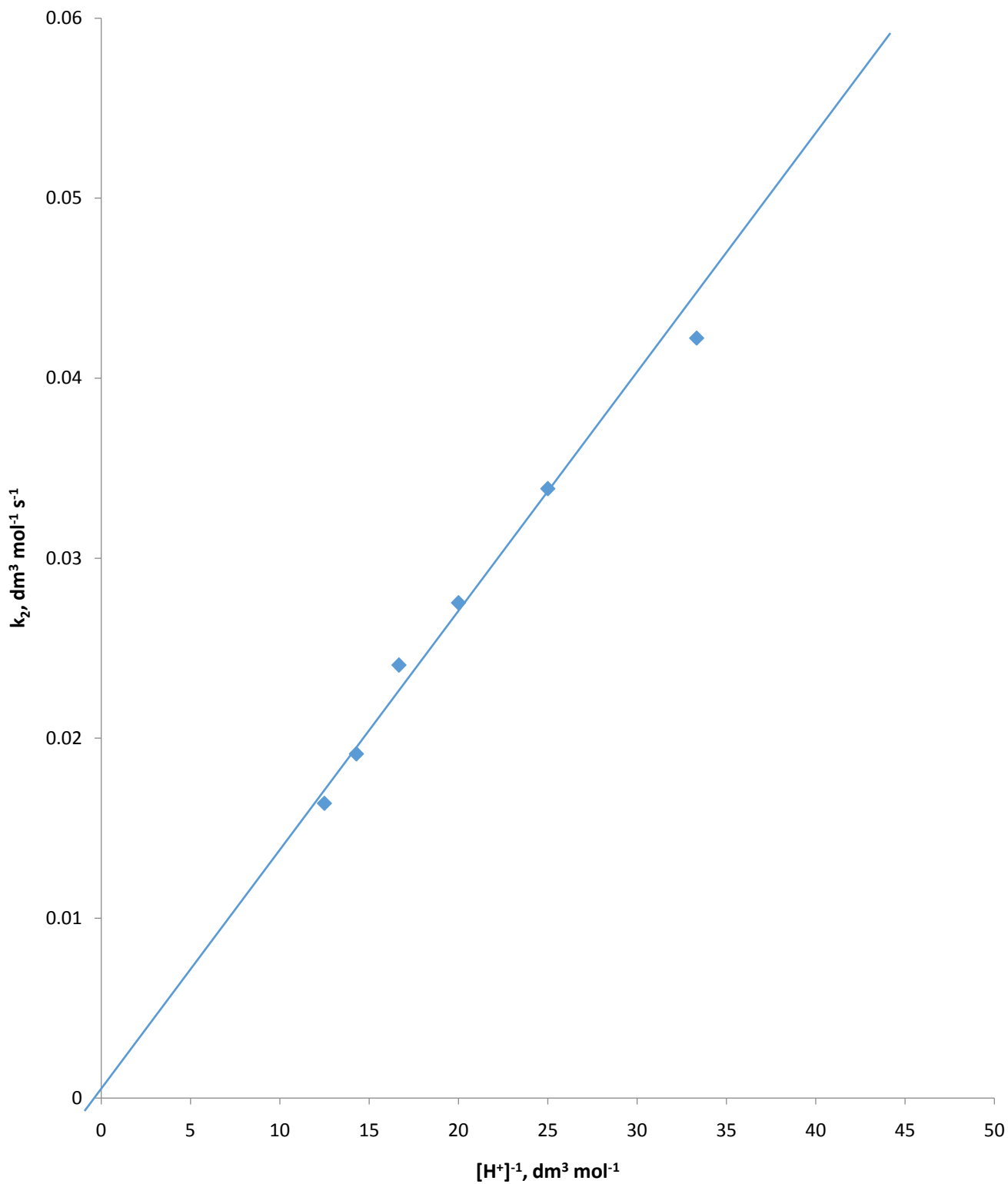
**Figure 4.9:** Plot of  $\log k_{obs}$  versus  $\log [S_2O_8^{2-}]$  for the reaction of  $[Co^{II}EDTA]^{2-}$  with  $S_2O_8^{2-}$  at  $[Co^{II}EDTA^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[Ag^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{max} = 520 \text{ nm}$



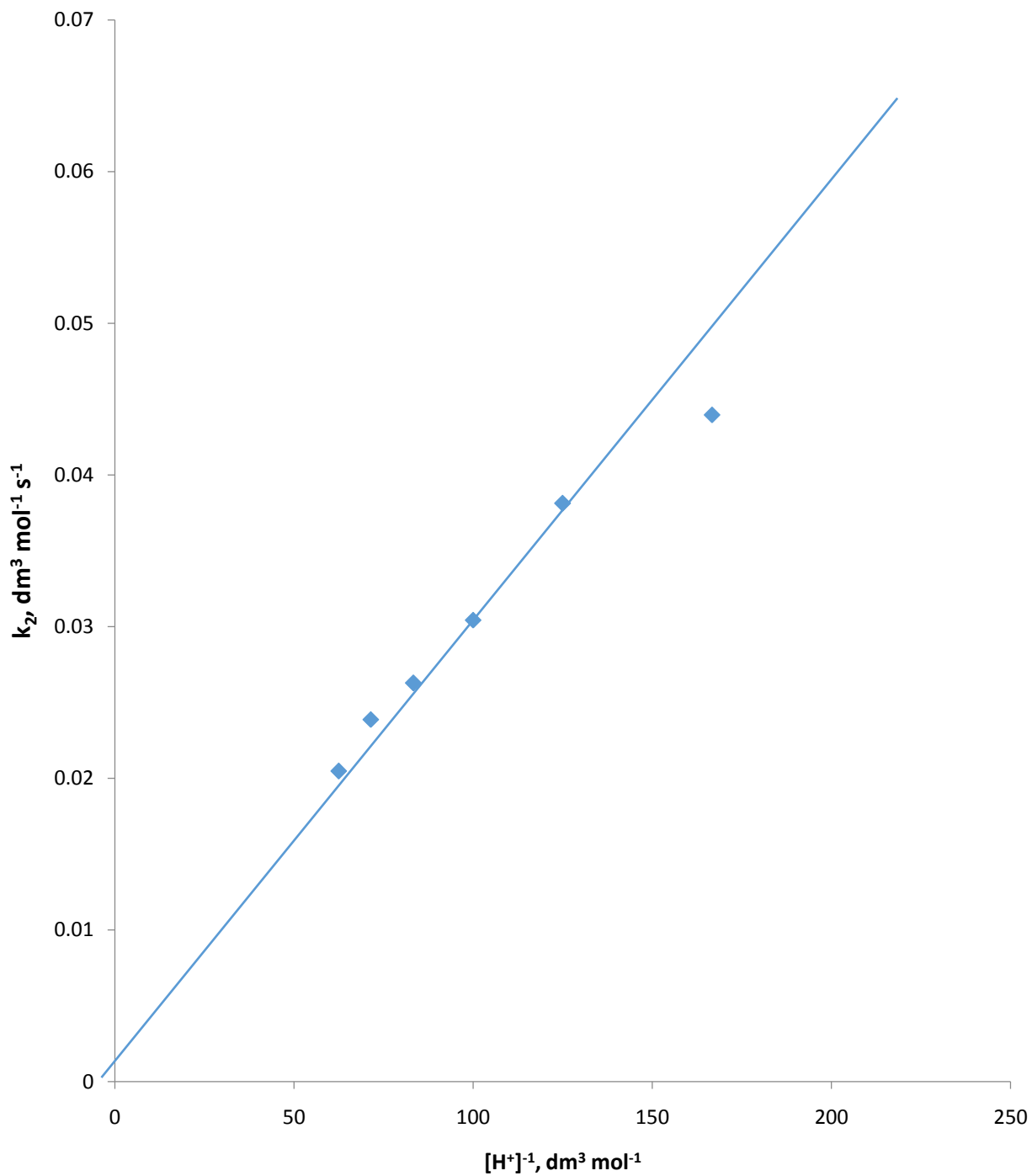
**Figure 4.10:** Plot of  $\log k_{\text{obs}}$  versus  $\log [\text{ClO}^-]$  for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



**Figure 4.11:** Plot of  $\log k_{\text{obs}}$  versus  $\log [\text{ClO}^-]$  for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)]^-$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{HEDTA}(\text{OH}_2)] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

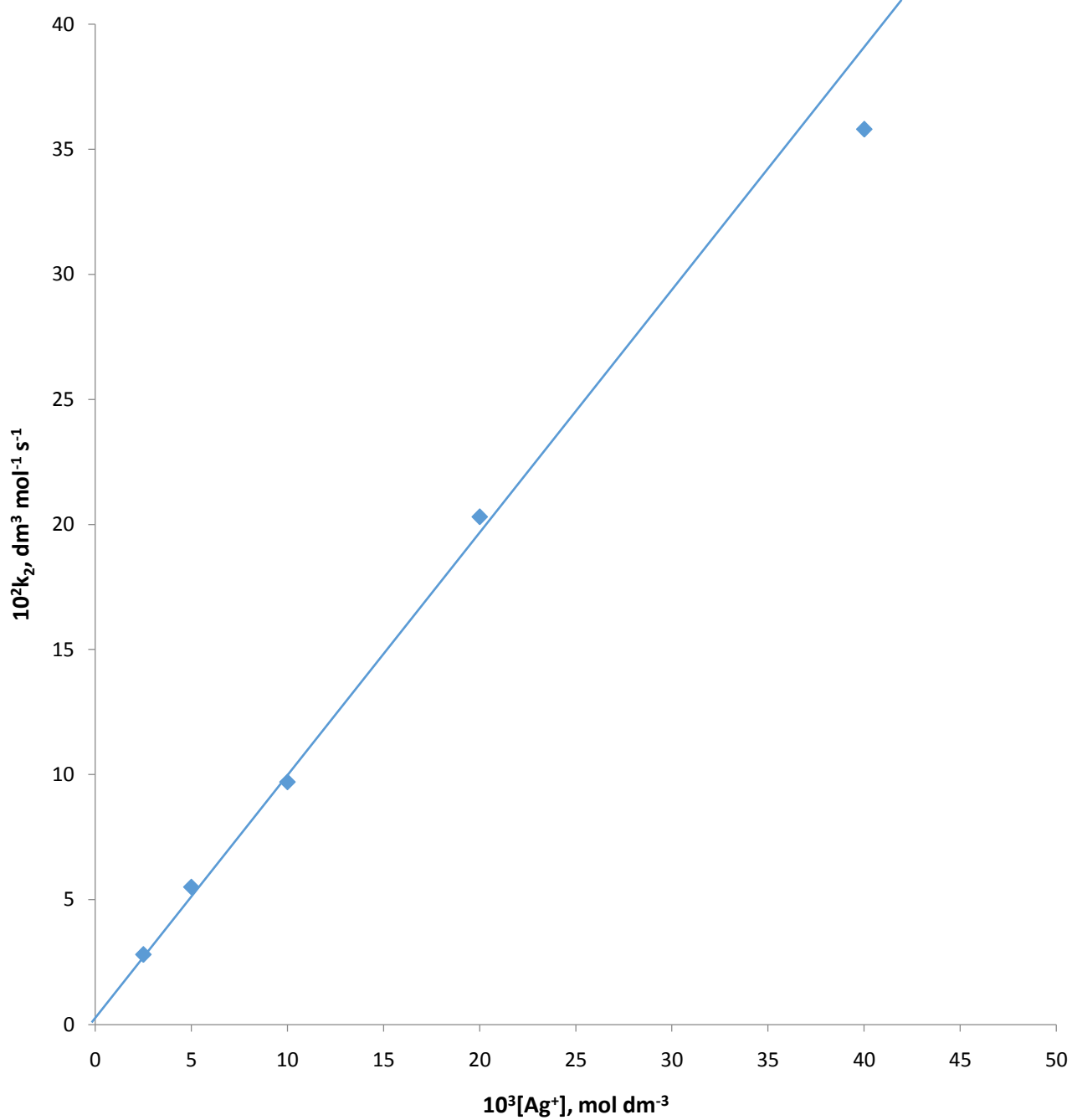


**Figure 4.12:** Plot of  $k_2$  versus  $[H^+]^{-1}$  for the reaction of  $[Co^{II}EDTA]^{2-}$  with  $ClO^-$  at  $[Co^{II}EDTA^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $ClO^- = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1K$  and  $\lambda_{max} = 520 \text{ nm}$

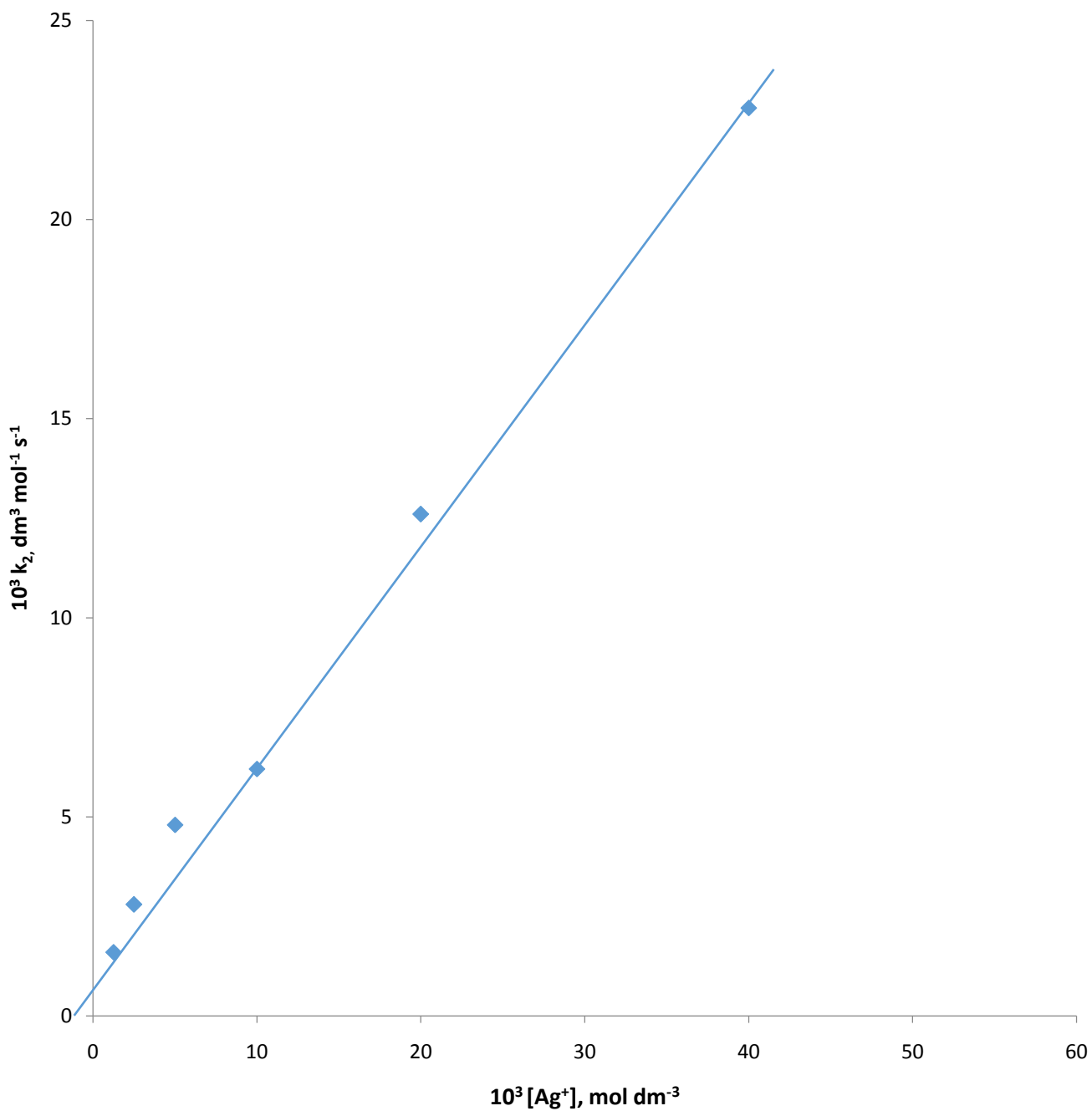


**Figure 4.13:** Plot of  $k_2$  versus  $[H^+]^{-1}$  for the reaction of  $[Co^{II}HEDTA]^-$  with  $ClO^-$  at  $[Co^{II}HEDTA] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $ClO^- = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

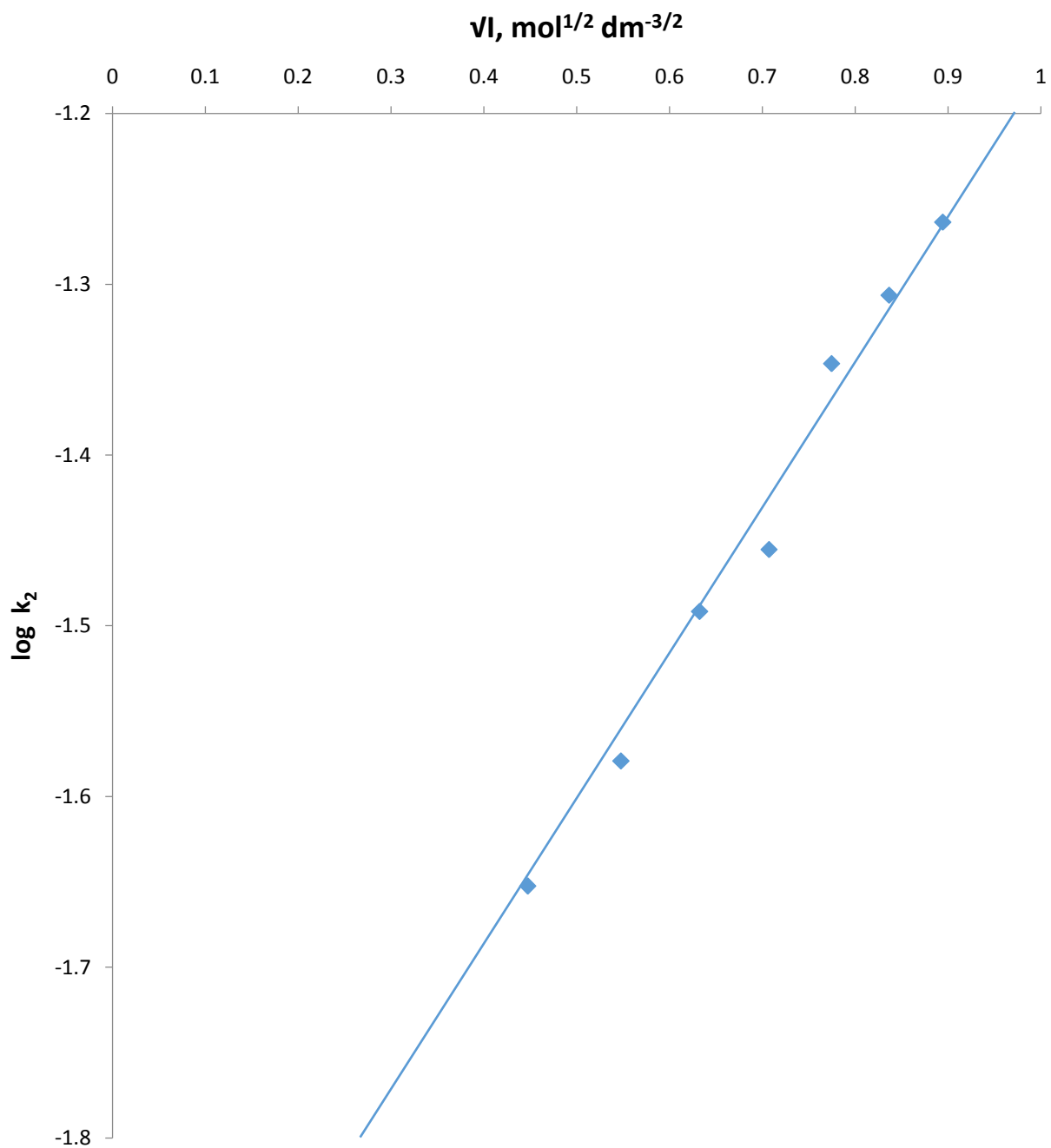




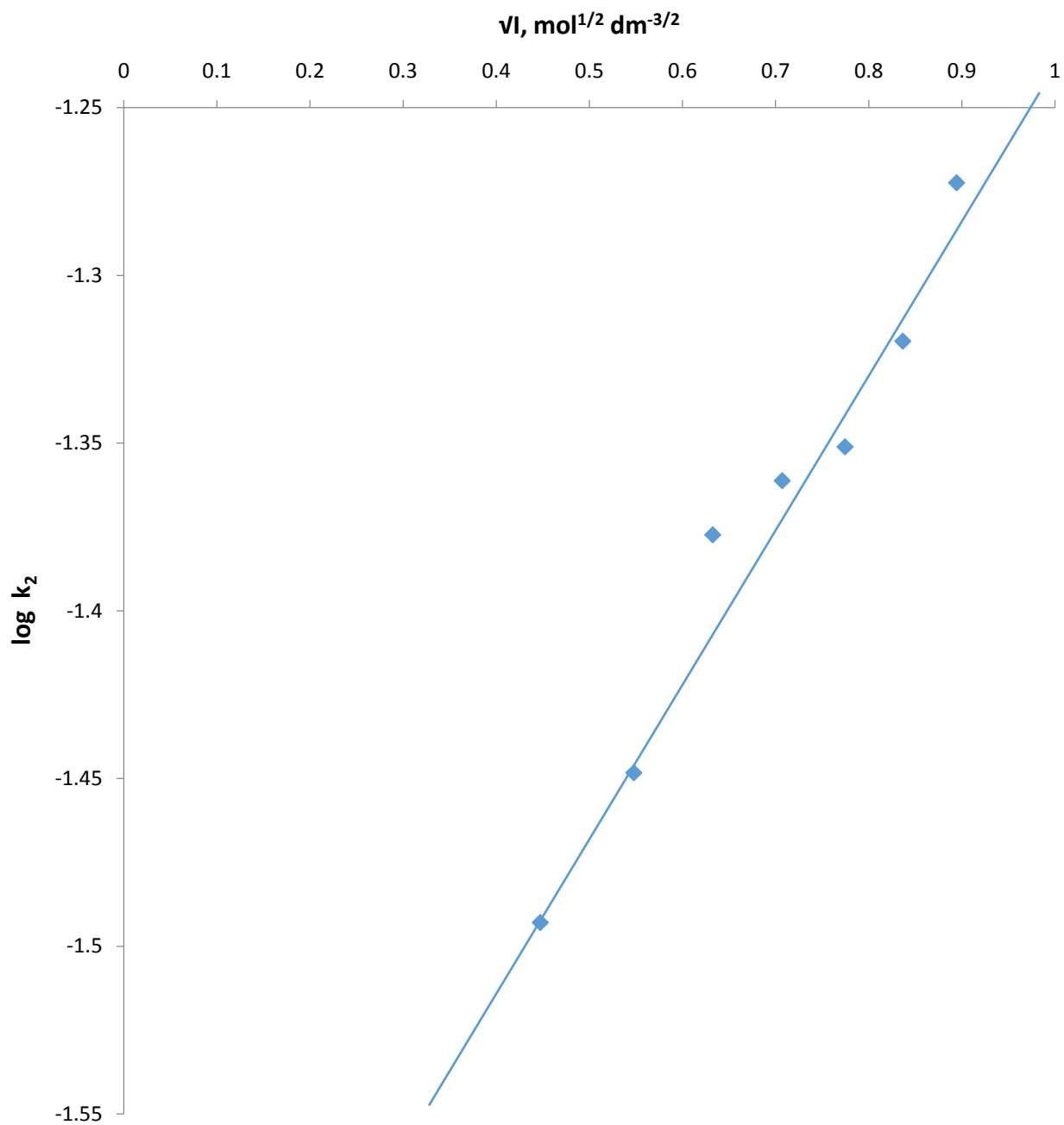
**Figure 4.14:** Plot of  $k_2$  versus  $[\text{Ag}^+]$  for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{S}_2\text{O}_8^{2-} = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



**Figure 4.15:** Plot of  $10^3 k_2$  versus  $[\text{Ag}^+]$  for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}]^-$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{HEDTA}]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{S}_2\text{O}_8^{2-} = 16.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$



**Figure 4.16:** Plot of  $\log k_2$  versus  $\sqrt{I}$  for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{ClO}^- = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



**Figure 4.17:** Plot of  $\log k_2$  versus  $\sqrt{I}$  for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}]^-$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{HEDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{ClO}^- = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

**Table 4.5:** Effect of Dielectric constant on the rate of reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

D	$10^3 1/D$	$10^3 k_{\text{obs}}, \text{ s}^{-1}$	$10^2 k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
80.10	12.48	4.84	9.67
77.39	12.92	4.84	9.67
74.68	13.39	4.84	9.67
71.96	13.90	4.84	9.67
69.25	14.44	4.81	9.62
66.54	15.03	4.81	9.62

**Table 4.6:** Effect of Dielectric constant on the rate of reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}]^-$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}(\text{II})\text{HEDTA}(\text{OH}_2)^-] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 16.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

<b>D</b>	$10^3 1/D$	$10^3 k_{\text{obs}}$ , $\text{s}^{-1}$	$10^3 k_1$ , $\text{s}^{-1}$
80.10	12.48	6.00	6.00
75.83	13.19	6.22	6.22
71.55	13.98	6.22	6.22
67.28	14.86	6.00	6.00
63.01	15.87	6.00	6.00
58.73	17.03	6.00	6.00

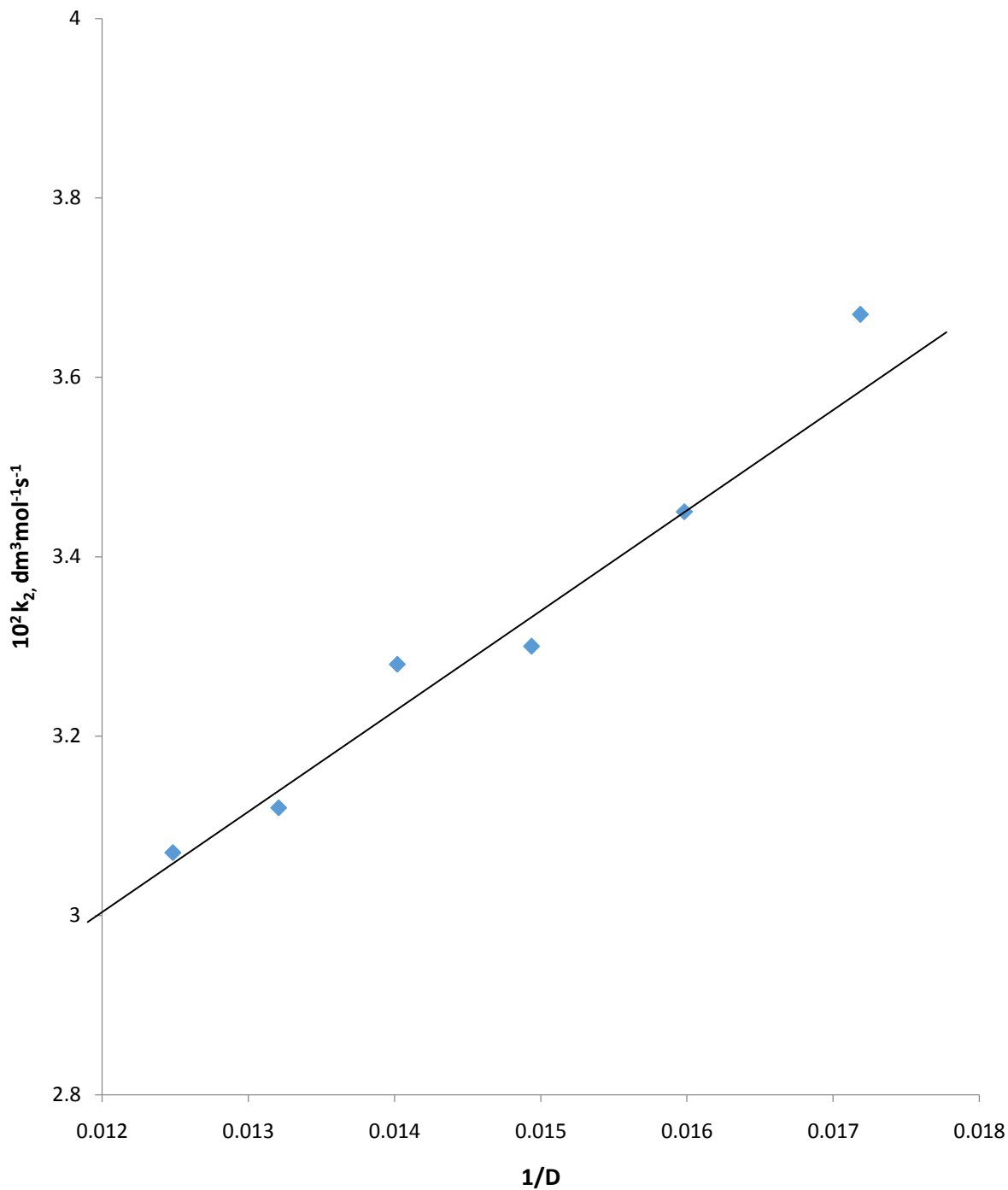
**Table 4.7:** Effect of Dielectric constant on the rate of reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}]^-$  with  $\text{ClO}^-$  at  $[\text{Co}(\text{II})\text{HEDTA}(\text{OH}_2)^-] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

D	$10^3 1/D$	$10^3 k_{\text{obs}}, \text{ s}^{-1}$	$10^3 k_2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
80.10	12.48	2.76	3.07
79.07	12.65	2.72	3.02
78.03	12.82	2.95	3.28
77.00	12.99	2.98	3.31
75.96	13.16	2.92	3.25
74.93	13.35	2.83	3.15

**Table 4.8:** Effect of Dielectric constant on the rate of reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}(\text{II})\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

<b>D</b>	<b><math>10^3 1/D</math></b>	<b><math>10^3 k_{\text{obs}}</math></b> <b><math>\text{s}^{-1}</math></b>	<b><math>10^3 k_2</math></b> <b><math>\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}</math></b>
80.10	12.48	2.76	3.07
75.72	13.21	2.81	3.12
71.33	14.02	2.95	3.28
67.95	14.94	2.97	3.30
62.57	15.98	3.11	3.45
58.19	17.19	3.29	3.67





**Figure 4.18:** Plots of  $k_2$  against  $1/D$  for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}(\text{II})\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1 \text{ K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

#### 4.5 Effect of Temperature on the Reaction Rates

Activation parameters obtained from the slopes ( $-\frac{\Delta H^*}{R}$ ) and intercepts ( $\ln\frac{k_b}{h} + \frac{\Delta S^*}{R}$ ) of the plot of  $\ln\left(\frac{k_2}{T}\right)$  against  $\frac{1}{T}$  (Figures 4.19 - 4.20) using the Eyring's equation (3.1) are presented in Tables 4.9 - 4.10. The slopes of -3448 and -6389 with intercepts of 3.226 and 10.09 are recorded respectively for  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{S}_2\text{O}_8^{2-}$  and  $[\text{Co(II)HEDTA}]^-$ -  $\text{S}_2\text{O}_8^{2-}$  systems. However, the reactions of  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{ClO}^-$ , and  $[\text{Co(II)HEDTAOH}_2]^-$ -  $\text{ClO}^-$  were too fast to carry out this study.

#### 4.6 Effect of Added Ions on the Reaction Rates

The results of both added cations ( $\text{K}^+$  and  $\text{Li}^+$ ) and added anions ( $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$ ) for all the reaction systems were reported in Tables 4.11 - 4.18.

#### 4.7 Spectroscopic Test

This was carried out to determine the presence of reactive intermediate indicated by a shift in  $\lambda_{\text{max}}$  as the reaction progresses (Figures 4.21 – 4.24).

#### 4.8 Free Radical Test

The test was carried out by the addition of about 0.5 g of acrylamide to partially reacted mixtures in the presence of excess methanol for all the reaction systems in order to detect the presence of free radicals species during the course of the reactions.

#### 4.9 Michaelis – Menten Plot

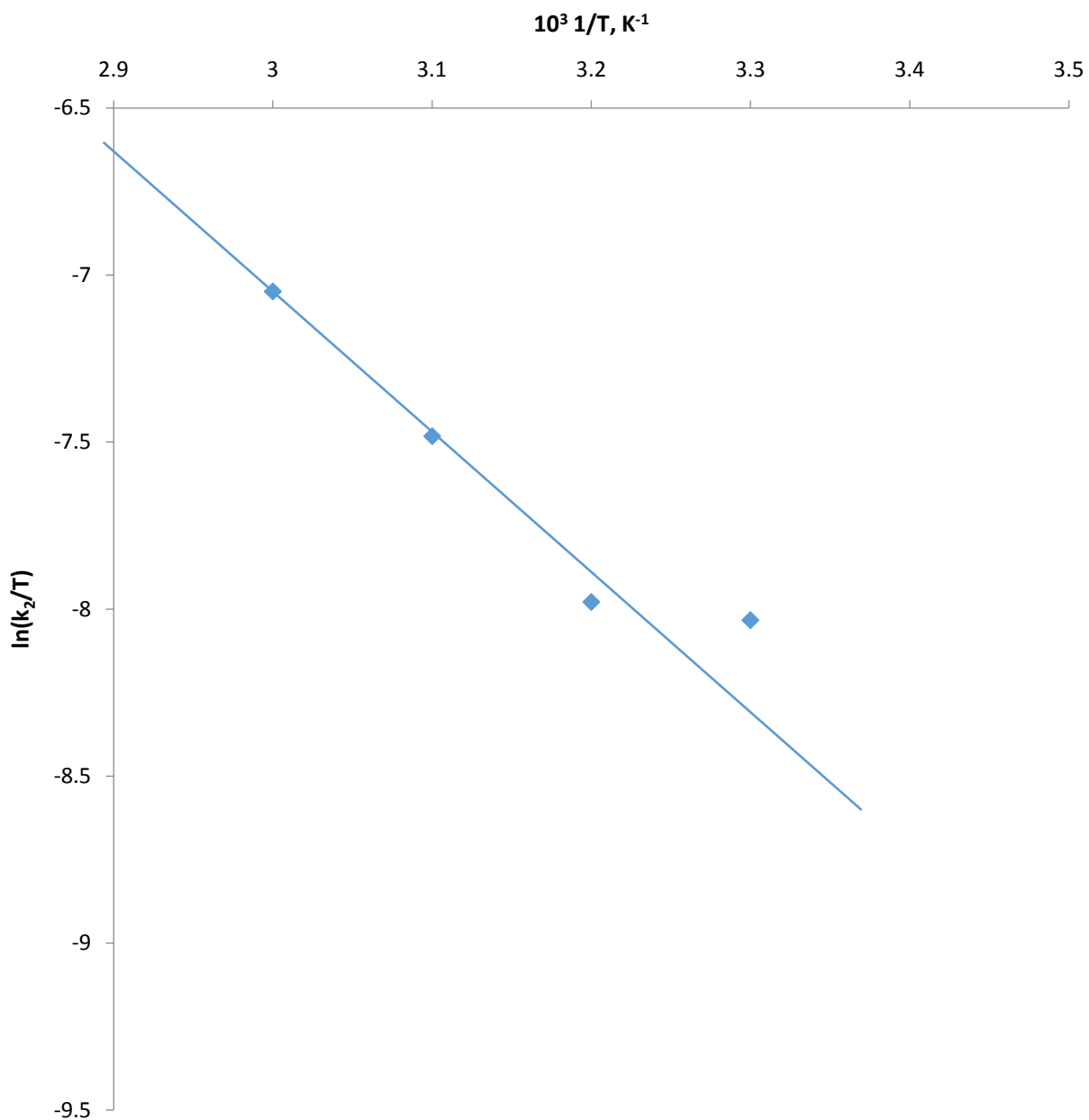
The Michaelis-Menten plot of  $1/k_{\text{obs}}$  versus  $1/[\text{oxidant}]$  was linear without an intercept for  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{S}_2\text{O}_8^{2-}$ ,  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{ClO}^-$  and  $[\text{Co(II)HEDTA}]^-$ -  $\text{ClO}^-$  systems (Figures 4.25 – 4.27).

**Table 4.9:** Activation parameters of the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

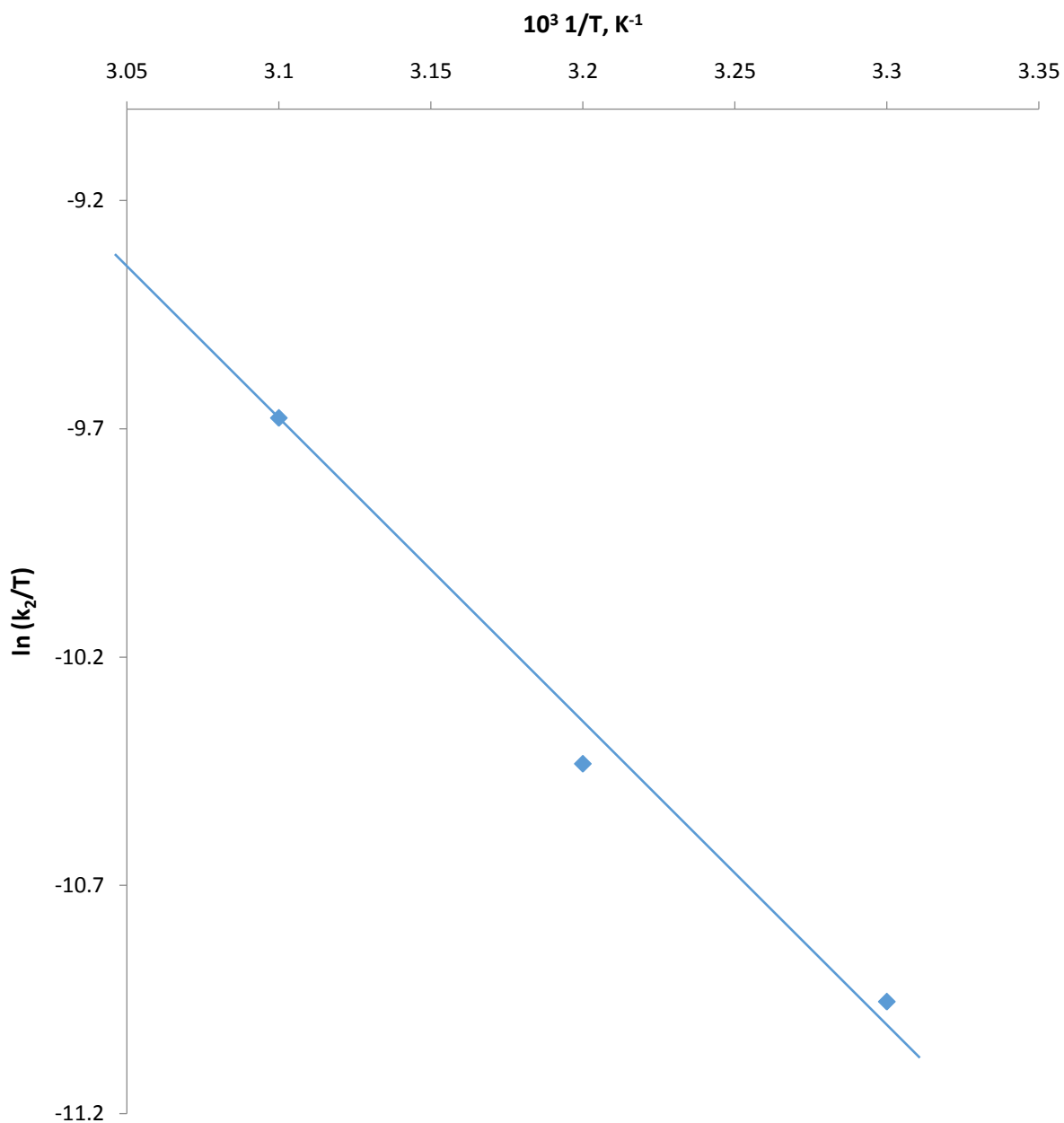
Temperature, K	$10^3 k_{\text{obs}}$ , $\text{s}^{-1}$	$10^2 k_2$ , $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
299	4.84	9.67
309	5.30	10.59
319	8.98	17.96
329	14.28	28.56
$\Delta H^* = +28.67 \text{ KJmol}^{-1}$		$\Delta S^* = -170.72 \text{ JK}^{-1} \text{mol}^{-1}$

**Table 4.10:** Activation parameters of the reaction of  $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co(II)HEDTA(OH}_2\text{)}]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 16.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

Temperature, K	$10^3 k_{\text{obs}}$ , $\text{s}^{-1}$	$10^3 k_1$ , $\text{s}^{-1}$
303	6.00	6.00
313	9.21	9.21
323	20.27	20.27
$\Delta H^* = +53.12 \text{ KJmol}^{-1}$		$\Delta S^* = -113.65 \text{ JK}^{-1}\text{mol}^{-1}$



**Figure 4.19:** Plot of  $\ln\left(\frac{k_2}{T}\right)$  versus  $\left(\frac{1}{T}\right)$  for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



**Figure 4.20:** Plot of  $\ln\left(\frac{k_2}{T}\right)$  versus  $\left(\frac{1}{T}\right)$  for the reaction of  $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co(II)HEDTA(OH}_2\text{)}^-] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 16.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

**Table 4.11:** Effect of added cation on the reaction rate of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

X	$10^2 [\text{X}]$ , mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	$10^2 k_2$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
K <sup>+</sup>	0.00	4.84	9.67
	1.00	4.74	9.48
	2.00	4.74	9.48
	3.00	4.75	9.50
	4.00	4.75	9.50
	5.00	4.74	9.48
Li <sup>+</sup>	0.00	4.84	9.67
	1.00	4.78	9.56
	2.00	4.78	9.56
	3.00	4.79	9.58
	4.00	4.78	9.56
	5.00	4.80	9.60

**Table 4.12:** Effect of added cation on the reaction rate of  $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co(II)HEDTA(OH}_2\text{)}]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 16.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

X	$10^2 [\text{X}]$ , mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	$10^3 k_1$ , s <sup>-1</sup>
K <sup>+</sup>	0.00	6.22	6.22
	1.00	6.00	6.00
	2.00	6.00	6.00
	3.00	6.22	6.22
	4.00	6.22	6.22
	5.00	6.00	6.00
Li <sup>+</sup>	0.00	6.22	6.22
	1.00	6.06	6.06
	2.00	6.10	6.10
	3.00	6.22	6.22
	4.00	6.22	6.22
	5.00	6.10	6.10



**Table 4.13:** Effect of added cations on the reaction rate of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

<b>X</b>	<b><math>10^3 [\text{X}]</math>,</b> <b><math>\text{mol dm}^{-3}</math></b>	<b><math>10^3 k_{\text{obs}}</math>,</b> <b><math>\text{s}^{-1}</math></b>	<b><math>10^2 k_2</math>,</b> <b><math>\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}</math></b>
<b>K<sup>+</sup></b>	0.00	3.00	3.33
	1.00	2.90	3.22
	2.00	2.90	3.33
	3.00	2.86	3.17
	4.00	2.65	2.94
	5.00	2.07	2.30
<b>Li<sup>+</sup></b>	0.00	3.00	3.33
	1.00	2.85	3.17
	2.00	2.78	3.09
	3.00	2.71	3.01
	4.00	2.54	2.82
	5.00	2.20	2.44

**Table 4.14:** Effect of added cations on the reaction rate of [Co(II)HEDTA]<sup>-</sup> with ClO<sup>-</sup> at [Co(II)HEDTA]<sup>-</sup> = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [ClO<sup>-</sup>] = 9.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.2 mol dm<sup>-3</sup>, T = 300 ± 1K and λ<sub>max</sub> = 525 nm

X	10 <sup>3</sup> [X], mol dm <sup>-3</sup>	10 <sup>3</sup> k <sub>obs</sub> , s <sup>-1</sup>	10 <sup>2</sup> k <sub>2</sub> , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
K <sup>+</sup>	0.00	2.76	3.07
	1.00	2.78	3.09
	2.00	3.03	3.36
	3.00	2.46	2.74
	4.00	3.13	3.48
	5.00	3.22	3.58
Li <sup>+</sup>	0.00	2.76	3.07
	1.00	2.79	3.10
	2.00	2.82	3.13
	3.00	2.80	3.11
	4.00	3.00	3.33
	5.00	3.10	3.44

**Table 4.15:** Effect of added anion on the reaction rate of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

X	$10^2 [\text{X}]$ , mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	$10^2 k_2$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
HCOO <sup>-</sup>	0.00	4.84	9.67
	1.00	5.07	10.13
	2.00	5.99	11.98
	3.00	6.45	12.90
	4.00	6.68	13.36
	5.00	7.14	14.28
CH <sub>3</sub> COO <sup>-</sup>	0.00	4.61	9.21
	1.00	5.30	10.59
	2.00	5.30	10.59
	3.00	6.22	12.44
	4.00	5.76	11.52
	5.00	6.22	12.44

**Table 4.16:** Effect of added anions on the reaction rate of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

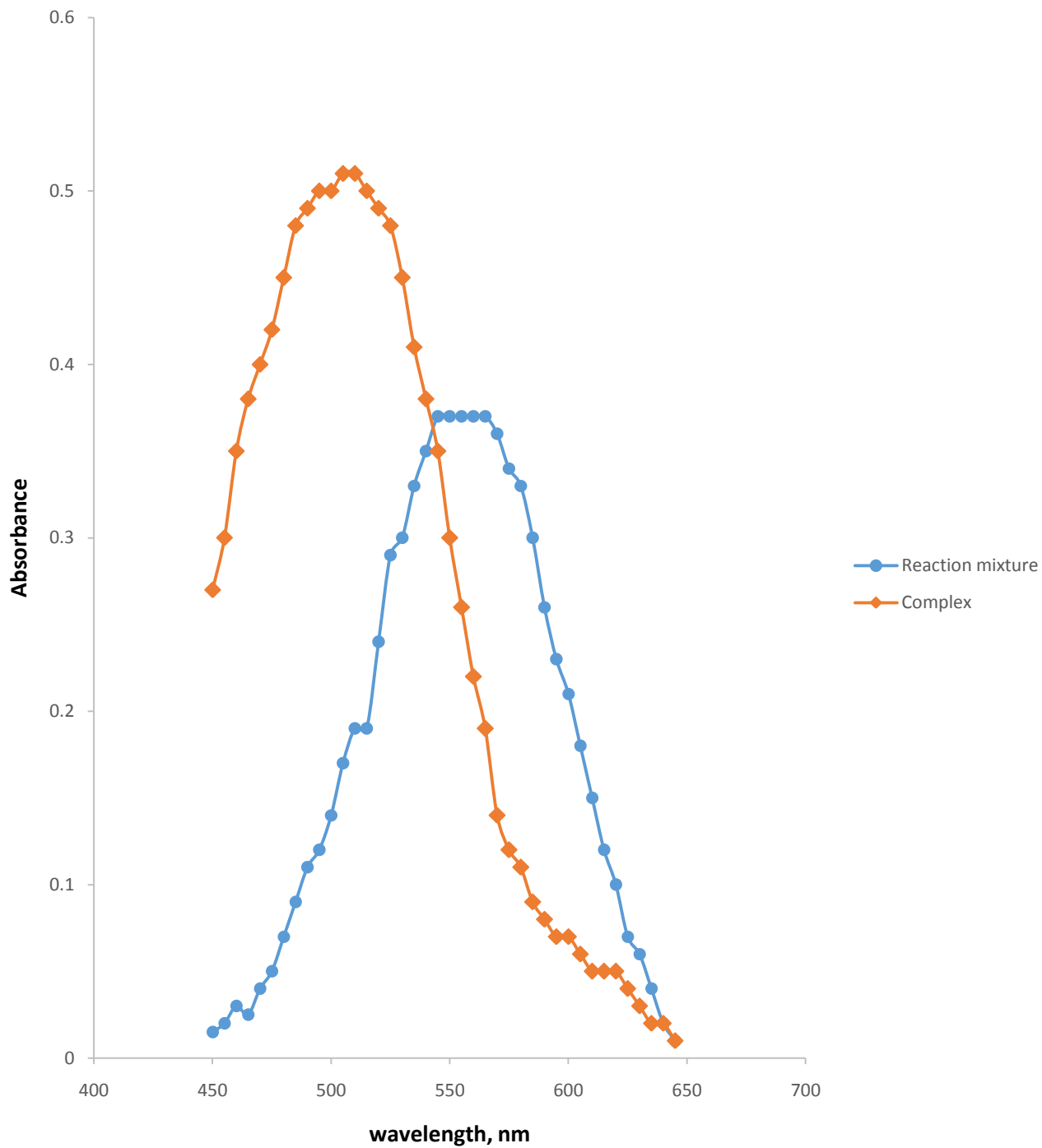
X	$10^3 [\text{X}]$ , mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	$10^2 k_2$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
CH <sub>3</sub> COO <sup>-</sup>	0.00	3.00	3.33
	1.00	4.15	4.61
	2.00	4.61	5.12
	3.00	5.30	5.89
	4.00	5.53	6.14
	5.00	6.00	6.65
HCOO <sup>-</sup>	0.00	3.00	3.33
	1.00	4.61	5.12
	2.00	6.91	7.68
	3.00	9.21	10.24
	4.00	11.52	12.79
	5.00	13.82	15.35

**Table 4.17:** Effect of added anions on the reaction rate of  $[\text{Co(II)HEDTA(OH}_2\text{)}]^-$  with  $\text{ClO}^-$  at  $[\text{Co(II)HEDTA(OH}_2\text{)}]^- = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

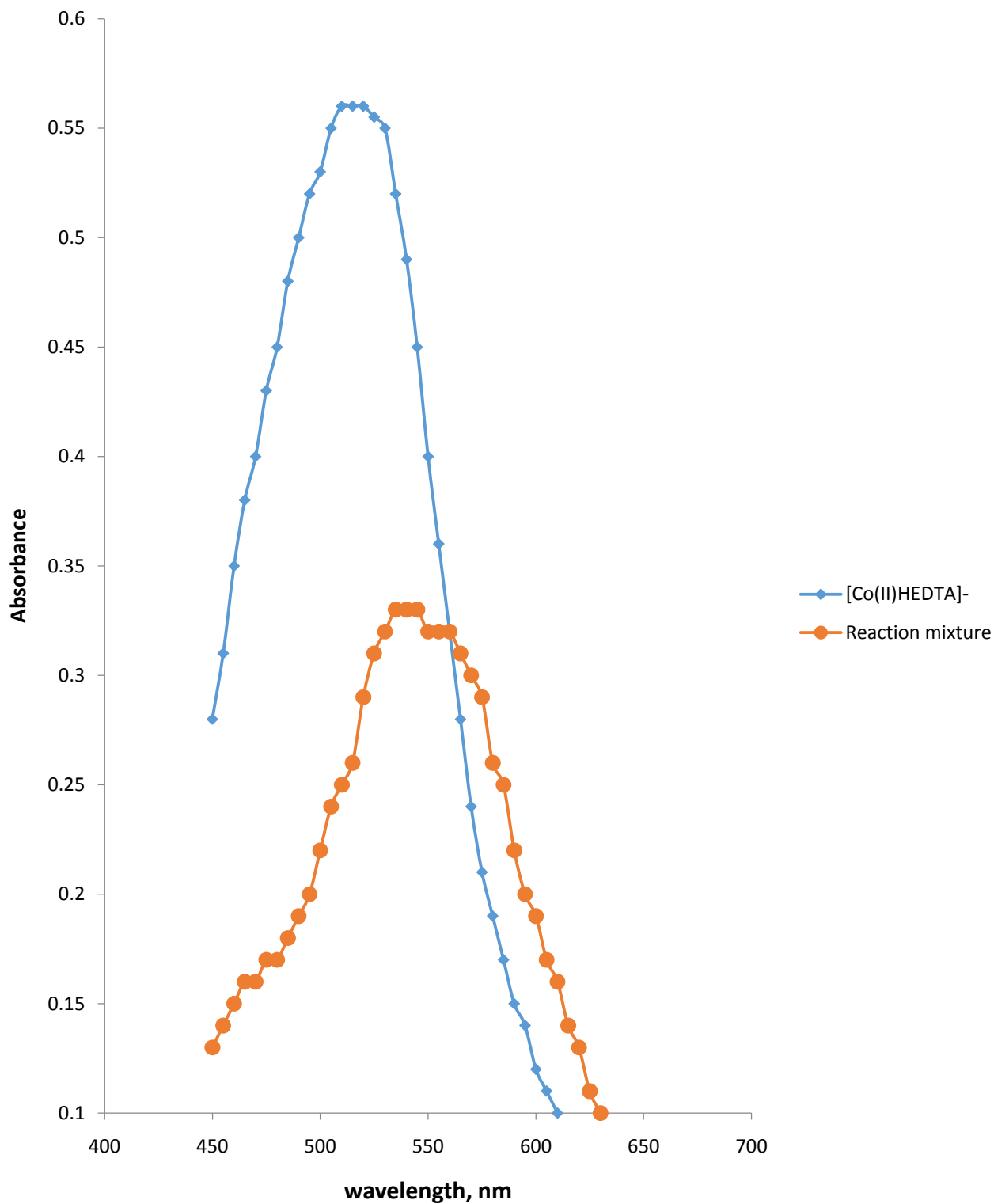
X	$10^2 [\text{X}]$ , mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ , s <sup>-1</sup>	$10^2 k_2$ , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
CH <sub>3</sub> COO <sup>-</sup>	0.00	2.76	3.07
	1.00	2.70	3.00
	2.00	2.64	2.93
	3.00	2.51	2.79
	4.00	2.82	3.13
	5.00	2.30	2.56
HCOO <sup>-</sup>	0.00	2.76	3.07
	1.00	2.70	3.00
	2.00	2.63	2.92
	3.00	3.02	3.36
	4.00	2.84	3.16
	5.00	2.58	2.87

**Table 4.18:** Effect of added anion on the reaction rate of [Co(II)HEDTA(OH<sub>2</sub>)]<sup>-</sup> with S<sub>2</sub>O<sub>8</sub><sup>2-</sup> at [Co(II)HEDTA(OH<sub>2</sub>)]<sup>-</sup> = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] = 16.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 1.0 mol dm<sup>-3</sup>, [Ag<sup>+</sup>] = 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, T = 299 ± 1K and λ<sub>max</sub> = 525 nm

X	10 <sup>2</sup> [X], mol dm <sup>-3</sup>	10 <sup>3</sup> k <sub>obs</sub> , s <sup>-1</sup>	10 <sup>3</sup> k <sub>1</sub> , s <sup>-1</sup>
CH <sub>3</sub> COO <sup>-</sup>	0.00	6.00	6.00
	1.00	6.00	6.00
	2.00	6.45	6.45
	3.00	6.22	6.22
	4.00	6.00	6.00
	5.00	6.22	6.22
HCOO <sup>-</sup>	0.00	6.22	6.22
	1.00	6.00	6.00
	2.00	6.00	6.00
	3.00	6.22	6.22
	4.00	6.00	6.00
	5.00	6.22	6.22

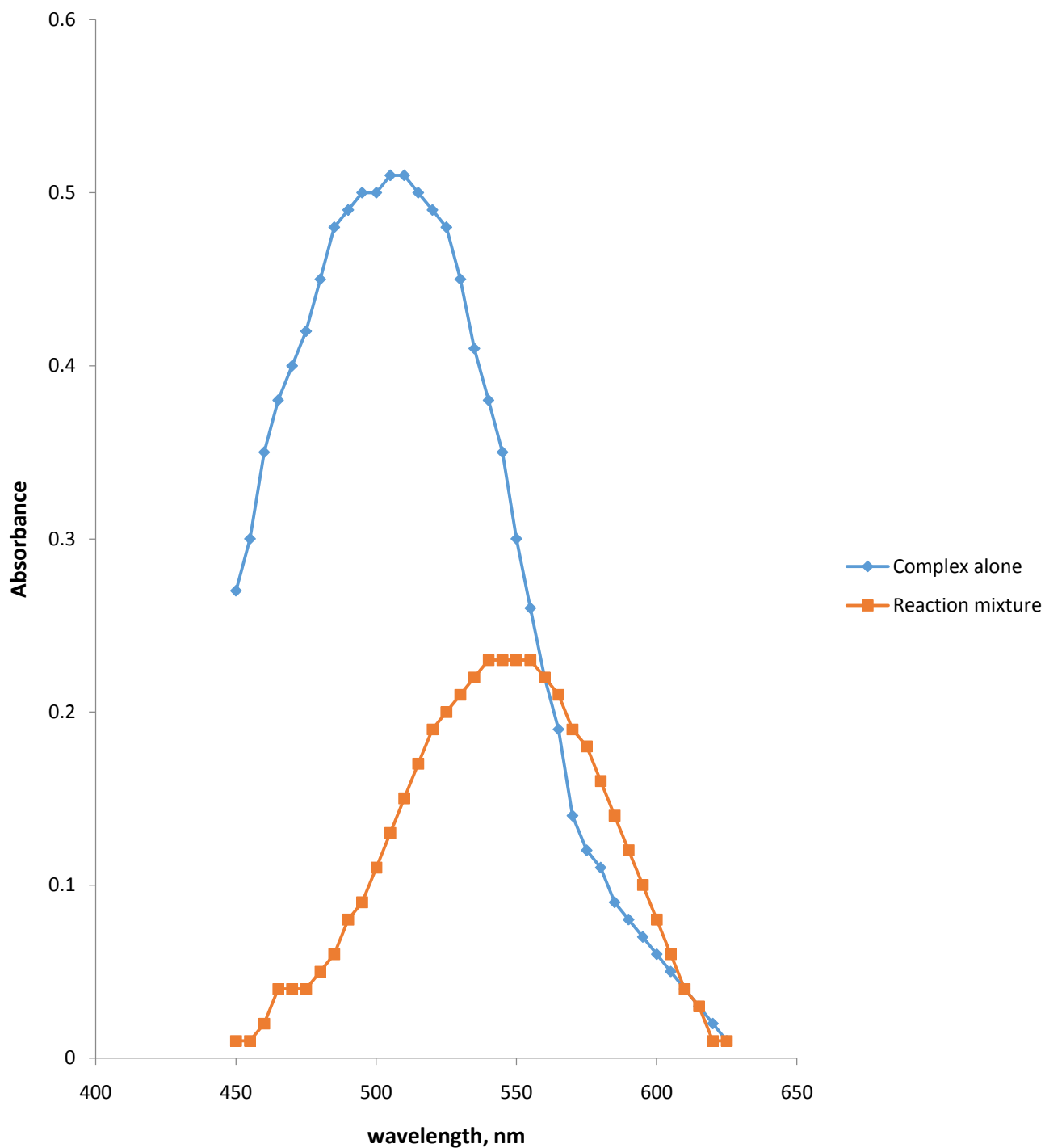


**Figure 4.21:** The spectrum of spectrophotometric test for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$

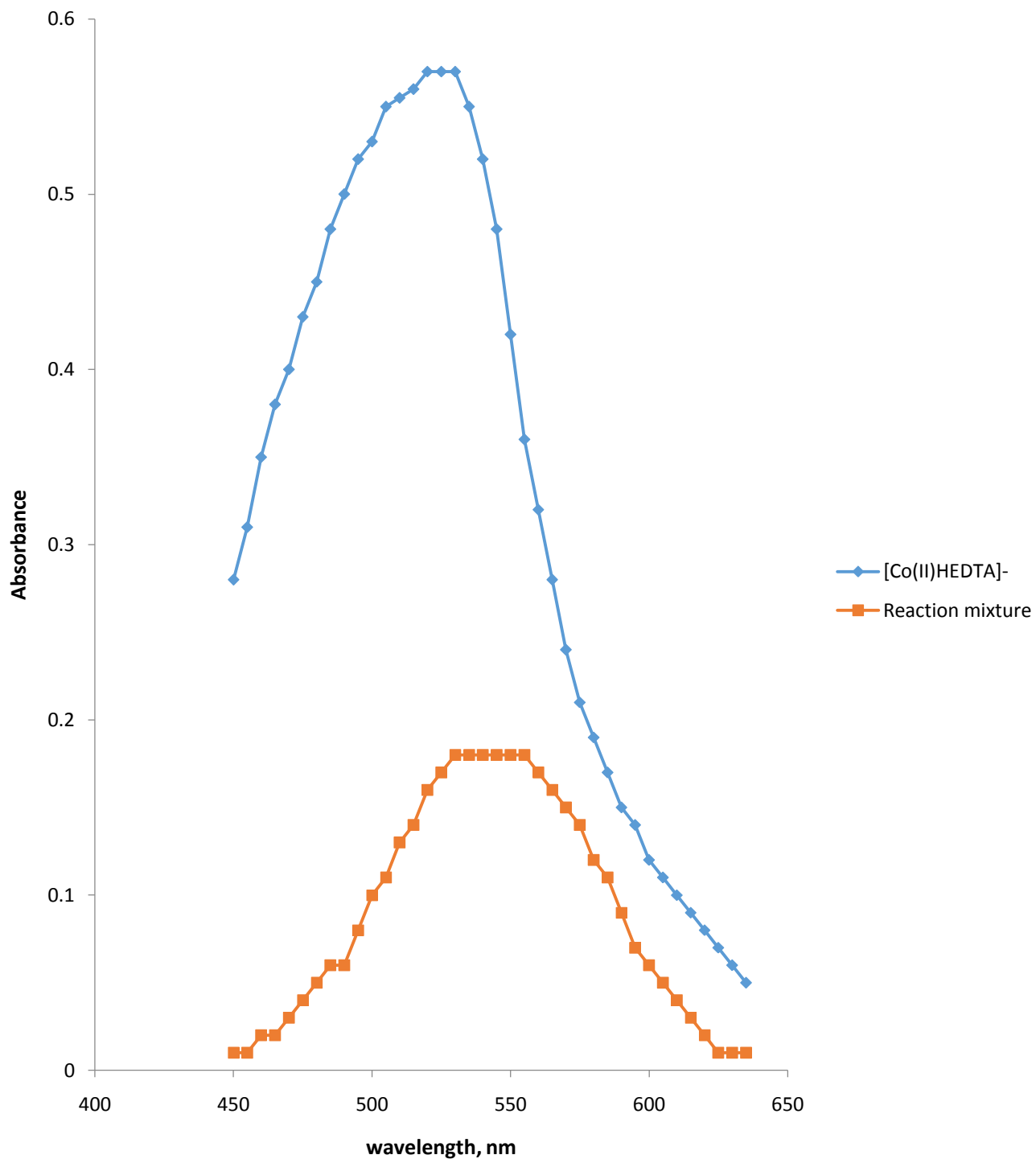


**Figure 4.22:** The spectrum of spectrophotometric test for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}]^-$  with  $\text{S}_2\text{O}_8^{2-}$  at  $[\text{Co}^{\text{II}}\text{HEDTA}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{S}_2\text{O}_8^{2-}] = 16.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{Ag}^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

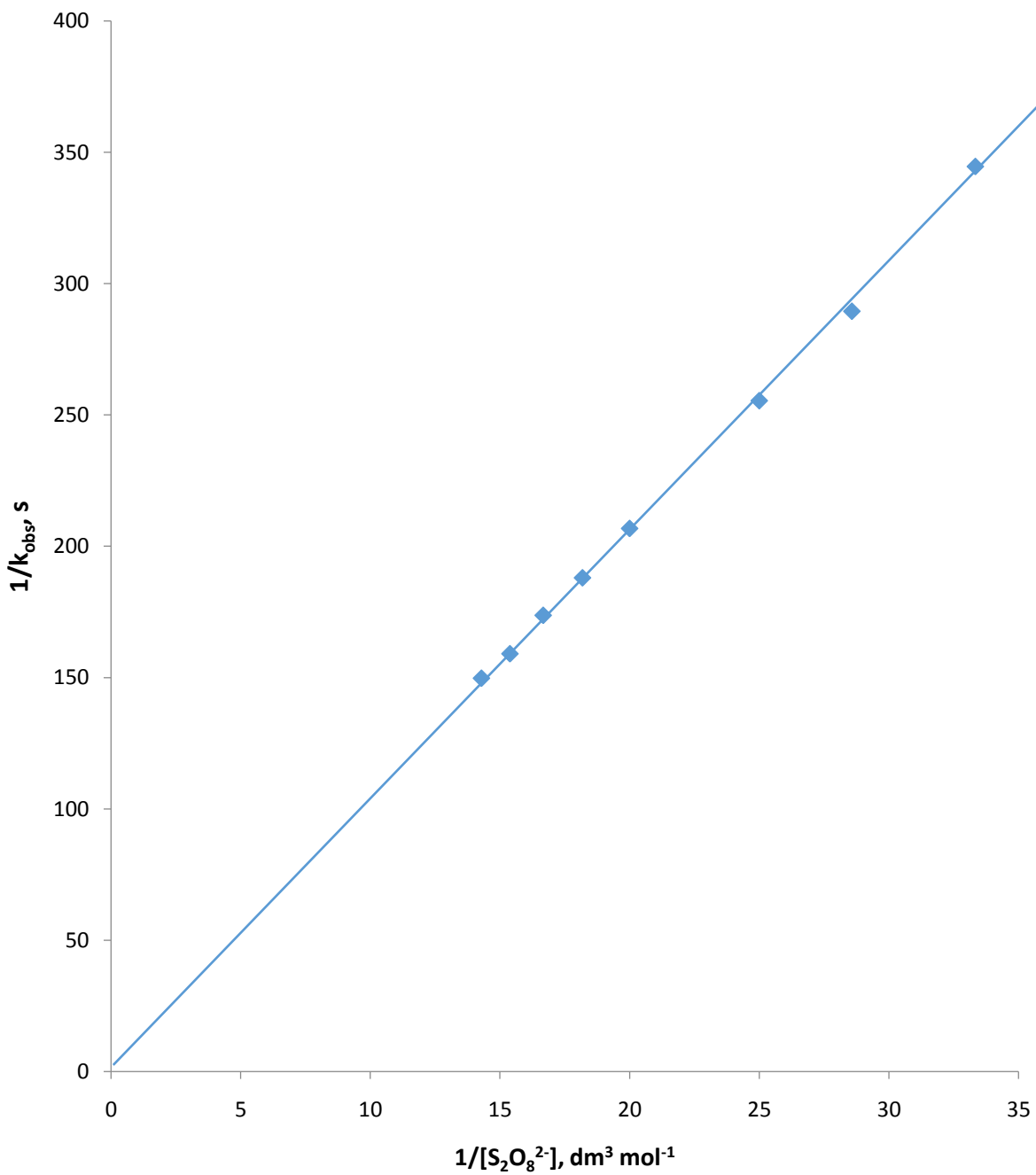




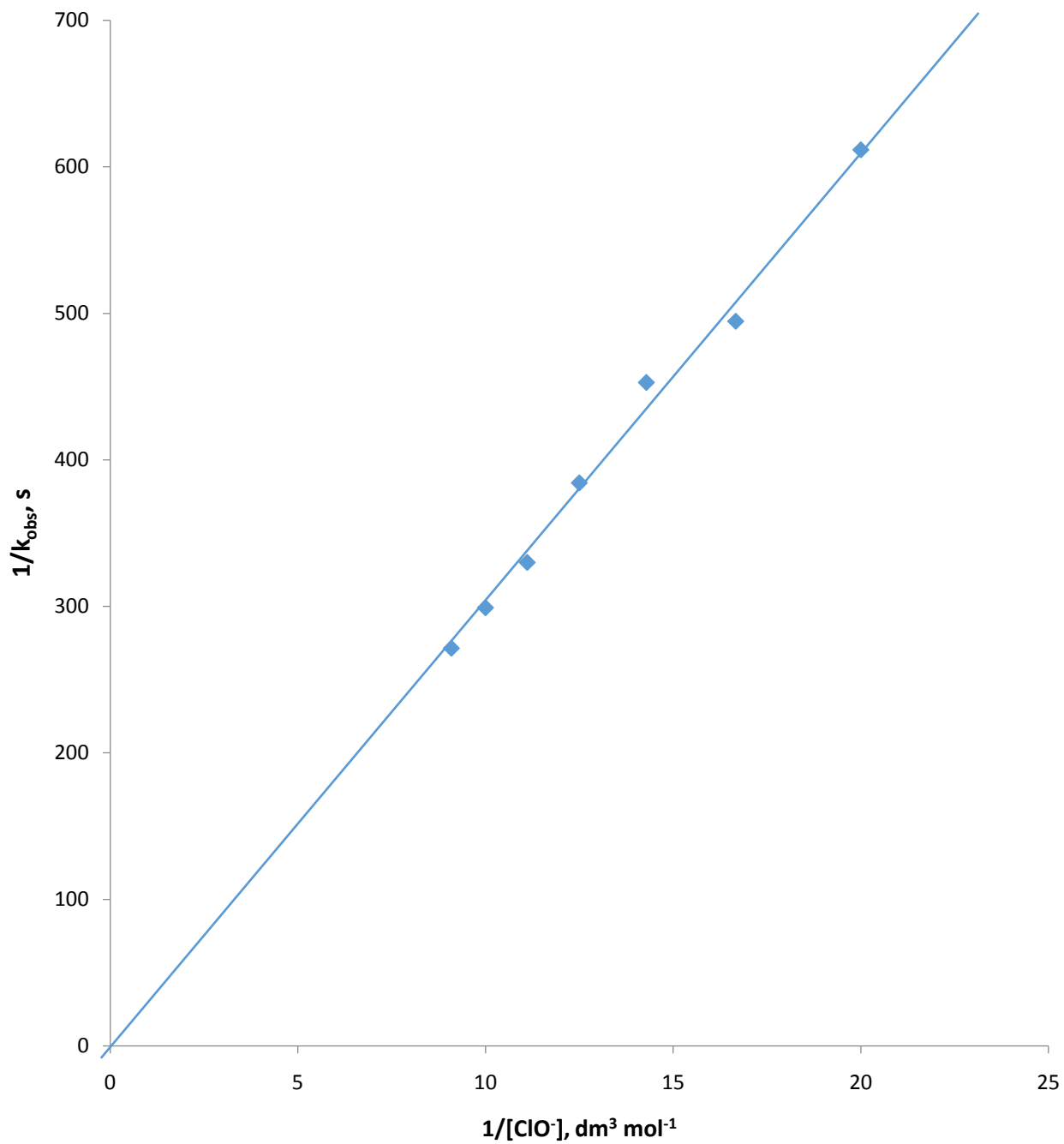
**Figure 4.23:** The spectrum of spectrophotometric test for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1 \text{ K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



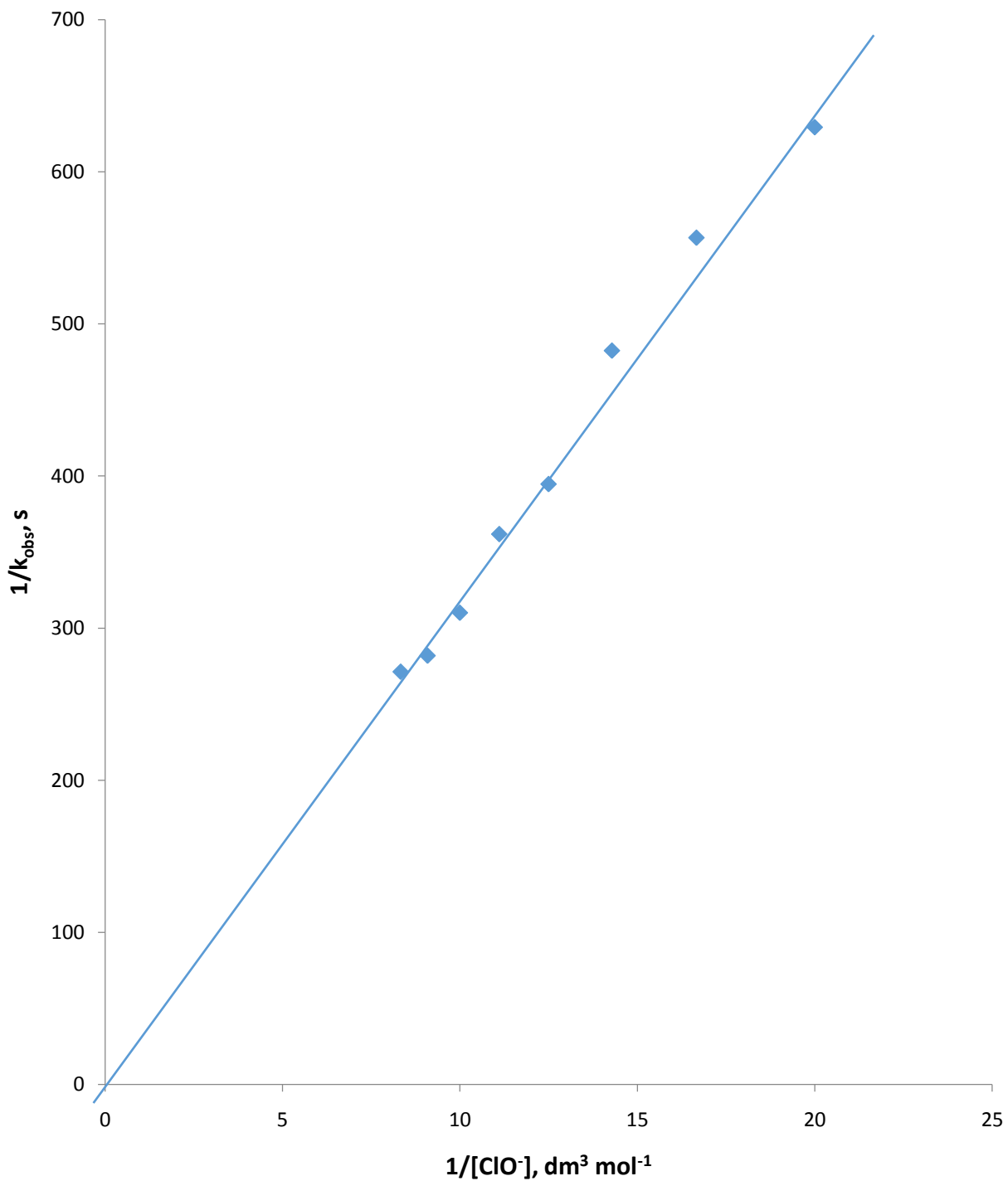
**Figure 4.24:** The spectrum of spectrophotometric test for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}]^-$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{HEDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{ClO}^-] = 9.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$



**Figure 4.25:** Michaelis-Menten plot for the reaction of  $[Co^{II}EDTA]^{2-}$  with  $S_2O_8^{2-}$  at  $[Co^{II}EDTA^{2-}] = 5.0 \times 10^{-3} mol dm^{-3}$ ,  $I = 0.5 mol dm^{-3}$ ,  $[Ag^+] = 1.0 \times 10^{-2} mol dm^{-3}$ ,  $T = 299 \pm 1K$  and  $\lambda_{max} = 520 nm$



**Figure 4.26:** Michaelis-Menten plot for the reaction of  $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{EDTA}^{2-}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $T = 299 \pm 1\text{K}$  and  $\lambda_{\text{max}} = 520 \text{ nm}$



**Figure 4.27:** Michaelis-Menten plot for the reaction of  $[\text{Co}^{\text{II}}\text{HEDTA}]^-$  with  $\text{ClO}^-$  at  $[\text{Co}^{\text{II}}\text{HEDTA}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.2 \text{ mol dm}^{-3}$ ,  $T = 300 \pm 1 \text{ K}$  and  $\lambda_{\text{max}} = 525 \text{ nm}$

#### 4.10 Products Analysis

The spectrum of the solution of the product of the reactions obtained using Carey series 300 UV-Visible spectrophotometre showed two maximum peaks (Figures 4.28 – 4.31).

The  $\text{SO}_4^{2-}$  ion product of  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{S}_2\text{O}_8^{2-}$  and  $[\text{Co(II)HEDTAOH}_2]^-$ -  $\text{S}_2\text{O}_8^{2-}$  reactions was confirmed by the formation of white precipitate insoluble in excess dilute HCl when  $\text{BaCl}_2$  was added to each of the solution (Vogel, 1996). Also the presence of  $\text{Cl}_2$  gas was detected as one of the reaction products of  $[\text{Co(II)EDTA}]^{2-}$  with  $\text{ClO}^-$  and  $[\text{Co(II)HEDTAOH}_2]^-$  with  $\text{ClO}^-$  by changing the colour of blue litmus paper to red when placed on the mouth of the tube (Ojokuku, 2012).

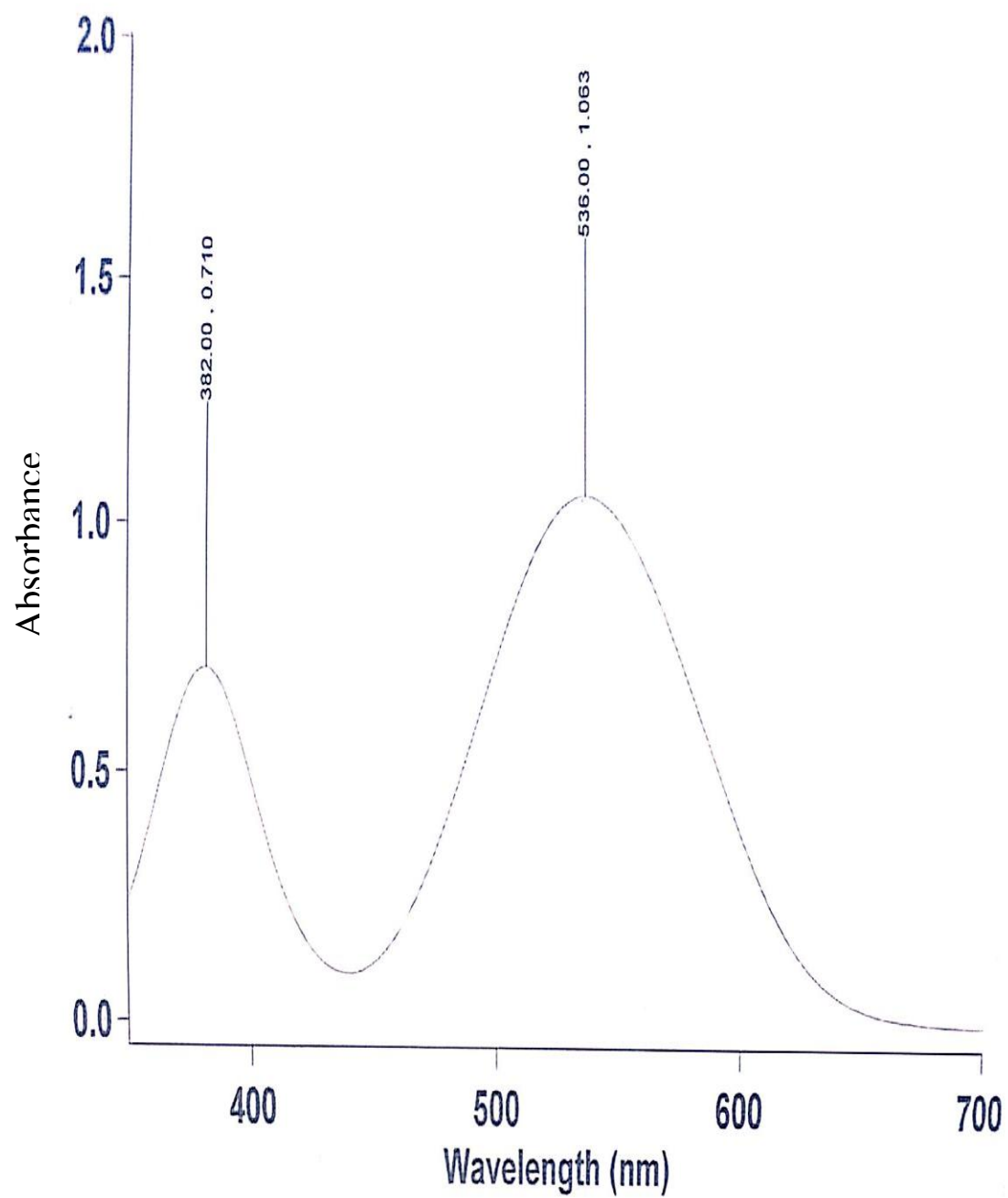
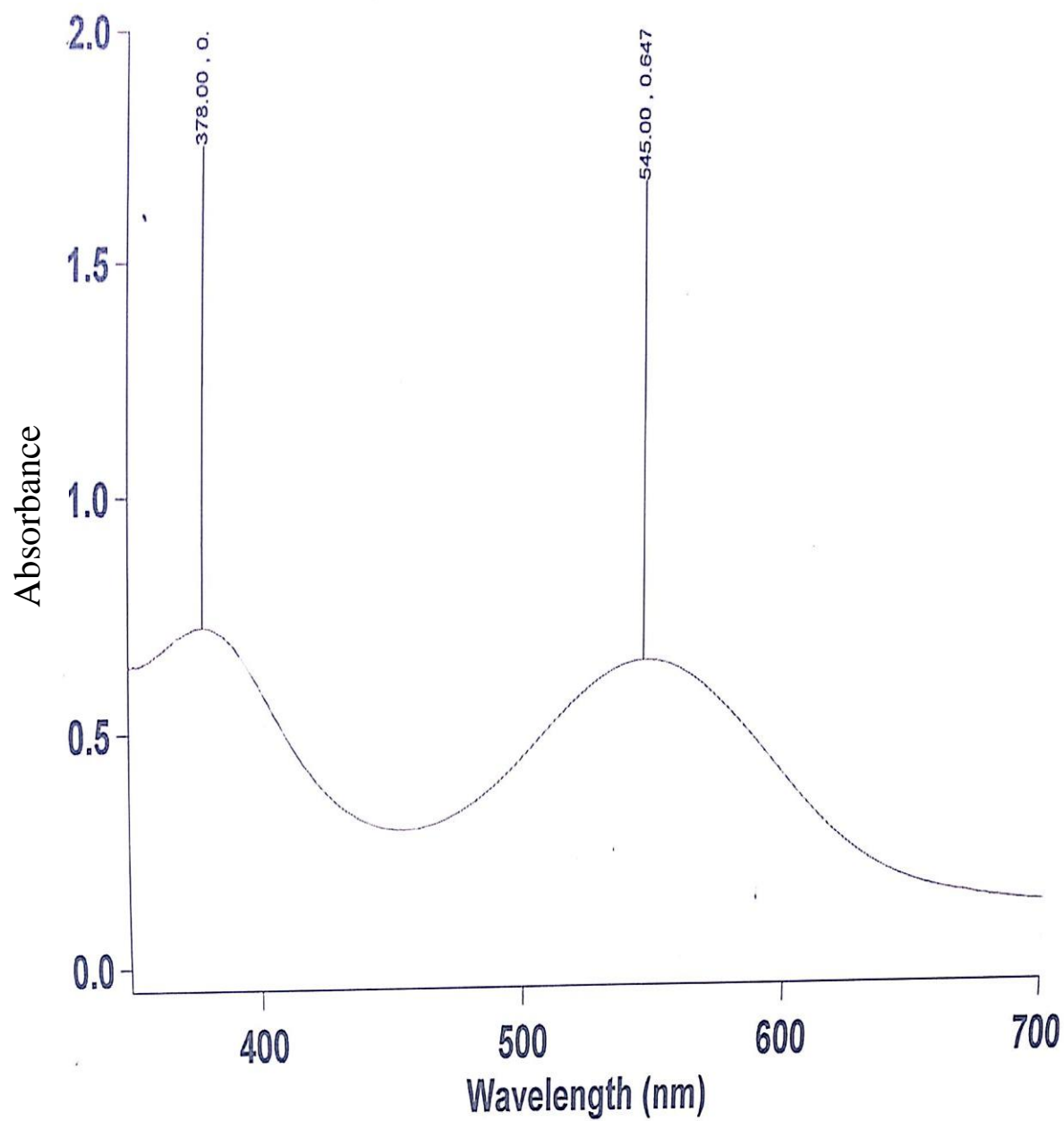


Figure 4.28: UV-visible spectrum of the product of  $[\text{Co(II)EDTA}]^{2-}$  -  $\text{S}_2\text{O}_8^{2-}$  reaction



**Figure 4.29: UV-visible spectrum of the reaction product of  $[\text{Co(II)HEDTAOH}_2]^- \text{S}_2\text{O}_8^{2-}$  reaction**



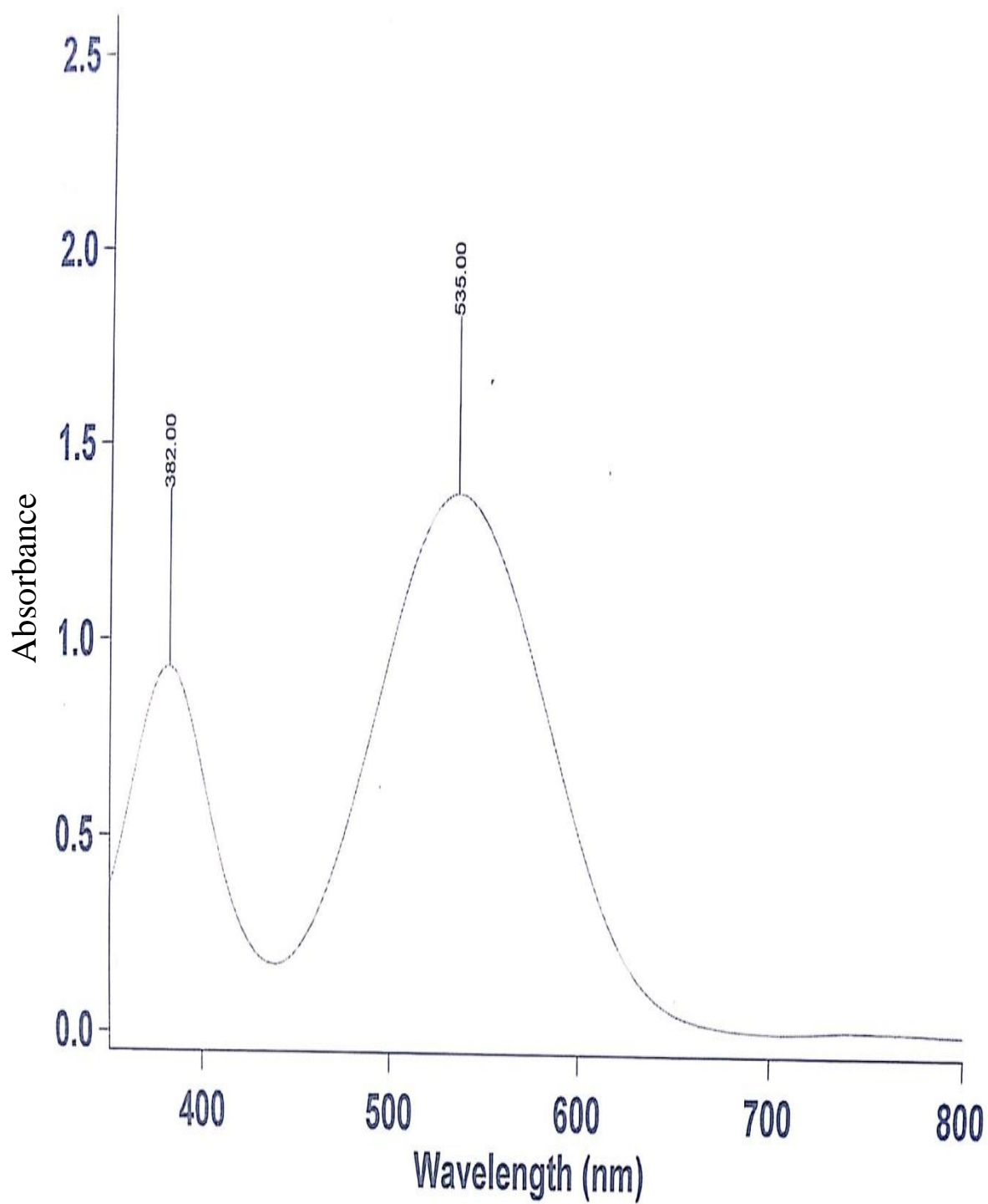
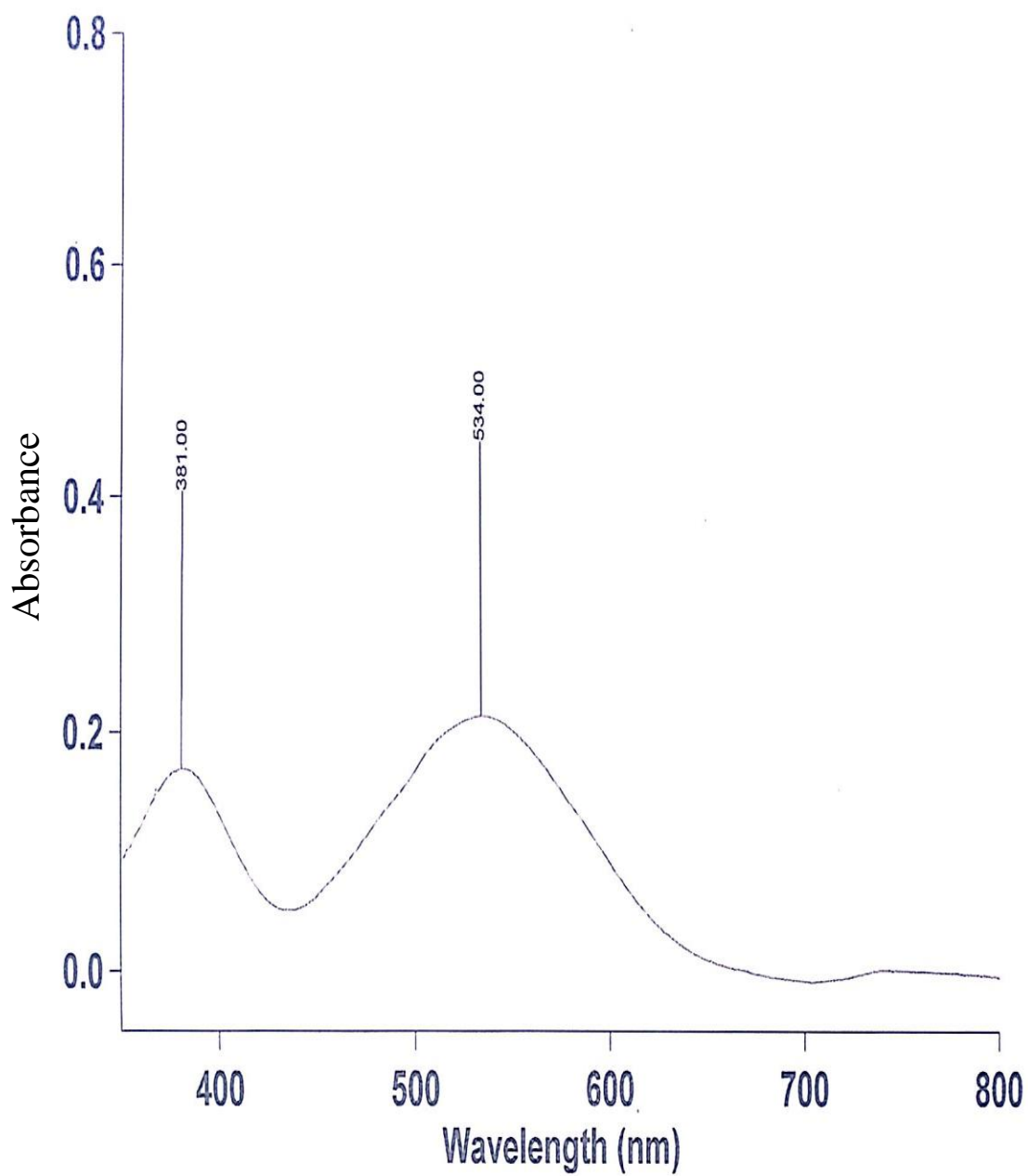


Figure 4.30: UV-visible spectrum of the product of  $[\text{Co(II)EDTA}]^{2-}$  -  $\text{ClO}^-$  reaction



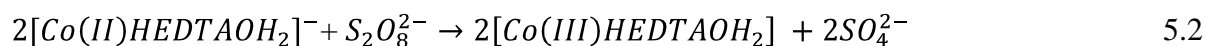
**Figure 4.31: UV-visible spectrum of the reaction product of  $[\text{Co}(\text{II})\text{HEDTAOH}_2]^- \text{ClO}^-$  reaction**

## CHAPTER FIVE

### 5.0 DISCUSSIONS

#### 5.1 Oxidation of $[Co(II)EDTA]^{2-}$ and $[Co(II)HEDTAOH_2]^-$ by Persulphate Ion

The result of spectrophotometric titration showed that two moles of the reductants, were oxidised by one mole of the oxidant for  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  and  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$  systems respectively. The spectrum of each of the two reaction products showed two maxima at 382, 536 and 378, 545 nm for the two systems respectively typical of Co(III) (Mansur, 2003; Peeveen *et al.*, 2013 and Onu *et al.*, 2009, 2015 and 2016). While qualitative analyses confirmed the presence of  $SO_4^{2-}$  ion. Based on these, the overall equations for the redox reactions can be represented in equations 5.1 – 5.2.



The stoichiometry of 2:1 is common to the redox reaction of aminocarboxylatocobaltate(II) complex with some oxidants (Onu *et al.*, 2015). Similar result was reported for the reaction of transition metal complex with persulphate ion (Gupta, 1986). This may be attributed to the fact that persulphate ion requires two electrons to form  $SO_4^{2-}$  ion (Busari, 2007).

The results of the kinetic study (Figures 4.5, 4.6 and 4.9) showed first order dependence with respect to both  $[Co(II)EDTA]^{2-}$  and  $[S_2O_8^{2-}]$  (slope = 0.980) for  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  system, while first order and zero order dependence with respect to  $[Co(II)HEDTA]^-$  and  $[S_2O_8^{2-}]$  (slope = 0.019) respectively were observed for  $[Co(II)HEDTA]^- - S_2O_8^{2-}$  system, thus, second order and first order overall for the two systems respectively. Similarly, first order dependence on  $[S_2O_8^{2-}]$  was reported on its redox reaction with malachite green (El-Idris *et al.*, 1991 and

Mohammed *et al.*, 2010). Zero order with respect to  $[S_2O_8^{2-}]$  showed that the rate of reaction is independent of the concentration of  $S_2O_8^{2-}$ . This could be attributed to the dissociation of the complex,  $[Co(II)HEDTAOH_2]^-$  at rate determining step followed by rapid reaction of the product of dissociation with persulphate ion (Burgess, 1999). Therefore,  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$  reaction is first order overall at constant  $[H^+]$  and  $[Ag^+]$  concentrations. The rate equation for the reactions can be represented by the equations 5.3 – 5.4:

$$\frac{d[Co(III)EDTA^-]}{dt} = k_2[Co(II)EDTA^{2-}][S_2O_8^{2-}] \quad 5.3$$

where  $k_2 = (9.70 \pm 0.1) \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

$$\frac{d[Co(III)HEDTA]}{dt} = k_1[Co(II)HEDTA^-] \quad 5.4$$

where  $k_1 = (6.00 \pm 0.1) \times 10^2 \text{ s}^{-1}$

Variation of hydrogen ion concentration showed no effect on the reaction rate for all the two systems within the concentration range investigated. This may be due to dependence of the reactions on the concentration of catalyst. This implies that the reactions were not catalyzed by acid and that none of the species was protonated during the course of the reaction. Hence, the reactions followed the acid independent pathway. Similar results have been reported for redox reaction of  $S_2O_8^{2-}$  (Rao *et al.*, 1987 and El-Idris, 1991). This may be due to non-protonation of  $S_2O_8^{2-}$  (El-Idris, 1991). However, the slopes obtained from the logarithmic plot of  $k_{\text{obs}}$  versus  $[Ag^+]$  were 0.92 and 0.78 for these systems respectively indicating first order dependence with respect to  $[Ag^+]$ , similar to that obtained by Ayoko *et al.* (1992) in the Ag(I) catalysed reduction of persulphate ion by 12-tungstocobaltate(II) ion. Even though the electrode potential for the process (Equation 2.5) portrays persulphate to be a strong oxidant, but its electron transfer

reaction is slow due to the strong  $-O-O-$  bond in the  $O_3S-O-O-SO_3$  which should be broken enroute to the formation of the  $SO_4^{2-}$  product (Burgess, 1999). Hence the role of catalyst in the reaction involving the oxidant becomes very germane. From Figures 4.14 – 4.15, the catalyst dependence rate constants for the reaction systems can be represented as:

$k_2 = a[Ag^+]$ , where  $a = 5.90 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  system

$k_2 = b[Ag^+]$ , where  $b = 5.4 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $[Co(II)HEDTA]^- - S_2O_8^{2-}$  system

Therefore, the overall rate equation in the catalyst concentration range investigated for each system is given as:

$$\frac{d[Co(III)EDTA^-]}{dt} = a[Ag^+][Co(II)EDTA^{2-}][S_2O_8^{2-}] \quad 5.5$$

$$\frac{d[Co(III)HEDTA]}{dt} = b[Ag^+][Co(II)HEDTA^-] \quad 5.6$$

The rates of the reactions showed no significant effect with change in ionic strength of the reaction medium in the concentration range investigated (Tables 4.1 and 4.2) suggesting a zero Brønsted-Debye salt effect (Atkins and de Paula, 2002). Zero Brønsted-Debye salt effect has however been ascribed to the formation of activated complex from redox partners which either one or both are neutral (Atkins and de Paula, 2002) or due to ion-pair effect (Naik *et al.*, 2007). This zero salt effect is surprising given that the reactant species are negatively charged and a positive salt effect would have been expected. However, the effect may have been occasioned due to ion-pair effect. This tendency is further supported by the negative value of activation entropy for  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  ( $\Delta S^* = -170.72 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $[Co(II)HEDTA]^- - S_2O_8^{2-}$  ( $\Delta S^* = -113.65 \text{ J K}^{-1} \text{ mol}^{-1}$ ) systems which are indicative of a more orderliness of species at the activated complex. These observations were also supported by the observation that the reactions rate constants remain the same upon variation of a dielectric

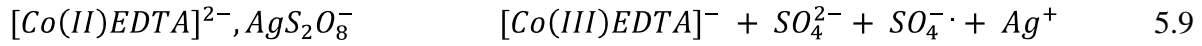
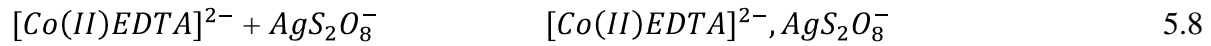
constant of the reactions media. Similar effects have been reported by Naik *et al.*, (2007). Free radical tests were positive which indicate the presence of free radical species in one of the reactions steps.

The  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  reaction is catalysed by the presence of added anions which suggest the outer sphere pathway but showed no effect upon addition of cations, which could be due to an ion-pair. However spectroscopic evidence indicated shift in  $\lambda_{max}$  suggesting that there was intermediate complex formation, but the shift could be attributed to the wavelength of the product, Co(III) formed, during the course of the reaction which has higher  $\lambda_{max}$  than the starting material. This is further supported by the observation that, Michaelis - Menten plot of  $1/k_{obs}$  versus  $1/S_2O_8^{2-}$  had zero intercept which suggests the absence of an intermediate in the rate determining step, thus, an outer-sphere mechanism is likely to be in operation.

However, the  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$  reaction is uncatalysed by the presence of both added cations and anions which suggest that the reaction proceeds via an inner-sphere mechanism or due to an ion-pair. Again, Michaelis - Menten plot of  $1/k_{obs}$  versus  $1/S_2O_8^{2-}$  had intercept which suggests the presence of an intermediate in the rate determining step, thus, an inner-sphere mechanism is likely to be in operation. Though spectroscopic evidence indicated shift in  $\lambda_{max}$  but it may be attributed to the wavelength of the product, Co(III) formed, during the course of the reaction which has higher  $\lambda_{max}$  than the starting Co(II) complex. Moreover, the high negative activation entropy could be ascribed to the decrease in the degree of freedom of reactants during the formation of activated complex (Mansour, 2003). This decrease in degree of freedom suggests that inner-sphere mechanism may be in operation.

In view of the above results, the following reaction mechanisms are hereby proposed via an outer-sphere and inner-sphere mechanism for  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  and  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$  systems respectively.

***Mechanistic pathway of  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  system***



$$\frac{d[Co(III)EDTA^-]}{dt} = k_3[Co(II)EDTA^{2-}, AgS_2O_8^-] \quad 5.11$$

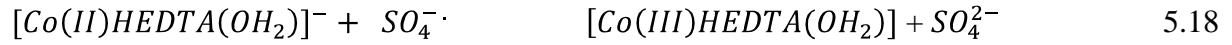
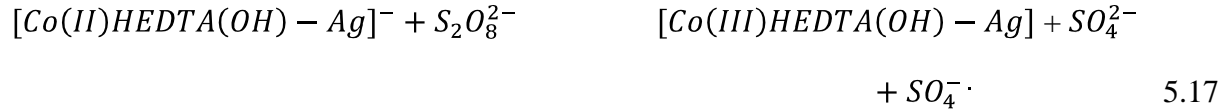
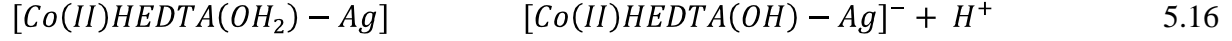
$$\text{But } [Co(II)EDTA^{2-}, AgS_2O_8^-] = K_2[Co(II)EDTA^{2-}][AgS_2O_8^-] \quad 5.12$$

$$\text{Also } [AgS_2O_8^-] = K_1[Ag^+][S_2O_8^{2-}] \quad 5.13$$

$$\text{Therefore, } \frac{d[Co(III)EDTA^-]}{dt} = (K_1K_2k_3[Ag^+])[Co(II)EDTA^{2-}][S_2O_8^{2-}] \quad 5.14$$

This is analogous to Eq. 5.5, where  $a = K_1K_2k_3$

**Mechanistic pathway of  $[Co(II)HEDTA(OH_2)]^- - S_2O_8^{2-}$  system**



$$\frac{d[Co(III)HEDTA(OH_2)]}{dt} = k_2[Co(II)HEDTA(OH_2) - Ag] \quad 5.22$$

$$\text{But } K_1 = \frac{[Co(II)HEDTA(OH_2) - Ag]}{[Ag^+][Co(II)HEDTA(OH_2)]^-} \quad 5.23$$

$$\text{Hence, } [Co(II)HEDTA(OH_2) - Ag] = K_1[Ag^+][Co(II)HEDTA(OH_2)]^- \quad 5.24$$

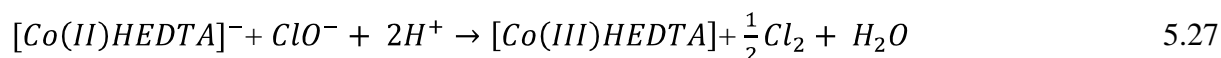
$$\text{Therefore, } \frac{d[Co(III)HEDTA(OH_2)]}{dt} = K_1 k_2 [Ag^+][Co(II)HEDTA(OH_2)]^- \quad 5.25$$

This is analogous to Eq. 5.6, where  $b = K_1 k_2$



## 5.2 Oxidation of $[Co(II)EDTA]^{2-}$ and $[Co(II)HEDTAOH_2]^-$ by Hypochlorite Ion

The result of spectrophotometric titration showed that one mole of the reductants was oxidised by one mole of the oxidant each for  $[Co(II)EDTA]^{2-} - ClO^-$  and  $[Co(II)HEDTA]^- - ClO^-$  reactions respectively. The spectrum of each of the two reaction products showed two maxima at 382, 535 nm and 381, 534 nm for  $[Co(II)EDTA]^{2-} - ClO^-$  and  $[Co(II)HEDTAOH_2]^- - ClO^-$  systems respectively. These are typical of Co(III) (Mansur, 2003; Peeveen *et al.*, 2013 and Onu *et al.*, 2009, 2015 and 2016). While qualitative analyses confirmed the presence of  $Cl_2$  gas. These results are in conformity with equations 5.26 and 5.27.



The stoichiometry (1:1) may be attributed to the fact that,  $ClO^-$  is transforming towards more stable  $Cl_2$  molecule. Similar results have been reported in the conversion of  $Ce^{3+}$  to  $Ce^{4+}$  by hypochlorite ion (Perumareddiet *al.*, 2003).

The kinetic study of the reaction (Figures 4.7, 4.8, 4.10 and 4.11) showed first order dependence with respect to each of the reductant and oxidant in the two reactions. The slopes obtained were 1.029 and 1.031 indicating first order dependence with respect to  $[ClO^-]$  in each of the  $[Co(II)EDTA]^{2-} - ClO^-$  and  $[Co(II)HEDTA]^- - ClO^-$  reactions. The observed first order dependence of the reaction rates on both [reductants] and  $[ClO^-]$  is a common feature of hypochlorite ion reactions (Jiann-Kuo, 1987; Idriset *al.*, 2015; Abdulsalam, 2015 and Ibrahim 2016). The rate equation for the reactions can be presented in equations 5.28 and 5.29.

$$\frac{d[Co(III)EDTA^-]}{dt} = k_2[Co(II)EDTA^{2-}][ClO^-] \quad 5.28$$

where  $k_2 = (3.31 \pm 0.07) \times 10^{-2} dm^3 mol^{-1} s^{-1}$

$$\frac{d[\text{Co(III)HEDTA}]}{dt} = k_2[\text{Co(II)HEDTA}^-][\text{ClO}^-] \quad 5.29$$

where  $k_2 = (3.13 \pm 0.09) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Acid dependent study showed that the reaction rate decreased with increase in hydrogen ion concentration for all the two systems as presented in Tables 4.3 and 4.4. The slopes obtained from the logarithmic plot of  $k_{\text{obs}}$  versus  $[\text{H}^+]$  (Figures 4.12 – 4.13) were -0.84 and -0.70 for  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{ClO}^-$ , and  $[\text{Co(II)HEDTA}]^-$ -  $\text{ClO}^-$  systems respectively, indicating negative first order with respect to  $[\text{H}^+]$ . These inverse acid dependences implies that there is deprotonation pre-equilibrium step prior to electron transfer (Wilkins, 2002 and Onu *et al.*, 2009, 2015 and 2016). The plots of  $k_2$  versus  $[\text{H}^+]^{-1}$  were linear with zero intercept implying that only the deprotonated species are reactive. Similar inverse dependence on the acid has been reported (Onu *et al.*, 2009, 2015 and 2016) for reaction involving these complexes with some oxyanions. From Figures 4.12 – 4.13, the acid dependence rate constants for the reaction systems can be represented as:

$k_2 = c[\text{H}^+]^{-1}$ , where  $c = 1.23 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $[\text{Co(II)EDTA}]^{2-}$ -  $\text{ClO}^-$  system

$k_2 = d[\text{H}^+]^{-1}$ , where  $d = 2.28 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for  $[\text{Co(II)HEDTA}]^-$ -  $\text{ClO}^-$  system

Therefore, the overall rate equations showing acid dependence effect for the two systems are expressed in equations 5.30 and 5.31.

$$\frac{d[\text{Co(III)EDTA}^-]}{dt} = c[\text{H}^+]^{-1}[\text{Co(II)EDTA}^{2-}][\text{ClO}^-] \quad 5.30$$

$$\frac{d[\text{Co(III)HEDTA}]}{dt} = d[\text{H}^+]^{-1}[\text{Co(II)HEDTA}^-][\text{ClO}^-] \quad 5.31$$

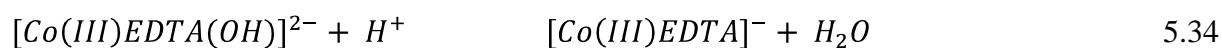
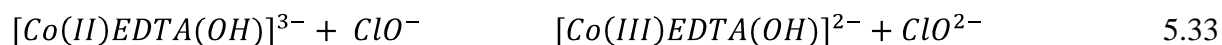
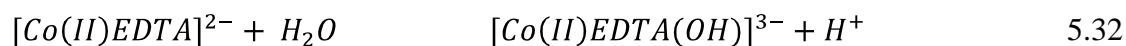
The rates of the reactions increased with increase in ionic strength of the reaction medium (Tables 4.3 and 4.4) suggesting positive Brønsted-Debye salt effect which shows that similar

charged species formed the activated complex (Atkins and de Paula, 2002). The effect was further supported by the observation that the reaction rate increased with decrease in dielectric constant of the reactions medium for  $[Co(II)EDTA]^{2-} - ClO^-$  system. However, negligible effect of dielectric constant was observed for  $[Co(II)HEDTAOH_2]^- - ClO^-$  system. Free radical test did not form gel. This indicates that the involvement of free radicals in the both two reactions is unlikely.

Both  $[Co(II)EDTA]^{2-} - ClO^-$  and  $[Co(II)HEDTAOH_2]^- - ClO^-$  reactions were catalysed by the presence of both added anions and cations which suggest the outer sphere pathway. The shifts in  $\lambda_{max}$  observed in each of the reactions however cannot be ascribed to presence of intermediate complex which is characteristic of inner-sphere mechanism, rather the shifts may be attributed to the product, Co(III) formed, which absorb at a higher  $\lambda_{max}$ . That detectable intermediate is not important in these reactions is further supported by the zero intercept obtained in the Michaelis - Menten plots of  $1/k_{obs}$  versus  $1/ClO^-$  for each of the reactions.

In view of the above results, the following reaction mechanisms are hereby proposed via an outer-sphere for  $[Co(II)EDTA]^{2-} - ClO^-$  and  $[Co(II)HEDTAOH_2]^- - ClO^-$  system

***Mechanistic pathway of  $[Co(II)EDTA]^{2-} - ClO^-$  system***



$$\frac{d[Co(III)EDTA^-]}{dt} = k_2[Co(II)EDTA(OH)^{3-}][ClO^-] \quad 5.36$$

$$\text{But } [Co(II)EDTA(OH)^{3-}] = \frac{K_1[Co(II)EDTA^{2-}][H_2O]}{[H^+]} \quad 5.37$$

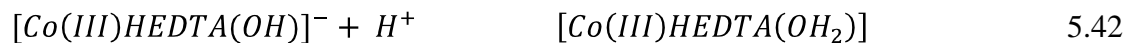
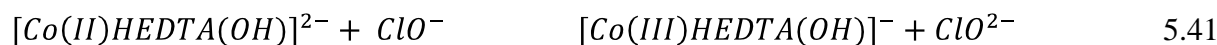
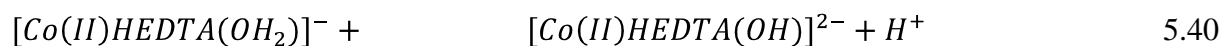
$$\frac{d[Co(III)EDTA^-]}{dt} = \frac{K_1 k_2}{[H^+]} [Co(II)EDTA^{2-}][ClO^-][H_2O]$$

$$5.38[H_2O] \approx 1$$

$$\text{Hence, } \frac{d[Co(III)EDTA^-]}{dt} = \frac{K_1 k_2}{[H^+]} [Co(II)EDTA^{2-}][ClO^-] \quad 5.39$$

This is analogous to Eq. 5.27, where  $c = K_1 k_2$

***Mechanistic pathway of  $[Co(II)HEDTA(OH_2)]^- - ClO^-$  system***



$$\frac{d[Co(III)HEDTA(OH_2)]}{dt} = k_2[Co(II)HEDTA(OH)^{2-}][ClO^-] \quad 5.44$$

$$\text{But } [Co(II)HEDTA(OH)^{2-}] = \frac{K_1[Co(II)HEDTA(OH_2)]^-}{[H^+]} \quad 5.45$$

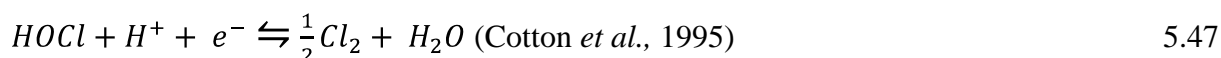
$$\text{Hence, } \frac{d[Co(III)HEDTA(OH_2)]}{dt} = \frac{K_1 k_2}{[H^+]} [Co(II)HEDTA(OH_2)]^- [ClO^-] \quad 5.46$$

This is analogous to Eq. 5.27, where  $d = K_1 k_2$

**5.3 Comparison of the  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  with  $[Co(II)EDTA]^{2-} - ClO^-$  reaction**

The rate constants,  $k_2$  for the oxidation of  $[Co(II)EDTA]^{2-}$  by  $S_2O_8^{2-}$  and  $ClO^-$  oxidants varied in the order  $9.70 \pm 0.1 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  ( $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$ )  $> 3.31 \pm 0.07 \times$

$10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} ([Co(II)EDTA]^{2-} - ClO^-)$ . The variation in the rate of reactions could be attributed to the differences in the oxidants present in the reaction medium. The persulphate,  $S_2O_8^{2-}$  ion being the better oxidant than hypochlorite,  $ClO^-$ , is one of the strongest oxidant ( $E = +2.01V$ ) known in aqueous solution (Mcheik and Jamal, 2013). However, even though, hypochlorite  $ClO^-$  is the strongest oxidizing agent of the chlorine oxyanions (Mohammed *et al.*, 2010), its redox potential (+1.63) for:



is lower than that of persulphate,  $S_2O_8^{2-}$  ion, hence, lower oxidizing ability.

#### 5.4 Comparison of the $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$ with $[Co(II)HEDTAOH_2]^- - ClO^-$ reaction

Also, in the oxidation of  $[Co(II)HEDTA]^-$  by the same oxidants, the reaction rates followed similar pattern, in the order  $6.00 \pm 0.1 \times 10^{-2} s^{-1} ([Co(II)HEDTA]^- - S_2O_8^{2-}) > 3.13 \pm 0.09 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} ([Co(II)HEDTA]^- - ClO^-)$ . This variation in the rates of reactions could be attributed to the differences in the oxidants oxidising the reductants. The persulphate,  $S_2O_8^{2-}$  ion is a better oxidant than hypochlorite,  $ClO^-$  due to above reason (Equation 5.35). The result is that, the rate of oxidizing similar reductant by these two oxidants is expected to be higher with  $S_2O_8^{2-}$  ion than with  $ClO^-$ .

#### 5.5 Comparison of the $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$ with $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$ reaction

The rate constants,  $k_2$  and  $k_1$  for the oxidation of  $[Co(II)EDTA]^{2-}$  and  $[Co(II)HEDTA]^-$  by  $S_2O_8^{2-}$  oxidant respectively varied in the order  $9.70 \pm 0.1 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} ([Co(II)EDTA]^{2-} - S_2O_8^{2-}) > 6.00 \pm 0.1 \times 10^{-2} s^{-1} ([Co(II)HEDTA]^- - S_2O_8^{2-})$ . This difference in rate constants could be attributed to the effect of ligands binding the metal Co(II), one being

hexadentate(EDTA) and the other pentadentate (HEDTA). It is known that ligands moderate the electron potential of metal ions (Burgess, 1999) and by extension reactivity. For example the redox potential of:



But when complexed with EDTA, the redox potential for the process:



The nature and specific chemical properties of metal ions and that of the ligands are known to determine this reactivity. The trend is surprising due to the fact that EDTA is known to bind more strongly to Co(II) than HEDTA in forming  $[Co(II)EDTA]^{2-}$  and  $[Co(II)HEDTA]^{-}$  with stability constant of  $\log K = 16.31$  and  $14.4$  respectively (Onu, 2010). Hence, it is expected that the reaction will be faster when HEDTA is bound with Co(II) metal. The faster rate for the oxidation of  $[Co(II)EDTA]^{2-}$  could be attributed to its low value (easily release electron) of electron potential as stated in equation (5.48) above.

### 5.6 Comparison of the $[Co(II)EDTA]^{2-} - ClO^{-}$ with $[Co(II)HEDTAOH_2]^{-} - ClO^{-}$ reaction

However, the rate constants,  $k_2$  for the oxidation of  $[Co(II)EDTA]^{2-}$  and  $[Co(II)HEDTAOH_2]^{-}$  by  $ClO^{-}$  followed the order  $3.31 \pm 0.07 \times 10^{-2} dm^3 mol^{-1} s^{-1} ([Co(II)EDTA]^{2-} - ClO^{-}) > 3.13 \pm 0.09 \times 10^{-2} dm^3 mol^{-1} s^{-1} ([Co(II)HEDTA]^{-} - ClO^{-})$ . This negligible effect implies that, the reaction rate of oxidising Co(II) by  $ClO^{-}$  ion is independent of the identity of the ligand binding the metal, consequently the rate constants are slightly similar.

## CHAPTER SIX

### 6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

#### 6.1 Summary and Conclusion

The kinetics studies of the oxidation of aminocarboxylatocobaltate(II) complexes ( $[\text{Co(II)EDTA}]^{2-}$  and  $[\text{Co(II)HEDTA(OH}_2)]^-$ ) each by hypochlorite and silver-catalysed persulphate ions in aqueous acidic medium was carried out. The stoichiometric studies showed 2:1 mole ratio for  $[\text{Co(II)HEDTAOH}_2]^- - \text{S}_2\text{O}_8^{2-}$  and  $[\text{Co(II)EDTA}]^{2-} - \text{S}_2\text{O}_8^{2-}$  systems and 1:1 mole ratio for  $[\text{Co(II)EDTA}]^{2-} - \text{ClO}^-$  and  $[\text{Co(II)HEDTAOH}_2]^- - \text{ClO}^-$  systems.

The kinetic study showed a first order dependence with respect to  $[\text{S}_2\text{O}_8^{2-}]$  and  $[\text{ClO}^-]$  for all the system except  $[\text{Co(II)HEDTAOH}_2]^- - \text{S}_2\text{O}_8^{2-}$  system which showed zero order with respect to  $[\text{S}_2\text{O}_8^{2-}]$ . The rates of the reactions were independent of  $[\text{H}^+]$  but dependent on  $[\text{Ag}^+]$  for  $[\text{Co(II)EDTA}]^{2-} - \text{S}_2\text{O}_8^{2-}$  and  $[\text{Co(II)HEDTAOH}_2]^- - \text{S}_2\text{O}_8^{2-}$  systems, while for  $[\text{Co(II)EDTA}]^{2-} - \text{ClO}^-$  and  $[\text{Co(II)HEDTAOH}_2]^- - \text{ClO}^-$  systems, the rates were inversely dependent on  $[\text{H}^+]$ . The reactions rate laws are therefore in conformity with equations 5.5 – 5.6 and 5.30 – 5.31 stated earlier.

The rate constants for the various reaction systems were observed as follows:

$$[\text{Co(II)EDTA}]^{2-} - \text{S}_2\text{O}_8^{2-} \text{ reaction, } k_2 = (9.70 \pm 0.1) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$[\text{Co(II)HEDTAOH}_2]^- - \text{S}_2\text{O}_8^{2-} \text{ reaction, } k_1 = (6.00 \pm 0.1) \times 10^{-2} \text{ s}^{-1}$$

$[Co(II)EDTA]^{2-} - ClO^-$  reaction,  $k_2 = (3.31 \pm 0.07) \times 10^2 dm^3 mol^{-1} s^{-1}$

$[Co(II)HEDTAOH_2]^- - ClO^-$  reaction,  $k_2 = (3.13 \pm 0.09) \times 10^2 dm^3 mol^{-1} s^{-1}$

Increase in concentrations of ionic strength increase the reaction rates for  $[Co(II)EDTA]^{2-} - ClO^-$  and  $[Co(II)HEDTAOH_2]^- - ClO^-$  systems while it had negligible effect for  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  and  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$  systems. The thermodynamic parameters obtained from the temperature dependence study showed that the activated complexes are ordered for  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$  and  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$  systems.

Spectroscopic evidence showed a shift in  $\lambda_{max}$  for all the reactions which may be attributed to the product, Co(III) formed. Also, Michaelis – Menten plot of  $1/k_{obs}$  versus  $1/[oxidant]$  had zero intercept for all the reaction systems except for  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$ . Moreover, the reaction rates were catalysed by addition of ions for all the reaction systems except for  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$ , where both added cations and anions had no effect on the reaction rate.

From the results, the outer-sphere mechanism is proposed as the plausible mechanism for  $[Co(II)EDTA]^{2-} - S_2O_8^{2-}$ ,  $[Co(II)EDTA]^{2-} - ClO^-$  and  $[Co(II)HEDTAOH_2]^- - ClO^-$  systems while the inner-sphere mechanism is proposed for  $[Co(II)HEDTAOH_2]^- - S_2O_8^{2-}$  system.

## 6.2 Recommendation

It is recommended that further studies should be carried out using thermostatic UV-Visible spectrophotometre in order to get full insight on the thermodynamic parameters of these



reactions. Also other spectroscopic techniques should be carried out for the structural elucidation of possible products.

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