KINETICS AND MECHANISMS OF THE REDOX REACTIONS OF 2,6-DICHLOROPHENOL INDOPHENOL WITH OXYANIONS, HYDRAZINE AND HYDROGEN PEROXIDE IN AQUEOUS MEDIUM

BY

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FEBRUARY, 2018

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BY

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P14SCCH8008

A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER OF SCIENCE DEGREE IN INORGANIC CHEMSTRY

DEPARTMENT OF CHEMISTRY
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AHMADU BELLO UNIVERSITY, ZARIA
NIGERIA.

FEBRUARY, 2018

Declaration

I declare that the work in this dissertation entitled "Kinetics and mechanisms of the redox reactions of 2,6-dichlorophenol indophenol with oxyanions, hydrazine and hydrogen peroxide in aqueous medium" has been carried out by me in the Department of Chemistry Ahmadu Bello University, Zaria. No part of this dissertation was earlier presented for another degree or diploma at this or any other institution. The information derived from the literature has been duly acknowledged in the text and a list of references provided.

Suleiman Sani ILIYASU _____ _____

Signature Date

Certification

This dissertation entitled “Kinetics and mechanisms of the redox reactions of 2,6-dichlorophenol indophenol with oxyanions, hydrazine and hydrogen peroxide in aqueous medium” by Suleiman Sani ILIYASU meets the regulations governing the award of the Degree of Master of Science in Inorganic Chemistry of Ahmadu Bello University Zaria, and is approved for its contribution to knowledge and literary presentation.

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Dedication

This work is dedicated to my parents, Alh. Iliyasu Muhammed Sani and Haj. Aisha Ismail Baballe. May Allah (S.W.T) reward them abundantly! Amen.

Acknowledgements

All praise be to Almighty Allah, the Shelter and Sustainer of the world, The Most Gracious The Most Merciful, my past, present and future life guide. I bear witness that there is no God but Allah and Prophet Muhammed (S. A. W) is the messenger of Allah. May the Blessings of Allah be upon Prophet Muhammed (S. A.W), His household and His companions.

My profound gratitude goes to my supervisors, Prof. S. O. Idris and Dr. A. D. Onu for their contribution, tolerance and encouragement which led to the success of this work. May Almighty Allah guide and protect them. I will like to thank the Head of Department, Prof. A. O. Oyewale and the entire staff of the Department for their support. I really appreciate the support from Mrs. S. A. Hamza and Mr. I. Ibrahim, I am grateful for their contribution and encouragement.

I wish to express my appreciation to the entire Alh. Iliyasu Sani's Family, Haj. Aishat Ismail Baballe's family, Alh. Nasiru Abdul's family, Alh Sani's Family and Alh. Audu Custom's family. May Allah (S. W. T) continue to guide and protect them. To my friends and research workmates, Yusuf Ahmed, Usman Bello, Abiti Yakadi, Samuel Agbese, Habib Gambo Isari, Muhammed Zakari, Shuaib Sulaiman, Aminu Abba, Bashir Zubair, Umar Ibrahim Danja to mention but a few, thank you and I am really grateful.

To all personalities that contributed to the success of this work, I am grateful. May the Peace and Blessing of Almighty Allah (S. W. T) continue to shower upon you.

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Abstract

The kinetics of the redox reactions of 2,6-dichlorophenol indophenol (DCPIP) by metabisulphite ions ($S_2O_5^{2-}$), sulphite ions (SO_3^{2-}), hydrazine (N_2H_4) and hydrogen peroxide (H_2O_2) at 28 ± 1 °C was studied at λ_{max} of 600 nm in aqueous medium under pseudo-first order conditions at I = 0.2 mol dm^{-3} (NaCl). The stoichiometry of 1:1 was obtained for all the reactions except DCPIP - $S_2O_5^{2-}$ which was 2:1. The reactions were first order in [$S_2O_5^{2-}$], [N_2H_4], [H_2O_2] and zero order with respect to [SO_3^{2-}]. The reactions conform to the following rate equations:

$$\frac{d[DCPIP]}{dt} = k_2 [DCPIP] [S_2O_5^{2-}]$$

where $k_2 = 16.24 \pm 0.03$ dm^3 mol^{-1} s^{-1}

$$\frac{d[DCPIP]}{dt} = k_1[DCPIP]$$

where $k_1 = 1.79 \pm 0.02$ dm^3 mol^{-1} s^{-1}

$$\frac{d[DCPIP]}{dt} = k_2 [DCPIP] [N_2H_4]$$

where $k_2 = 0.13 \pm 0.02$ dm^3 mol^{-1} s^{-1}

$$\frac{d[DCPIP]}{dt} = k_2[DCPIP] [H_2O_2]$$

where $k_2 = 3.01 \pm 0.02$ dm^3 mol^{-1} s^{-1}. The rates of reactions displayed negative salt effect for DCPIP - $S_2O_5^{2-}$ reaction, positive salt effect for DCPIP - N_2H_4 reaction and zero salt effect for DCPIP - SO_3^{2-} and DCPIP - H_2O_2 reactions. Added cations catalysed the reaction of DCPIP - $S_2O_5^{2-}$ but had no significant effect in the reactions of DCPIP - SO_3^{2-}, DCPIP - N_2H_4 and DCPIP - H_2O_2. While added anions had negligible effect for all the reactions except DCPIP - N_2H_4 reaction. There was no evidence of formation of intermediate complex of significant stability for any of the reactions.

Free radicals were not detected in all the reactions. Based on the results obtained in these studies, outer-sphere mechanism was proposed for the reactions of DCPIP with $S_2O_5^{2-}$, SO_3^{2-}, H_2O_2 and inner-sphere mechanism for the reaction of DCPIP with N_2H_4.

CHAPTER ONE

1.0 INTRODUCTION

Inorganic chemistry is the chemistry of all elements in the periodic table and the compounds they form based on the concept of structure, bonding and reactivity (Cox, 2004). Areas of research in inorganic chemistry includes organometallic chemistry, synthetic inorganic chemistry, cluster chemistry, bioinorganic chemistry, industrial chemistry, kinetic and mechanistic inorganic chemistry (Miessler and Tarr, 2003).

In the last few decades, studies of electron transfer reaction in inorganic chemistry have developed tremendously both theoretically and experimentally as witnessed by large number of research articles (Gennady *et al.,* 2013). In chemical system, mechanism of electron transfer gives kinetic explanation of elementary steps by which the overall chemical reaction change occurs (Espenson, 2002). The mechanisms of such reactions have been generally grouped as either the inner-sphere mechanism; that involve formation of bridging ligand between the reacting species centre prior to electron transfer or the outer-sphere mechanism; that involve direct transfer of electron between reacting species without change in the coordination sphere of the species (Jagannadham, 2012).

2,6-Dichlorophenol indophenol (DCPIP) with a molecular formular of $C_{12}H_7Cl_2NO_2$ is a quinone imine dye that can be synthesized as a dark green powder, stable, odourless and freely soluble in water (Cabello *et al.,* 2009). Several kinetic process for its oxidation have been used for the determination of chemical reductants in food, as biological sample for making microscopic object more clearly visible than they would be when unstained and in pharmaceutical industries because of it chemical stability, systemic deliverability and membrane permeability (Cabello *et al.,* 2009).

Metabisulphite ion ($S_2O_5^{2-}$) is an inorganic compound with a wide range of application. It is a good reducing agent used as antioxidant, antimicrobial agent in variety of foods and drugs, antichloride and as sulphonating agent (Quanxi *et al*., 2015; Ivana *et al*., 2011), it is also used in wine and beer making to inhibit the growth of wild yeasts, bacteria and fungi (Miline, 2005).

Sulphite ion (SO_3^{2-}) is an inorganic compound that has a powerful reducing ability. Its sulphur atom is double-bonded to one oxygen atom and single-bonded to two other oxygen atoms that carries a formal charge of -1, together accounting for the -2 charge on the ion. It has a resonance equivalent structure due to the resonance hybrid involving pπ-pπ S-O bonding (Catherine and Alan, 2008). It is used in pharmaceutical industries, paper industries, textile industries, as oxygen scavenger in water treatment and also as preservative additive in food (Hassan and Neil, 2012).

Hydrogen peroxide can act both as oxidising and reducing agent. But, it is only in the presence of strong oxidising agents it act as reducing agent. It is the simplest peroxide that contain O-O single bond (Goor *et al.*, 2007). It is used as a bleaching agent, disinfectant, catalyst, in paper and pulp industries and water pollution control as well as biological and medicinal applications (Onu *et al.*, 2015; Hill, 2001).

Hydrazine, a good reducing agent, is a colourless liquid at room temperature. The compound and it derivatives have been used in agriculture as pesticide, deoxygenation of boiler water, chemical industries, pharmaceutical drugs, polymerization catalyst, fuel rocket, explosive and as mono propellants in gas turbine generators (Jean-Pierre and Paul, 2002).

1.1 Statement of the Research Problem

Dyes are coloured and ionizing compounds which have affinity toward the substrate to which it is being applied (Booth, 2000). DCPIP is used for the determination of ascorbic acid in food, as biological stain for the study of bacteria and related microorganism and in pharmaceutical industry (Cabello *et al.,* 2009). It also serves as good medium for disruption of cell proliferation, tissue angiogenesis and inflammation by directly or indirectly targeting specific cellular factors when delivered enclosed in specific nanoparticles (Fadee *et al.,* 2010). Despite these uses, the direct assessment of the redox activities of the dye with respect to the medium involved in control of cancer cells and proliferation is lacking (Wondrak, 2009; Fry *et al.*, 2005; Kumar and Acharya, 1999). Available literature collaborates the fact that not much have been done on the kinetics and mechanism of its redox reaction.

1.2 Justification

The kinetic data that would be generated from these studies will complement much needed kinetic information for quantitative comparison of various electron transfer reactions involving the dye, its uses as well as its handling. Furthermore, the kinetic data generated and the proposed mechanisms would contribute to conceptual development of mechanism of redox reactions of the dye.

1.3 Aim and Objectives

The research is aimed at studying the kinetics of the redox reactions of 2,6-dichlorophenol indophenol with $S_2O_5^{2-}$, SO_3^{2-}, H_2O_2 and N_2H_4 in aqueous medium and propose mechanisms for these reactions.

The objectives of the study are to:

i. determine the stoichiometry and order of the redox reactions,

ii. establish the rate law,

iii. investigate the effect of changes in ionic strength, added ions and dielectric constant on the reaction rates,

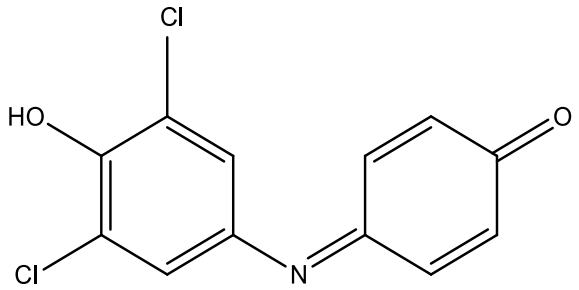
iv. test for intermediate complex formation, free radicals and

v. analyse the reaction products.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Reactions of 2,6-Dichlorophenol Indophenol



Structure of 2,6-dichlorophenol indophenol

The compound is a two-electron acceptor oxidant although in some cases like reactions catalysed by different oxidoreductases it takes part as a one-electron transfer oxidant (Christian *et al.,* 2005). Kinetic studies of DCPIP with reduced nicotinamide adenine dinucleotide phosphate (NADPH) has been reported (Dupuy *et al*., 1990), The reduced form of the dye is unstable and can transfer the accepted electron to any suitable electron acceptor, making the species to act as chemical catalyst in electron transfer reaction.

Similarly, kinetic studies of the dye with dithionate (Konidari and Karayannis,1988) and titanium dioxide aqueous suspension (Brezova *et al.*,1991) have been reported. Both reactions were first order with respect to DCPIP, dithionate and titanium dioxide.

Tiwari and Mishra (1991) investigated the electron transfer reaction of DCPIP with 2-mercaptobenzothiazole (MBT) in the presence of hydroxyl ion in acetone – water medium (60%, v/v), two moles of MBT was oxidized by one mole of DCPIP, the reaction was half order to [DCPIP] and second order with respect to [MBT], increase in ionic strength of the medium did not influence the rate but the rate increased with increase in dielectric constant of the medium.

2.2 Reactions of Metabisulphite Ions

Reactions of metabisulphite with crystal violet (Abdulsalam, 2015), methylene blue (Babatunde *et al*., 2013) and rosaniline (Onu and Iyun, 2001) in aqueous acidic medium have been studied. Results from the spectrophotometric titration gave stoichiometry of 1:1 for the reactions of metabisulphite with rosaniline and crystal violet and 1:3 for the reaction of metabisulphite with methylene blue. Both reactions were first order with respect to both reactants and rate of reaction enhanced with increase in hydrogen ion concentration. Increase in ionic concentration of the reaction medium decrease the rate of reaction for all the reactions (negative salt effect). Results from spectroscopic investigation and Michaelis-Menten plot showed no evidence of formation of intermediate complex of significant stability for all the reactions and outersphere mechanism was proposed for the reactions.

Abbas and Nabeel (2010) investigated the reduction of potassium hexacyaoferrate(III) by sodium metabisulphite as a function of pH and temperature. The pH was varied between the range 2.6 – 4.7 using citric acid buffer and at temperatures between 15 – 30 °C. The reaction follow two paths; acid dependent and an inverse acid dependent.

Also, in the oxidation of metabisulphite by malachite green (MG^+), Imam (2016) reported that the reaction was first order with respect to both reactants. Stoichiometry of the reaction showed one mole of metabisulphite ion consumed one mole of malachite green. Increase in ionic strength of the reaction medium increased the rate of the reaction (positive salt effect) while increase in hydrogen ion concentration decreased the rate of the reaction. Michaelis-Menten plot showed no evidence of formation of complex intermediate. Outersphere mechanism was proposed as the possible reaction pathway.

2.3 Reactions of Sulphite Ions

Sulphite inhibit oxidation in beer during storage by acting as antioxidant and it react with carbonyl compound formed in beer to mask stale flavour (Luis, 2016). The stoichiometry and products of reactions involving sulphite allows a distinction to be made among one and two equivalent oxidizing agents (Erling and Tor, 2007).

Electron transfer reaction of 3,7-bis(dimethylamine)phenothionium chloride (MB^+) with sulphite showed first order in both reactants (Busari, 2007).

$$-\frac{d[MB^+]}{dt} = k_2[MB^+][SO_3^{2-}] \quad 2.1$$

The stoichiometry of the reaction could not be established because of the slow nature of the reaction. The rate showed no acid dependence but increase with change in ionic strength. Michaelis-Menten plot showed no evidence of formation of intermediate, outersphere mechanism was proposed for the reaction.

Kinetic studies of redox reaction of sulphite with toluidine blue (TB^+) (Jonnalagadda and Gollapalli, 2000) and non-toxic additive polyteraphthalate (PT) inhibitor (Cui *et al.*, 2012) have been reported. The reactions were found to be second order overall with first order dependence on both reactants for the reaction with toluidine blue and zero order for the reaction with PT inhibitor. Also, oxidation of sulphite by hydrogen peroxide in acidic medium has been investigated (Hoffmann and Edward, 1975). One mole of sulphite ion consumed one mole of hydrogen peroxide, the rate of reaction was found to be pH dependent.

Olajire and Olajide (2014) studied the kinetics of reduction of methylene blue with sodium sulphite in aqueous media. The reaction was carried out as a function of variables like concentration, pH, and temperature on rate of decolourisation. The rate of the reaction increase linearly with temperature and was found to be $[H^+]$ dependent. The reaction was first order in both $[MB^+]$ and $[SO_3^{2-}]$.

2.4 Reactions of Hydrazine

In the oxidation of hydrazine dihydrochloride by naphthol green B, Myek (2012) reported that the reaction was first order with respect to both reactants. Increase in ionic strength of the medium decreased the rate of the reaction while change in hydrogen ion concentration has no effect on the reaction rate. Outersphere mechanism was proposed as possible reaction pathway because Michaelis-Menten plot showed no evidence of formation of intermediate complex.

Kinetic studies of hydrazine and tetrachloroaurate(III) has been investigated (Bartlomiej *et al.,* 2014). The study shows that the rate of reaction increased with increase in temperature and change in ionic strength of the reaction medium showed negative salt effect. Mechanism involving one electron innersphere reaction was suggested.

Similarly, the kinetics of oxidation of hydrazine by chromium(VI) over pH range of 1.9 - 3.0 have been studied (Beck and Durham, 1970). The reaction was found to occur via two pathways with rate determining step involving the two-electron reduction of chromium(VI) to chromium(IV).

Hydrazine in deoxygenated aqueous solution quantitatively reduces superoxo complex $[(NH_3)_5Co^{III}$ (μ-superoxo) $Co^{III}(NH_3)_5]^{5+}$ to the corresponding peroxo complex $[(NH_3)_5Co^{III}$ (μ-peroxo) $Co^{III}(NH_3)_5]^{4+}$. The reaction was first order in hydrazine and $[(NH_3)_5Co^{III}$ (μ-superoxo) $Co^{III}(NH_3)_5]^{5+}$ and second order overall. Effect of acid shows inverse $[H^+]$ dependence on the reaction rate (Amit and Rupendranah, 2009).

In addition, John *et al.,* (2000) investigated the reduction of nitrobenzene to aniline by hydrazine with carbon as catalyst. The hydrazine served as a two electron reducing agent. The carbon served as adsorbent that made it possible for hydrazine to execute a four electron reduction process in two steps.

2.5 Reactions of Hydrogen Peroxide

Hydrogen peroxide can act as both oxidizing and reducing agent. It is used as bleaching agent, disinfectant, catalytic agent, for treatment of industrial chemical effluent, as well as biological and medicinal applications (Onu *et al.,* 2015; Hill, 2001)

Onu *et al.,* (2015) studied the kinetics of the redox reaction of hydrogen peroxide with aminocaboxylactocobaltate(II) complex ($[CoHEDTAOH_2]^-$) in aqueous acidic medium. The reaction followed 2:1 stoichiometry and the order of the reaction was found to be second order overall at constant hydrogen ion concentration. Michaelis-Menten plot showed no evidence of formation of intermediate complex. Outersphere mechanism was proposed as the preferred reaction pathway. Under experimental conditions employed, the rate of the reaction as deduced from the mechanism was proposed as:

$$\text{Rate} = k\,[H^+]\,[CoHEDTAOH_2^-]\,[H_2O_2] \qquad 2.2$$

where $k = k_1K_{eq}$.

Redox reaction for the oxidation of Sb(III) by hydrogen peroxide in aqueous medium has been studied (Quentel *et al.,* 2004). The rate was measured as a function of pH, temperature and ionic strength. The rate was found to be zero order with respect to Sb(III) and decreased with decrease in pH of the reaction medium. Similarly, in the oxidation of sulphite by hydrogen peroxide. One mole of hydrogen peroxide consumed one mole of sulphite ion and the rate of reaction was found to be pH dependent (Hoffmann and Edward, 1975).

In addition, Banerjee *et al.,* (1997) investigated the oxidation of hydrogen peroxide by dioxo-bridged manganese(III, IV) complex. The reaction was first order with respect to both reactants while the rate increased with increase in hydrogen ion concentration. Innersphere was proposed as plausible mechanism for the reaction.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

All solutions were prepared with distilled water. Chemicals and reagents used in this work were analar grade and were used without further purification except otherwise stated. Sodium chloride was used to maintain a constant ionic strength for all the reaction systems. Sodium metabisulphite, sodium sulphite, hydrazine and hydrogen peroxide were the reductants used. The rates of the reactions were monitored using Corning 254 colorimeter.

3.1.1 Preparation of stock 2,6-dichlorophenol indophenol solution.

Analar grade, 2,6-dichlorophenol indophenol was obtained from Alcon laboratories private limited. Stock solution (1.0×10^{-3} mol dm^{-3}) of the dye was prepared by dissolving 0.0268 g of the dye with distilled water in a 100 cm^3 volumetric flask and made up to the mark with distilled water. The electronic spectrum of the solution was run using a Jenway 6405 uv/vis spectrophotometer within a wavelength range of 400-780 nm. From the spectrum, the wavelength of maximum absorption (λ_{max}) of 600 nm was obtained.

3.1.2 Preparation of 0.4 mol dm^{-3} sodium metabisulphite ($Na_2S_2O_5$) solution

Stock solution (0.4 mol dm^{-3}) of sodium metabisulphite was prepared by dissolving 3.8024 g of the salt with distilled water in 50 cm^3 volumetric flask and made up to the mark with distilled water.

3.1.3 Preparation of 0.2 mol dm^{-3} sodium sulphite (Na_2SO_3) solution

Stock solution (0.2 mol dm^{-3}) of sodium sulphite was prepared by dissolving 1.2605 g of the salt with distilled water in 50 cm^3 volumetric flask and made up to the mark with distilled water.

3.1.4 Preparation of 0.1 mol dm^{-3} hydrazine hydrate ($N_2H_4.H_2O$) solution

Stock solution of $N_2H_4.H_2O$ (0.2 mol dm^{-3}) was prepared by transferring 1.63 cm^3 of 60 % $N_2H_4.H_2O$ solution (density 1.021 g cm^{-3}) into a 100 cm^3 volumetric flask and made up to the mark with distilled water.

3.1.5 Preparation of 0.1 mol dm^{-3} hydrogen peroxide (H_2O_2) solution

Stock solution of H_2O_2 (0.2 mol dm^{-3}) was prepared by transferring 2.04 cm^3 of 30 % H_2O_2 solution (density 1.11 g cm^{-3}) into a 50 cm^3 volumetric flask and made up to the mark with distilled water.

3.1.6 Preparation of 2.0 mol dm^{-3} sodium chloride solution

Stock solution of NaCl was prepared by dissolving 11.70 g of the salt with distilled water in 100 cm^3 volumetric flask and made up to the mark with distilled water.

3.1.7 Preparation of salts solution

Stock solutions of $MgCl_2$, $CaCl_2$, $NaNO_3$ and CH_3COONa were all prepared by dissolving known weight of the respective salt in known volume of distilled water. All salts were analar grade.

3.2 Methods

3.2.1 Stoichiometric studies

The stoichiometries of the reactions was determined by spectrophotometric titration, using the mole ratio method. The concentration of DCPIP was kept constant at 1.0×10^{-4} mol dm^{-3}, I = 0.20 mol dm^{-3} for all the systems, λ_{max} = 600 nm, T = 28 ± 1 ^oC for all the systems. [$S_2O_5^{2-}$], [SO_3^{2-}], [N_2H_4] and [H_2O_2] were varied in the range $(0.25 - 3.5) \times 10^{-4}$ mol dm^{-3}. The reactions were allowed to go to completion and the absorbance was recorded.

The stoichiometry was determined by a plot of absorbance against mole ratio.

3.2.2 Kinetic measurements

The rates of the reactions were monitored on a Sherwood Colorimeter 254. The rates were studied by monitoring decrease in absorbance of the dye at λ_{max} of 600 nm. All kinetic measurements were performed under pseudo first order conditions with the concentration of 2,6-dichlorophenol indophenol kept constant at 1.0×10^{-4} mol dm^{-3} and that of the reductants maintained at least 10 fold in excess over that of the dye. The following experimental conditions were maintained for the respective systems studied.

- 2,6-dichlorophenol indophenol – metabisulphite system:

$[S_2O_5^{2-}] = (0.5 - 2.25) \times 10^{-3}$ mol dm^{-3} ($Na_2S_2O_5$), I = 0.2 mol dm^{-3} (NaCl) and T = 28 ± 1°C.

- 2,6-dichlorophenol indophenol – sulphite system:

$[SO_3^{2-}] = (0.3 - 1.0) \times 10^{-2}$ mol dm^{-3} (Na_2SO_3), I = 0.2mol dm^{-3} (NaCl) and T = 28 ± 1°C.

- 2,6-dichlorophenol indophenol – hydrazine system:

$[N_2H_4] = (3.5 - 7.0) \times 10^{-2}$ mol dm^{-3} ($N_2H_4.H_2O$), I = 0.2 mol dm^{-3} (NaCl) and T = 28 ± 1°C

- 2,6-dichlorophenol indophenol – hydrogen peroxide system:

$[H_2O_2] = (1.0 - 4.5) \times 10^{-3}$ mol dm^{-3} (H_2O_2), I = 0.2 mol dm^{-3} (NaCl) and T = 28 ± 1°C

The pseudo first order rate constants for the reactions were obtained from the plots of the log ($A_t - A_\infty$) versus time, t (where A_∞ and A_t are the absorbances at the end of the reaction and at time, t) and from the slopes of the plots, the pseudo-first order rate constants, k_1, were determined. The second order rate constants (k_2) were obtained from the relation:

$$k_2 = k_1/[R] \qquad 3.1$$

where R= $S_2O_5^{2-}$, SO_3^{2-}, N_2H_4, H_2O_2

3.2.3 Effect of ionic strength and dielectric constant of reaction medium on the reaction rate

The effect of ionic strength on the rate of the reaction was investigated over a range of (0.01 - 0.5) mol dm^{-3} using NaCl as the inert electrolyte for all of the reactants, while other reaction conditions were kept constant. The ionic strength was caculated based on the relationship

$$I = \frac{1}{2}\sum C_i Z_i^{\,2} \qquad 3.2$$

where Z_i is the charge of an ion (positive for cations and negative for anions) and C_i is the concentration of the ion in solution.

Effect of changes in dielectric constant on the reaction rate was determined at different dielectric constants in the range 80.1 - 74.46 using water-acetone mixture at constant [DCPIP], [reductant] and [NaCl]

The dielectric constant for the reaction medium was calculated as:

$$D = \frac{D_{H2O} \times V_{H2O} + D_{Acetone} \times V_{Acetone}}{V_{H2O} + V_{Acetone}} \qquad 3.3$$

where D_{H2O} = dielectric constant of water, V_{H2O} = volume of water, $D_{Acetone}$ = dielectric constant of acetone, $V_{Acetone}$ = volume of acetone.

3.2.4 Effect of added ions on the reaction rate

The effect of added ions on the reaction rate was studied by addition of $(10 – 60) \times 10^{-3}$ mol dm^{-3} of the ions (Mg^{2+}, Ca^{2+}, NO_3^-, CH_3COO^-) while keeping all other parameters constant.

3.2.5 Test for intermediate complex

The spectra of the reaction mixtures were obtained over a wavelength range of 400 – 780 nm. These were carried out to determine whether intermediate complex were formed during the course of the reactions. Michaelis-Menten plots of $1/k_1$ versus 1/[reductant] were also made.

3.2.6 Free radical test

Acrylamide was added to partially oxidized reaction mixture of each reductant and 2,6-dichlorophenol indophenol. This was followed by a large excess of methanol. The acrylamide was also added to a solution of each reductant and 2,6-dichlorophenol indophenol separately. This served as control, formation of gel indicates the presence of free radical.

3.2.7 Products analysis

Presence of SO_4^{2-} ion (reduced product of $S_2O_5^{2-}$ and SO_3^{2-} ion) was tested by addition of $BaCl_2$ solution to the reaction mixture followed by dilute HCl (Vogel, 1996; Jeffery, 1991). Presence of H_2 was tested by holding a lighted splint near the opening of a closed tube of the reacting mixture. The lighted splint was exposed to the trapped gas in the closed tube (Emil *et al.*, 2011). Presence of O_2 was tested when a burning splint was blown out by shaking whilst the ember at the tip is still glowing hot. The ember tip was exposed to the trapped gas in the closed tube (John and Phil, 2001).

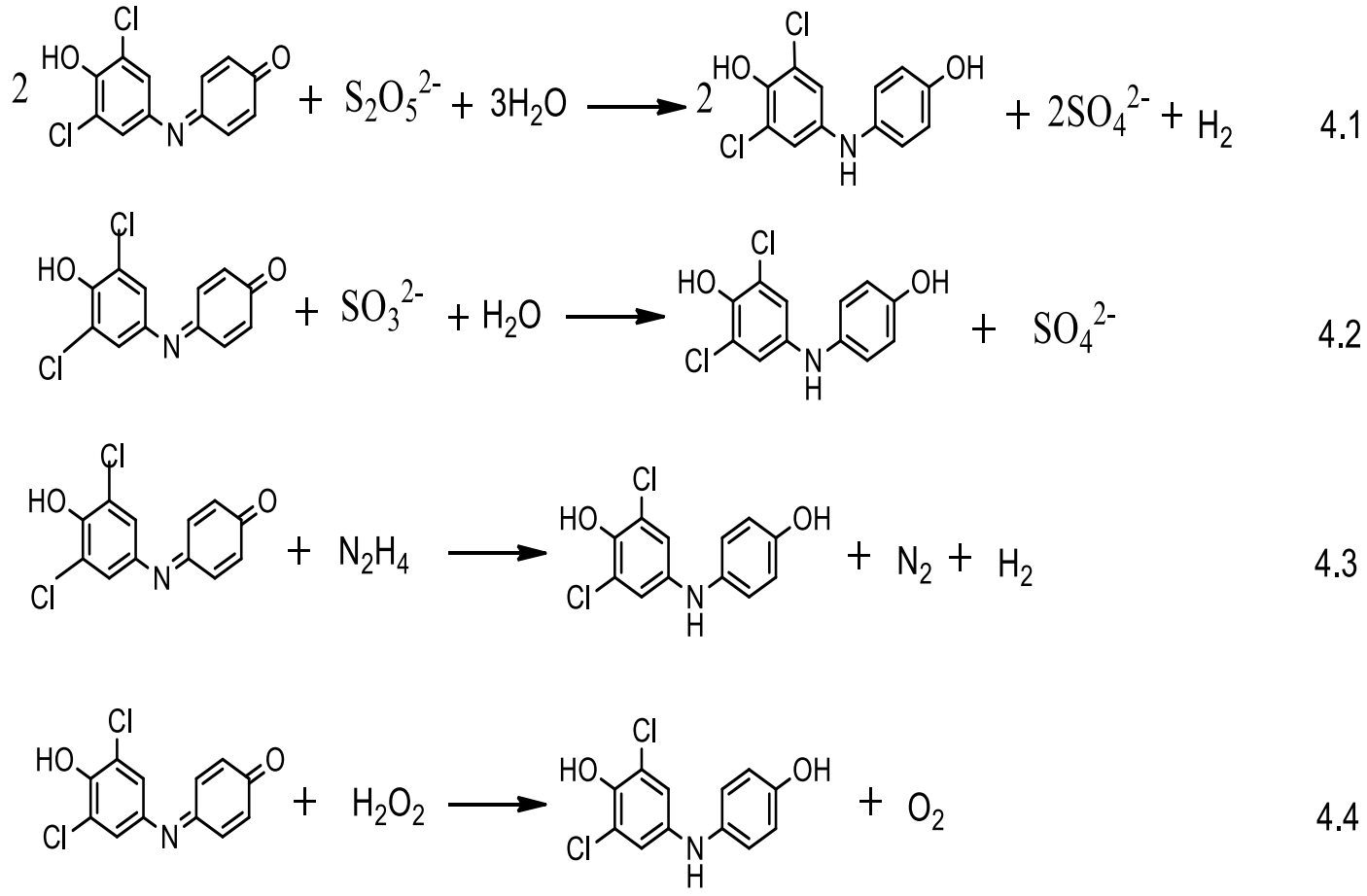
CHAPTER FOUR

4.0 RESULTS

4.1 Stoichiometry

Stoichiometric studies showed that one mole of 2,6-dichlorophenol indophenol was consumed by one mole each of sulphite ion, hydrazine and hydrogen peroxide, while two moles of 2,6-dichlorophenol indophenol was consumed by one mole of metabisulphite ion. The titration curves from which the stoichiometries were determined are presented in Figures 4.1 – 4.4.

On the basis of these results, the overall equation for the reactions can be presented as equations 4.1–4.4



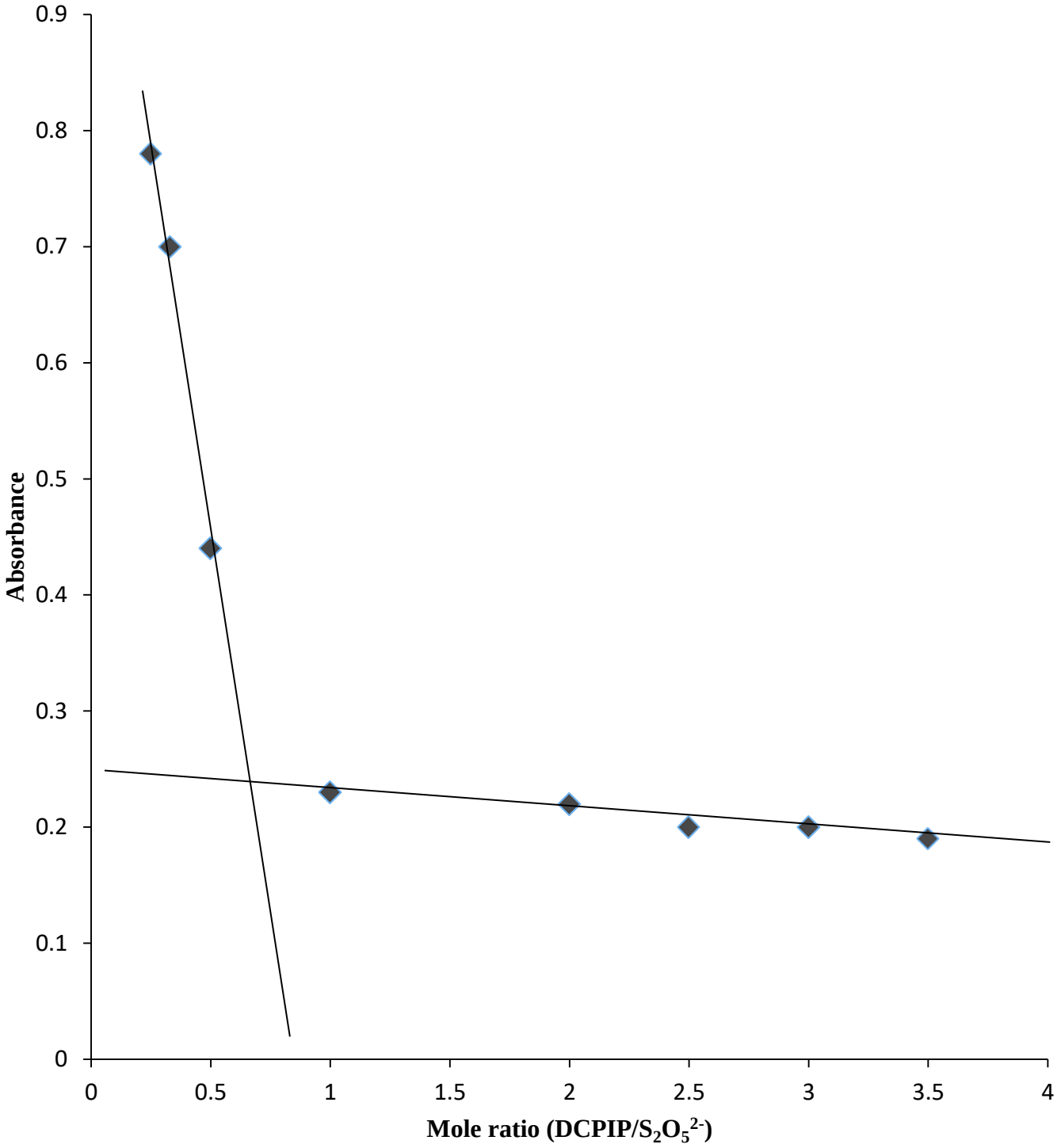


Figure 4.1: Plot of absorbance versus mole ratio for the redox reaction of 2,6-dichlorophenol indophenol with metabisulphite ion at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 28 ± 1 ˚C

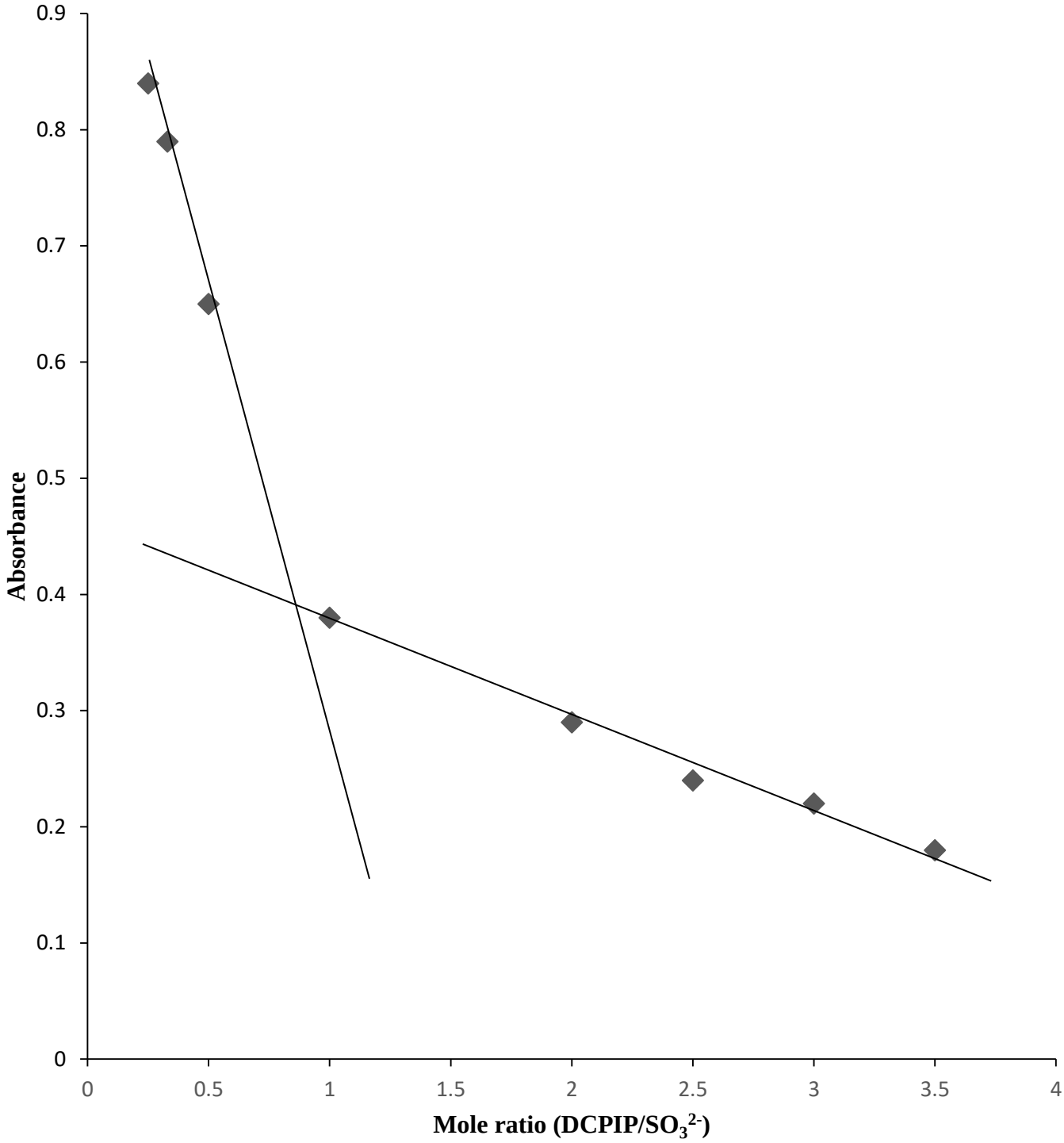


Figure 4.2: Plot of absorbance versus mole ratio for the redox reaction of 2,6-dichlorophenol indophenol with sulphite ion at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 28 ± 1 ˚C

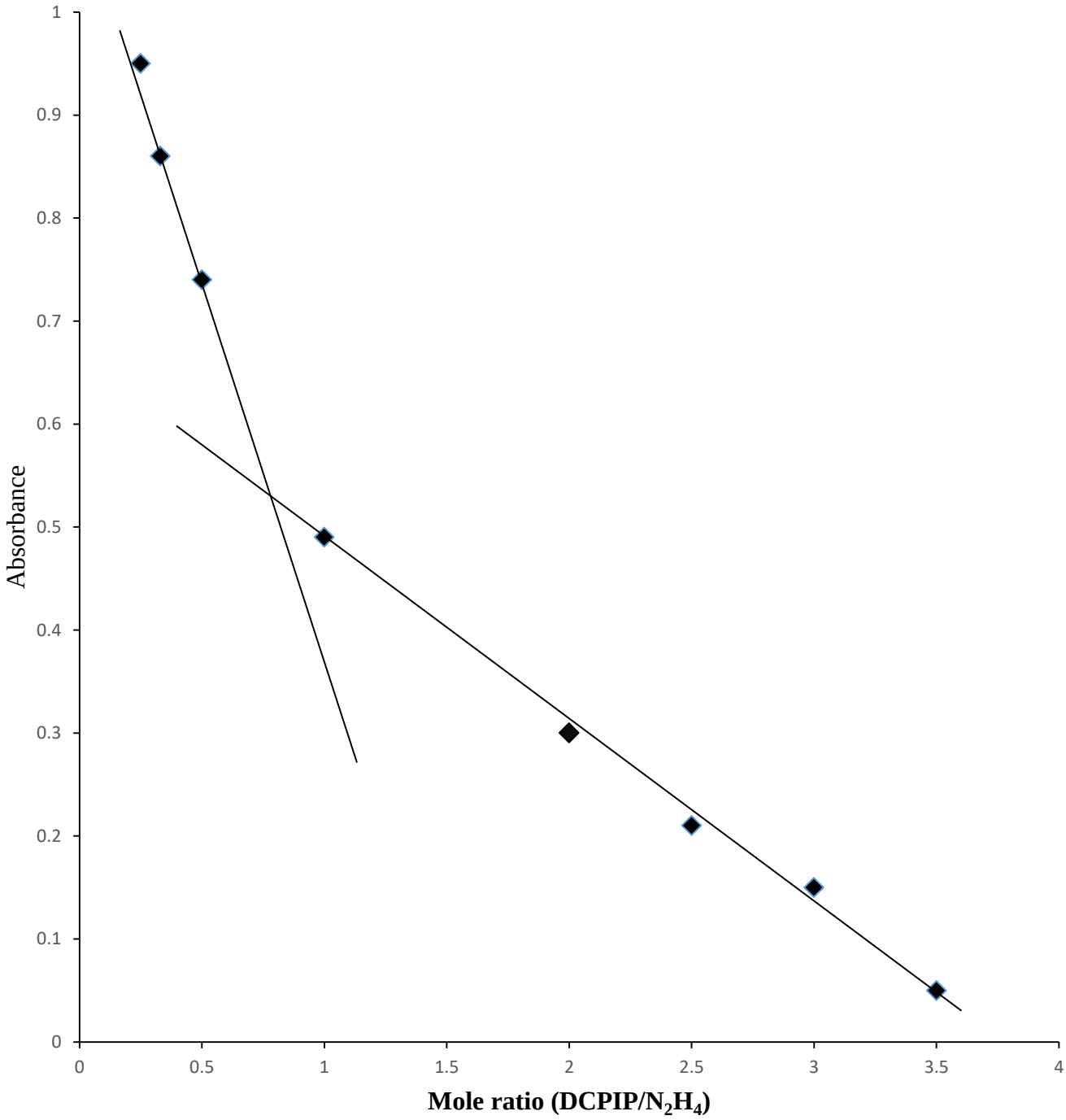


Figure 4.3: Plot of absorbance versus mole ratio for the redox reaction of 2,6-dichlorophenol indophenol with hydrazine at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 28 ± 1 ˚C

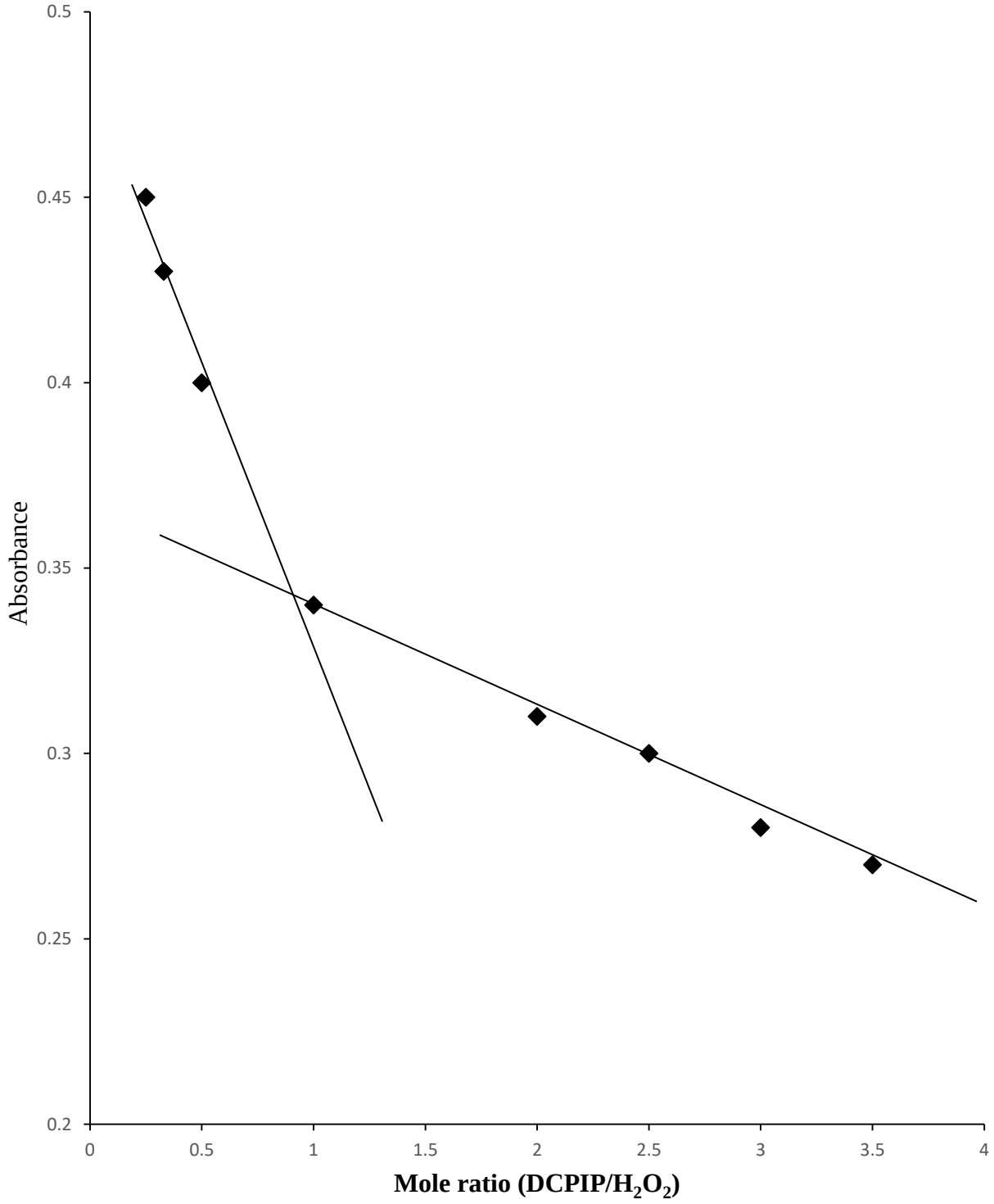


Figure 4.4: Plot of absorbance versus mole ratio for the redox reaction of 2,6-dichlorophenol indophenol with hydrogen peroxide at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 28 ± 1 ˚C

4.2 Determination of Order of the Reactions with Respect to the Reactants

The pseudo-first order plots of log (A_t - A_∞) versus time were linear to about 70% of the reaction. Linearity of these plots indicates that these reactions are first order with respect to [DCPIP]. The typical plots are presented in Figures (4.5 - 4.8). The pseudo-first order rate constants, k_1, were calculated from the slopes of these plots and are reported on Tables (4.1 - 4.4). Least square plots of log k_1 against log [reductants] gave a slope of 1.00, 1.07, 1.00 and 0.01 respectively for DCPIP-$S_2O_5^{2-}$, DCPIP-N_2H_4, DCPIP-H_2O_2 and DCPIP- SO_3^{2} reactions (Figures 4.9 - 4.11). These indicate first order dependence with respect to [$S_2O_5^{2-}$], [N_2H_4], [H_2O_2] and 0.01 indicates zero order with respect to [SO_3^{2-}]. The second order rate constant k_2, determined as $k_2 = k_1/[\text{reductant}]$ for $S_2O_5^{2-}$, N_2H_4 and H_2O_2, and first order determined as $k_1 = k_{obs}/[\text{reductant}]^0$ for SO_3^{2-} were fairly constant (Tables 4.1 - 4.4). On the basis of the above observations, the rate laws for these reactions can therefore be written as:

$$\frac{-d[DCPIP]}{dt} = k_2 [DCPIP][S_2O_5^{2-}] \qquad 4.5$$

where $k_2 = 16.24 \pm 0.03$ dm^3 mol^{-1} s^{-1}

$$\frac{-d[DCPIP]}{dt} = k_2 [DCPIP] [N_2H_4] \qquad 4.6$$

where $k_2 = 0.13 \pm 0.02$ dm^3 mol^{-1} s^{-1}

$$\frac{-d[DCPIP]}{dt} = k_2 [DCPIP] [H_2O_2] \qquad 4.7$$

where $k_2 = 3.01 \pm 0.02$ dm^3 mol^{-1} s^{-1}

$$\frac{-d[DCPIP]}{dt} = k_1 [DCPIP] \qquad 4.8$$

where $k_1 = 1.79 \pm 0.02$ s^{-1}

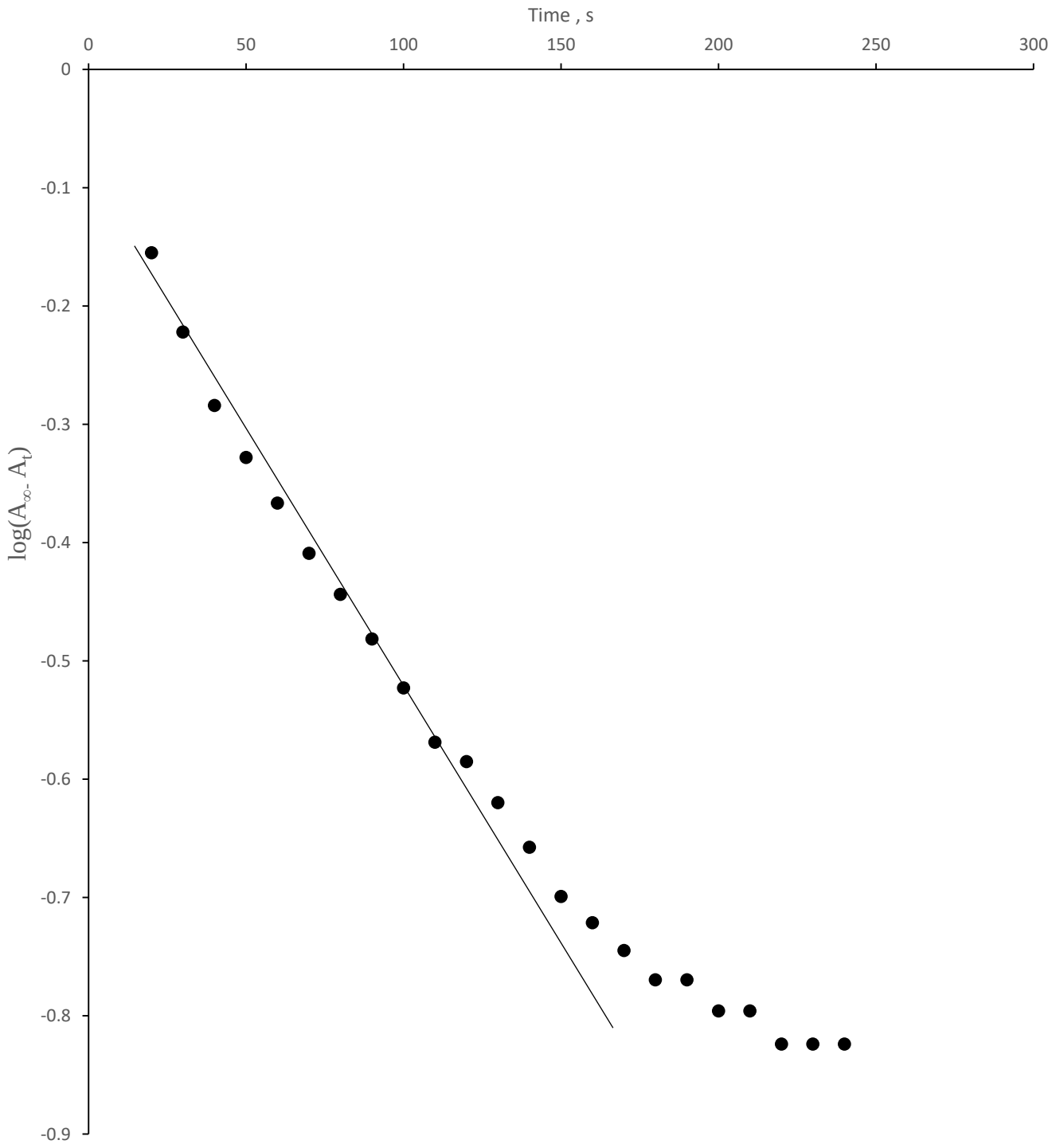


Figure 4.5: Typical pseudo-first order plot for the redox reaction of 2,6-dichlorophenol indophenol with metabisulphite ions at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, [$S_2O_5^{2-}$] = 1.0×10^{-3} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 28 ± 1 ºC

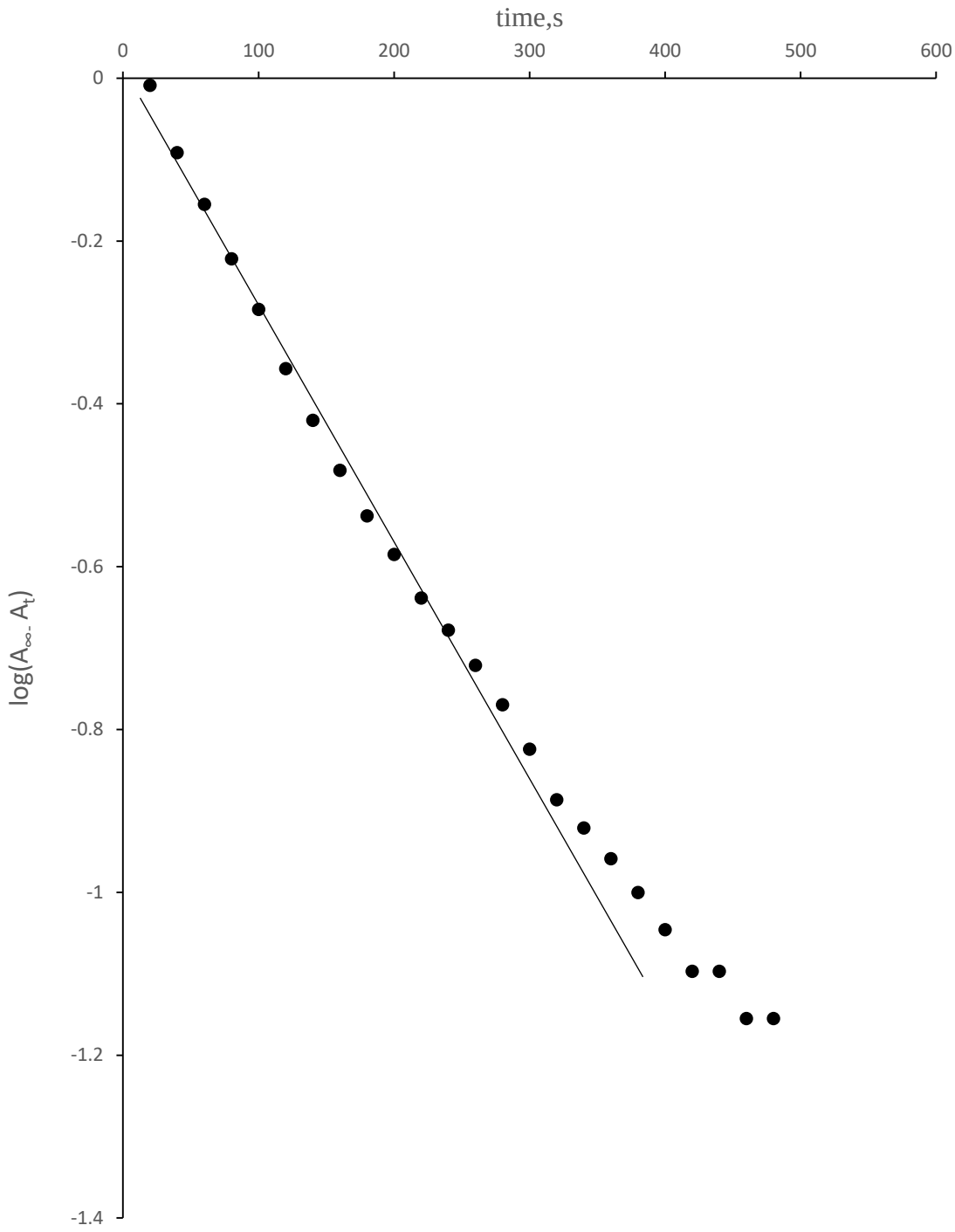


Figure 4.6: Typical pseudo-first order plot for the redox reaction of 2,6-dichlorophenol indophenol with hydrazine at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, [N_2H_4] = 4.0×10^{-2} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 28 ± 1 ºC

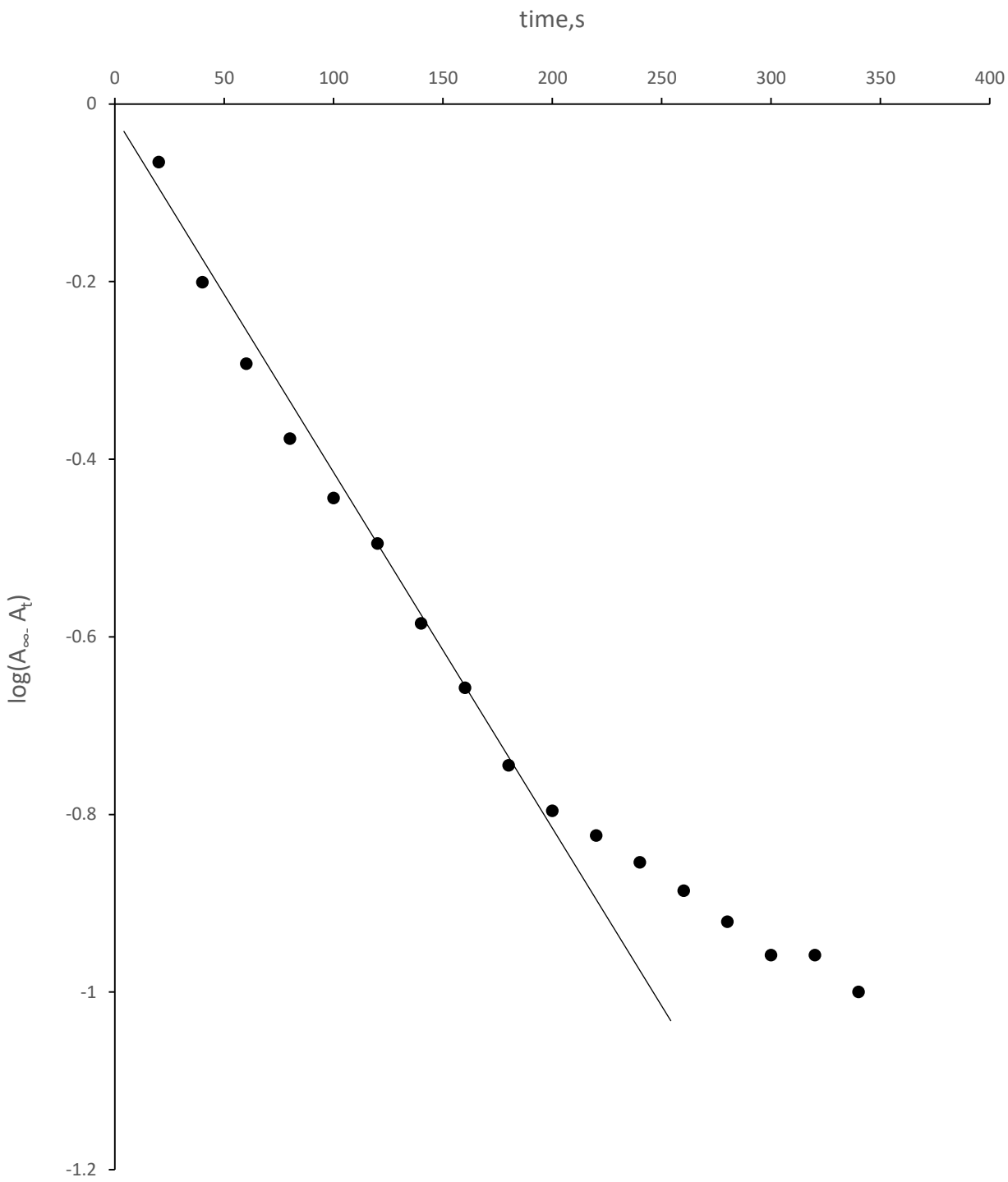


Figure 4.7: Typical pseudo-first order plot for the redox reaction of 2,6-dichlorophenol indophenol with hydrogen peroxide at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, [H_2O_2] = 2.0 × 10^{-3} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 28 ± 1 ºC

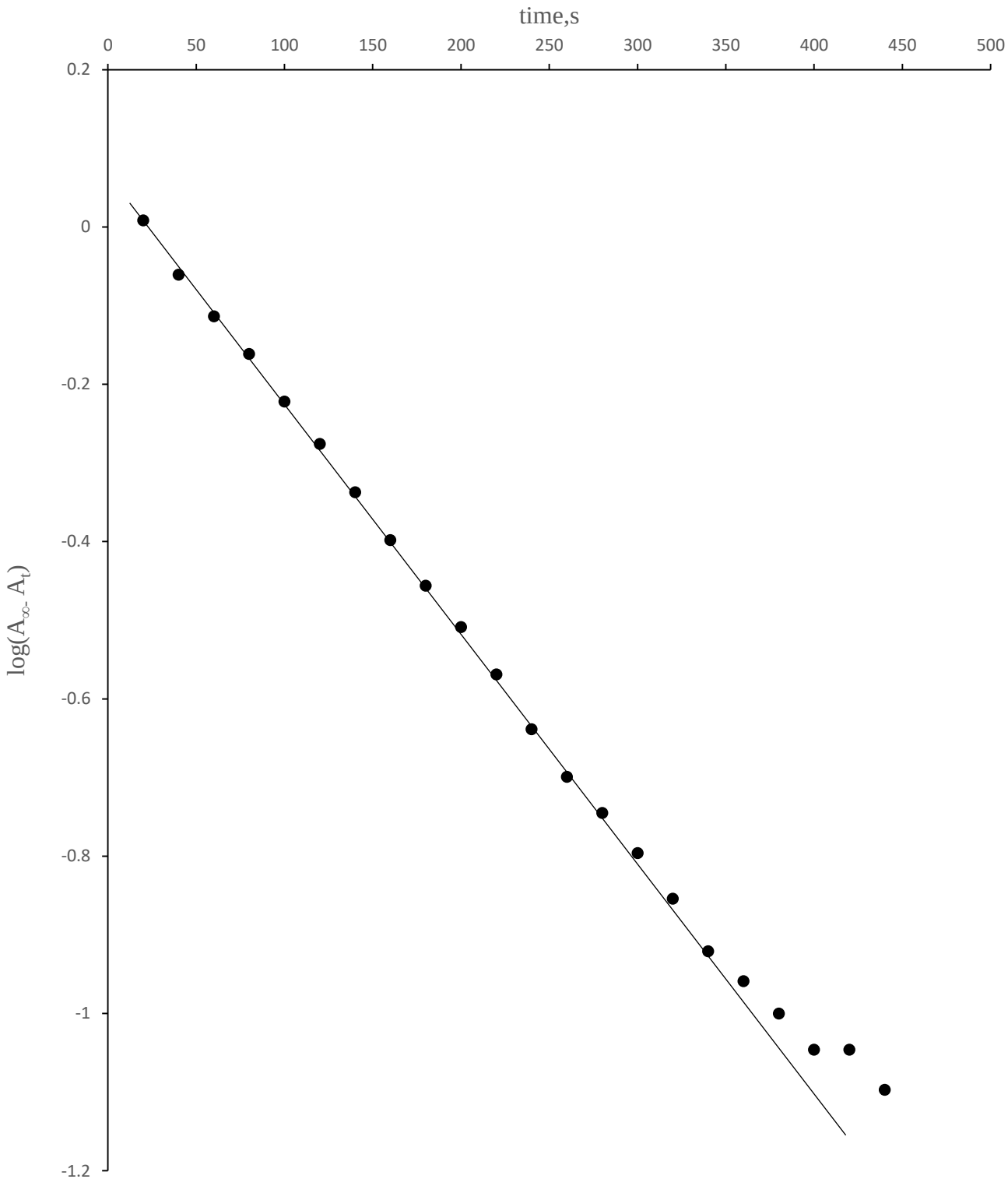


Figure 4.8: Typical pseudo-first order plot for the redox reaction of 2,6-dichlorophenol indophenol with sulphite ions at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, [SO_3^{2-}] = 3.0 × 10^{-2} mol dm^{-3}, I = 0.20 mol dm^{-3} and T = 28 ± 1 ºC

Table 4.1: Pseudo-first order and second order rate constants for the redox reaction of 2,6-dichlorophenol indophenol with metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, T= 28 ± 1˚C and λ_{max}= 600 nm

$10^3[S_2O_5^{2-}]$, mol dm^{-3}	I, mol dm^{-3}	10^2k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
0.50	0.20	0.81	16.21
0.75	0.20	1.22	16.27
1.00	0.20	1.62	16.21
1.25	0.20	2.03	16.25
1.50	0.20	2.43	16.21
1.75	0.20	2.84	16.24
2.00	0.20	3.24	16.22
2.25	0.20	3.64	16.21
1.00	0.05	2.06	20.65
1.00	0.08	1.94	19.43
1.00	0.10	1.85	18.49
1.00	0.15	1.70	17.02
1.00	0.20	1.62	16.24
1.00	0.25	1.56	15.58
1.00	0.30	1.48	14.73
1.00	0.40	1.36	13.57

Table 4.2: Pseudo-first order and second order rate constants for the redox reaction of 2,6-dichlorophenol indophenol with hydrazine in aqueous medium at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, T= 28 ± 1˚C and λ_{max}= 600 nm

$10^2[N_2H_4]$, mol dm^{-3}	I, mol dm^{-3}	10^2k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
3.50	0.20	0.45	0.13
4.00	0.20	0.54	0.14
4.50	0.20	0.59	0.13
5.00	0.20	0.64	0.13
5.50	0.20	0.71	0.13
6.00	0.20	0.76	0.13
6.50	0.20	0.87	0.13
7.00	0.20	0.96	0.14
4.00	0.01	0.27	0.06
4.00	0.05	0.35	0.09
4.00	0.10	0.43	0.11
4.00	0.20	0.54	0.14
4.00	0.30	0.65	0.16
4.00	0.40	0.74	0.19
4.00	0.50	0.90	0.22

Table 4.3: Pseudo-first order and second order rate constants for the redox reaction of 2,6-dichlorophenol indophenol with hydrogen peroxide in aqueous medium at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, T= 28 ± 1˚C and λ_{max}= 600 nm

$10^3[H_2O_2]$, mol dm^{-3}	I, mol dm^{-3}	10^3k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
1.00	0.20	3.03	3.03
1.50	0.20	4.54	3.02
2.00	0.20	6.03	3.01
2.50	0.20	7.53	3.01
3.00	0.20	9.07	3.02
3.50	0.20	10.06	3.01
4.00	0.20	12.09	3.02
4.50	0.20	13.55	3.01
2.00	0.01	6.03	3.01
2.00	0.05	6.04	3.02
2.00	0.10	6.03	3.01
2.00	0.20	6.03	3.01
2.00	0.30	6.05	3.03
2.00	0.40	6.03	3.01
2.00	0.50	6.03	3.03

Table 4.4: Pseudo-first order and first order rate constants for the redox reaction of 2,6-dichlorophenol indophenol with sulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, T= 28 ± 1°C and λ_{max}= 600 nm

$10^2[SO_3^{2-}]$, mol dm^{-3}	I, mol dm^{-3}	$10^2 k_{obs}$, s^{-1}	k_1, s^{-1}
3.00	0.20	1.78	1.78
4.00	0.20	1.79	1.79
5.00	0.20	1.78	1.78
6.00	0.20	1.79	1.79
7.00	0.20	1.79	1.79
8.00	0.20	1.78	1.78
9.00	0.20	1.78	1.78
10.00	0.20	1.78	1.78
3.00	0.05	1.79	1.79
3.00	0.10	1.79	1.79
3.00	0.15	1.78	1.78
3.00	0.20	1.79	1.79
3.00	0.30	1.79	1.79
3.00	0.40	1.78	1.78
3.00	0.50	1.78	1.78

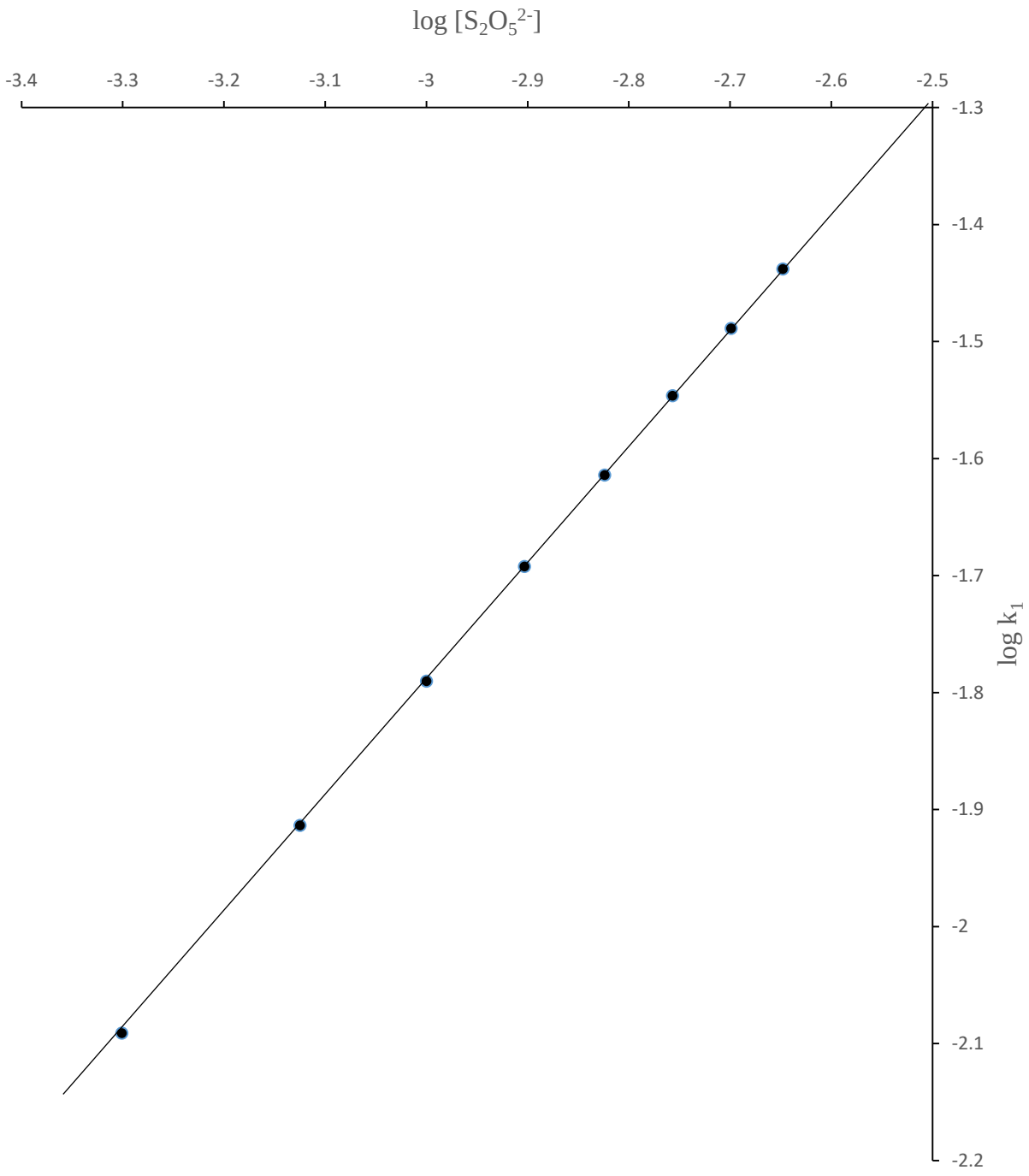


Figure 4.9: Plot of log k_1 versus log $[S_2O_5^{2-}]$ for the 2,6-dichlorophenol indophenol reduction by metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[S_2O_5^{2-}] = 1.0 \times 10^{-3}$ mol dm^{-3} T= 28 ± 1°C and λ_{max}= 600 nm

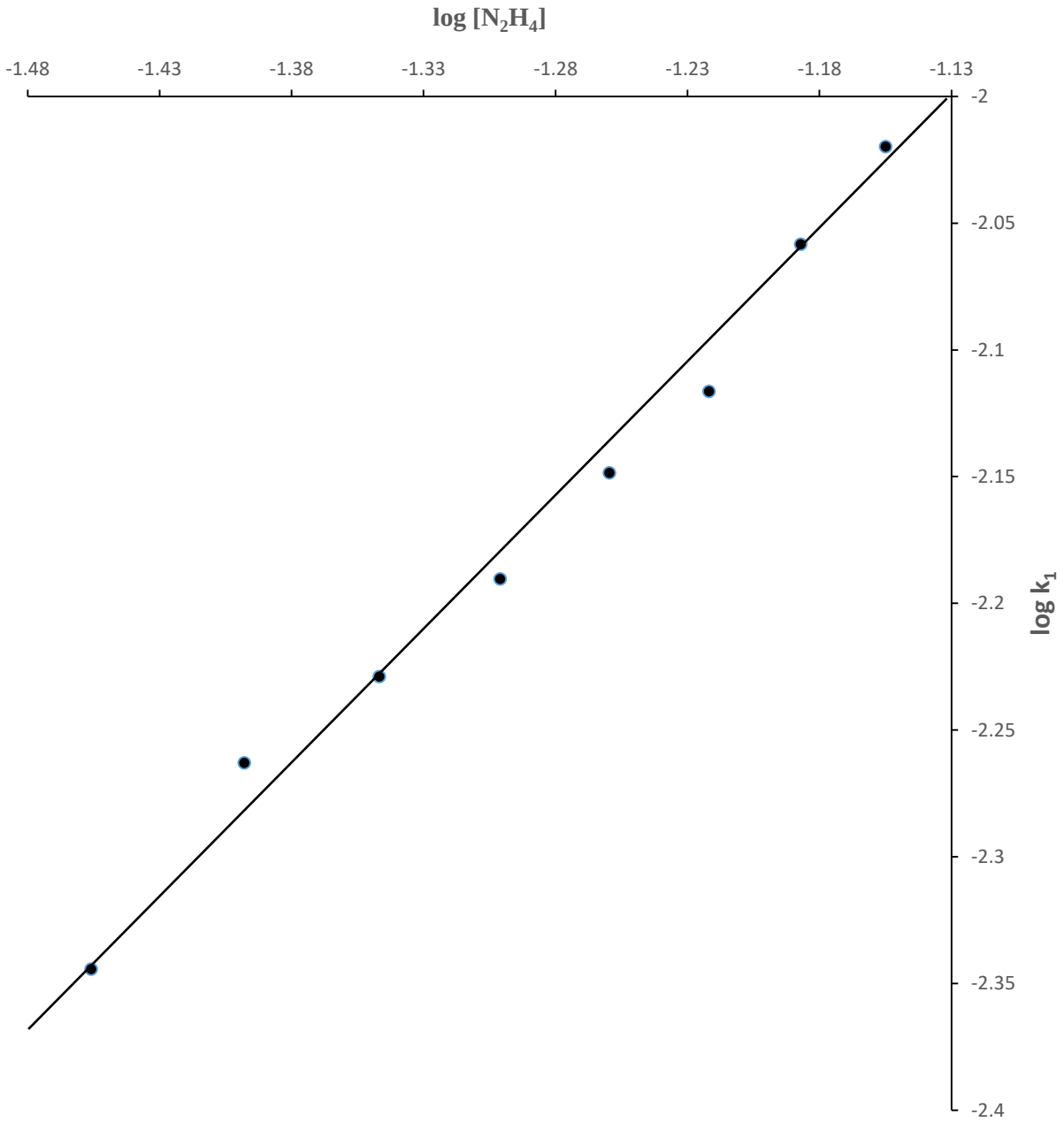


Figure 4.10: Plot of log k_1 versus log $[N_2H_4]$ for the 2,6-dichlorophenol indophenol reduction by hydrazine in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[N_2H_4]$ = 4.0×10^{-2} $moldm^{-3}$ T= 28 ± 1˚C and λ_{max}= 600 nm

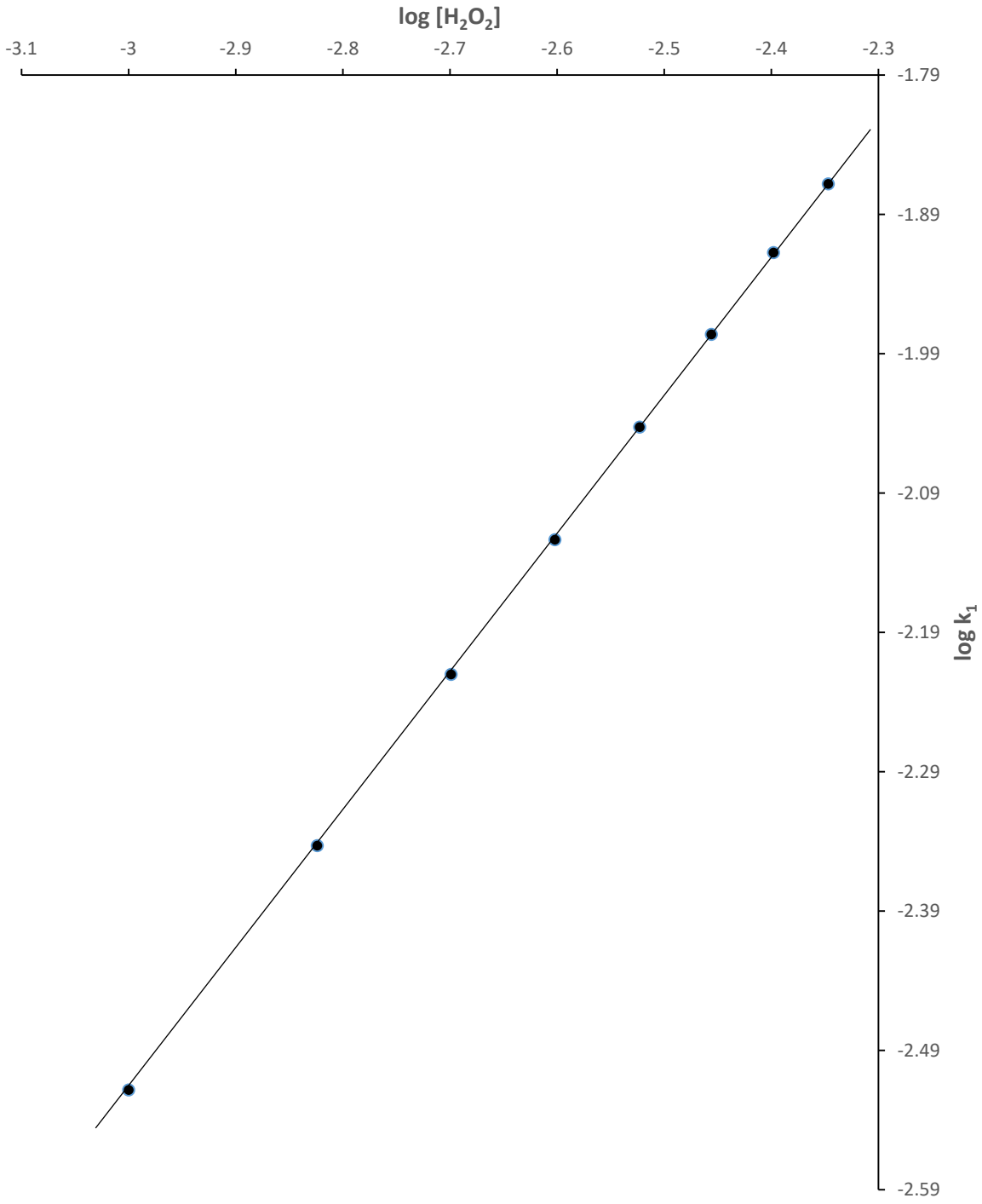


Figure 4.11: Plot of log k_1 versus log [H_2O_2] for the 2,6-dichlorophenol indophenol reduction by hydrogen peroxide in aqueous medium at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, [H_2O_2] = 2.0 × 10^{-3} $moldm^{-3}$ T= 28 ± 1˚C and λ_{max}= 600 nm

4.3 The Effect of Ionic Strength of the Reaction Medium on the Reaction Rate

The rate of reaction decreased with increase in ionic strength of the reaction medium for DCPIP-metabisulphite system, suggesting negative Brønsted-Debye salt effect. While the converse was the case for the DCPIP-hydrazine system, suggesting positive Brønsted-Debye salt effect. Increase in ionic strength has no effect on the reaction rate for the reactions with sulphite and hydrogen peroxide. The results are presented in Tables (4.1 – 4.4). The dependence of the rate constant on ionic strength of the reaction medium involving two reactant with charges Z_A and Z_B (Brønsted, 1922) are related by the equation 4.9

$$\log k = \log k_o + 2\beta Z_A Z_B \sqrt{I} \qquad 4.9$$

where k = the rate constant of the reactions, k_o = hypothetical rate constant in medium of infinite dielectric constant, I = ionic strength, β = constant (≈ 0.509 at 25°C)

If at 25°C, β = 0.50, then at this temperature, equation (4.9) becomes

$$\log k = \log k_o + 1.02 Z_A Z_B \sqrt{I} \qquad 4.10$$

The plot of log k versus √I should therefore be linear with slope equal to the products of the charges of the reacting partners $Z_A Z_B$ and intercept equal to log k_o (Brønsted, 1922). If Z_A and Z_B have the same sign, $Z_A Z_B$ is positive, and the rate constant increases with the ionic strength, while if Z_A and Z_B have different charge, $Z_A Z_B$ is negative, and the rate constant decreases with the ionic strength. But, if one of the reactant is uncharged, $Z_A Z_B$ is zero and the rate constant is independent of the ionic strength (Moore, 1999). The plots of log k_2 against √I are presented in Figures (4.13 – 4.14).

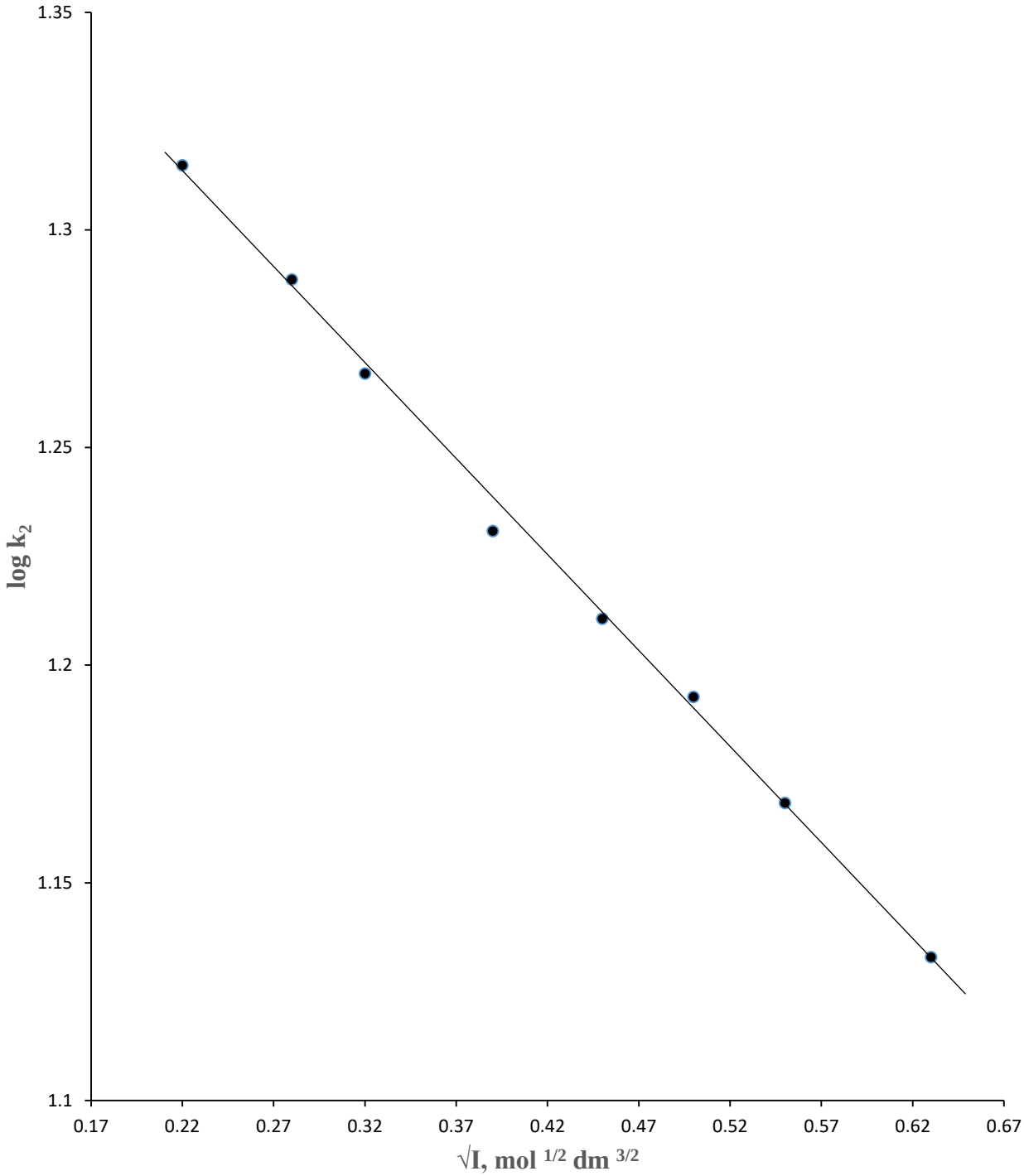


Figure 4.12: Plot of log k_2 versus √I for the reduction of 2,6-dichlorophenol indophenol by metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, [$S_2O_5^{2-}$] = 1.0×10^{-3} mol dm^{-3} T= 28 ± 1°C and λ_{max}= 600 nm

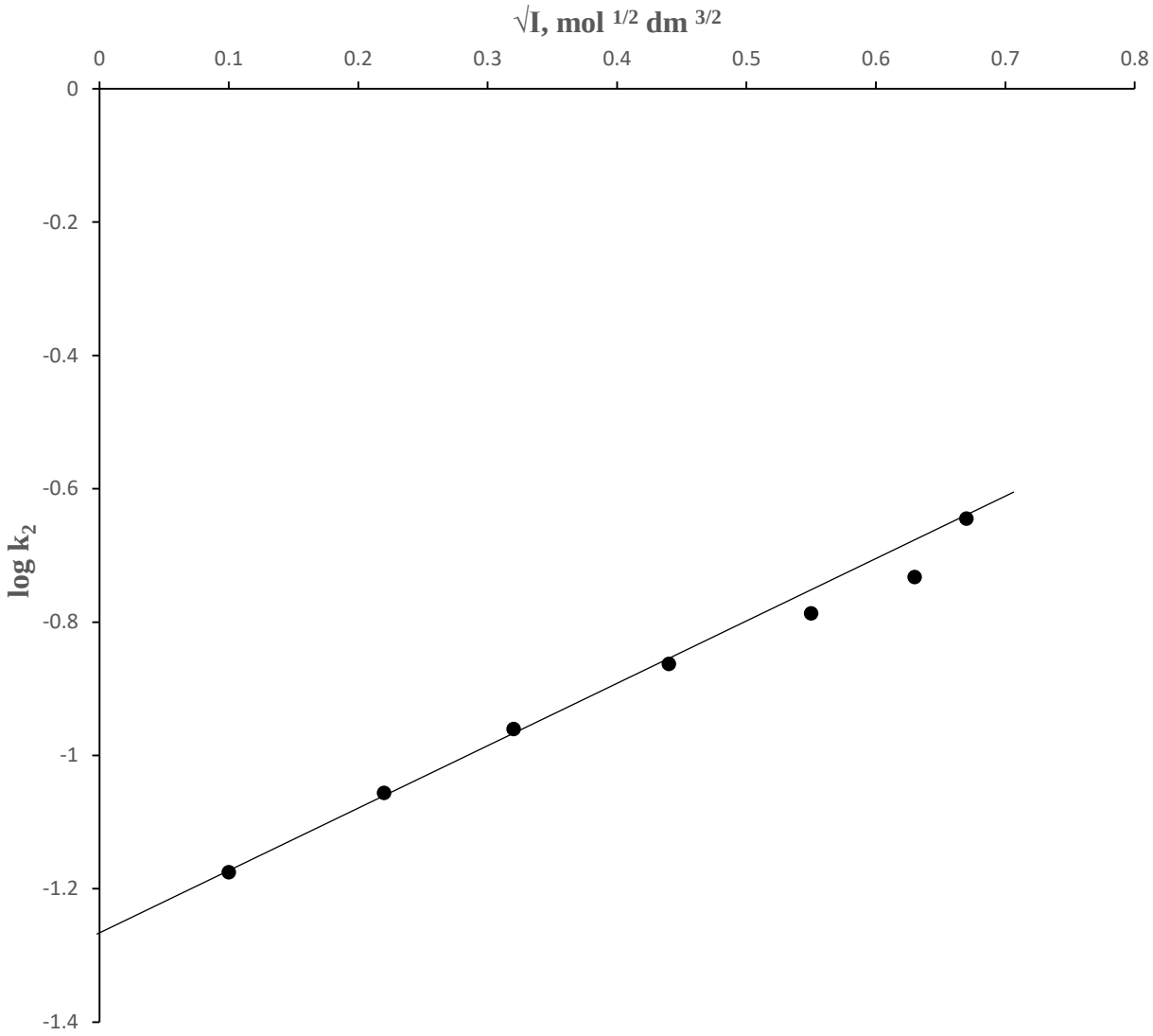


Figure 4.13: Plot of log k_2 versus √I for the reduction of 2,6-dichlorophenol indophenol by hydrazine in aqueous medium at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, [N_2H_4] = 4.0 × 10^{-2} mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

4.4 The Effect of the Changes in Dielectric Constant of the Reaction Medium on Reaction Rate

The dielectric constant of the medium was varied by addition of acetone to the reaction mixture. The corresponding effect of this on the rate of reaction was studied. The results for change in dielectric constant are presented in Tables (4.5 - 4.8). The rate of the reaction decreased on addition of acetone for the DCPIP-$S_2O_5^{2-}$ and DCPIP-N_2H_4 systems and has no effect on the rate of reaction for the DCPIP–SO_3^{2-} and DCPIP-H_2O_2 systems. The plots of dielectric constant dependent rate constants against 1/D for the DCPIP - $S_2O_5^{2-}$ and DCPIP-N_2H_4 systems are presented in Figures (4.15 and 4.16).

4.5 The Effect of Added Ions on the Reaction Rate

Increase in concentration of added anions (NO_3^- and CH_3COO^-) decreased the rate of reaction for all the systems studied except for the DCPIP - N_2H_4 system. The anion dependent rate constants are presented in Tables (4.9 - 4.12). Various plots of anion dependent rate constants against anion concentrations are presented in Figures (4.17 - 4.22).

It was observed that the rate of reaction decreased with increase in concentration of the added cations for DCPIP - $S_2O_5^{2-}$ reaction. For the DCPIP - SO_3^{2-}, DCPIP - N_2H_4 and DCPIP - H_2O_2 systems, cation concentration exhibited no effect in the rate of reaction. The result are presented in Tables (4.9 - 4.12). Plots of cation dependent rate constants against cation concentrations for DCPIP - $S_2O_5^{2-}$ are presented in Figures (4.23 and 4.24).

Table 4.5: Pseudo-first order and second order rate constants for the effect of change in dielectric constant of the medium on the redox reaction of 2,6-dichlorophenol indophenol with metasulphite ions at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [$S_2O_5^{2-}$]= 1.0×10^{-3} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

D	10^2 1/D	k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
80.10	1.24	16.24	16.24
79.72	1.25	2.24	2.24
79.34	1.26	2.12	2.12
78.58	1.27	1.45	1.45
77.44	1.29	0.61	0.61
76.30	1.31	0.30	0.30

Table 4.6: Pseudo-first order and second order rate constants for the effect of change in dielectric constant of the medium on the redox reaction of 2,6-dichlorophenol indophenol with sulphite ions at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [SO_3^{2-}]= 3.0×10^{-2} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

D	10^2 1/D	k_1 s^{-1}	k_2 $dm^3mol^{-1}s^{-1}$
80.10	1.24	1.78	1.78
79.16	1.26	1.79	1.79
78.22	1.27	1.78	1.78
77.28	1.29	1.78	1.78
76.34	1.30	1.78	1.78
75.40	1.32	1.79	1.79
74.46	1.34	1.79	1.79

Table 4.7: Pseudo-first order and second order rate constants for the effect of change in dielectric constant of the medium on the redox reaction of 2,6-dichlorophenol indophenol with hydrazine at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , $[N_2H_4] = 4.0 \times 10^{-2}$ mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1°C

D	$10^2 1/D$	k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
80.10	1.24	5.45	13.60
79.72	1.25	1.33	3.33
78.58	1.27	1.01	2.53
77.44	1.29	0.78	1.95
76.30	1.31	0.38	0.96
75.40	1.32	0.29	0.74
74.46	1.34	0.23	0.58

Table 4.8: Pseudo-first order and second order rate constants for the effect of change in dielectric constant of the medium on the redox reaction of 2,6-dichlorophenol indophenol with hydrogen peroxide at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [H_2O_2]= 2.0×10^{-3} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

D	$10^2 1/D$	k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
80.10	1.24	6.03	3.01
79.72	1.25	6.03	3.01
78.58	1.27	6.03	3.01
77.44	1.29	6.03	3.01
76.30	1.31	6.05	3.03
75.40	1.32	6.03	3.01
74.46	1.34	6.04	3.02

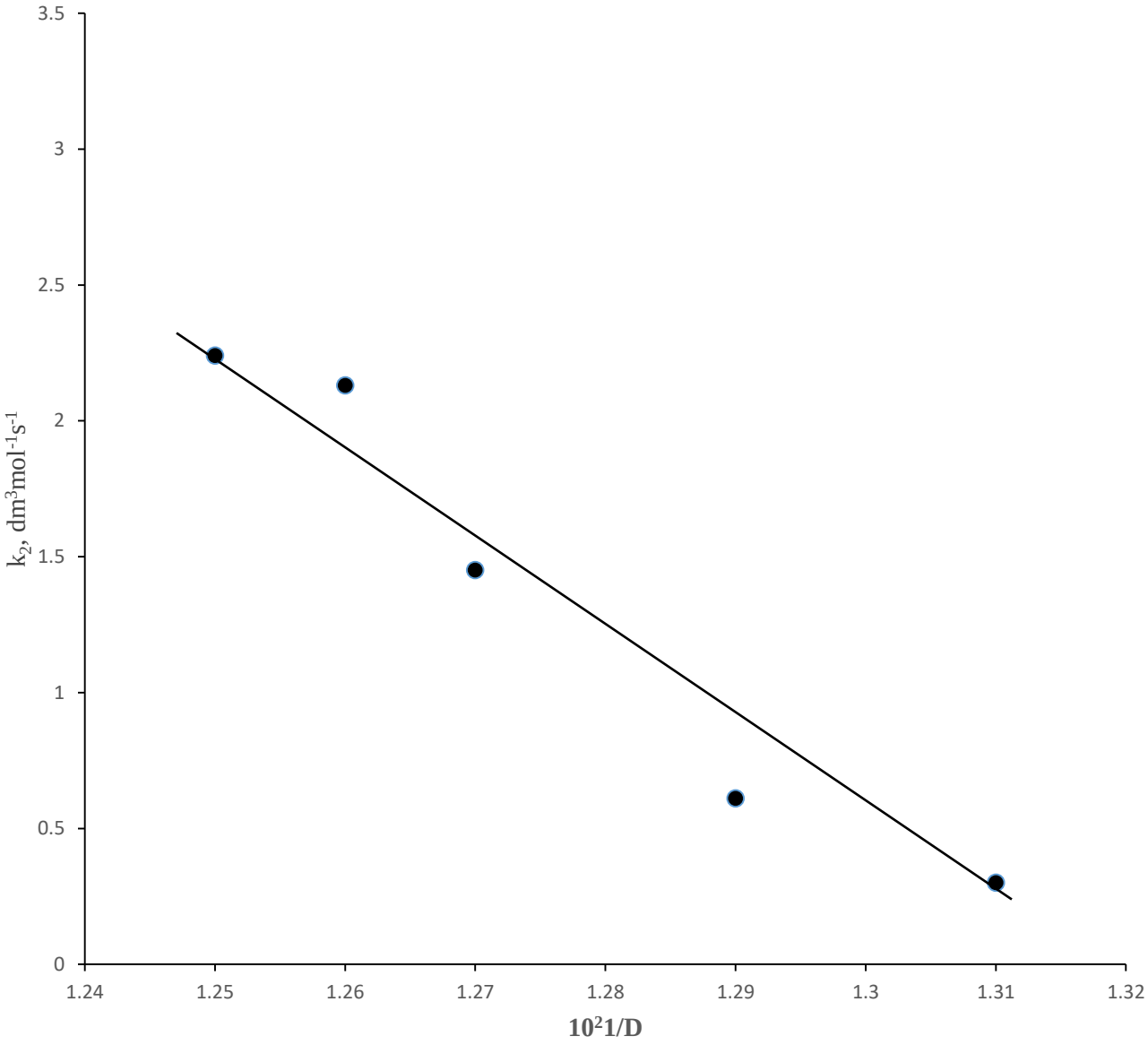


Figure 4.14: Plot of k_2 versus 1/D for the reduction of 2,6-dichlorophenol indophenol by metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, [$S_2O_5^{2-}$] = 1.0×10^{-3} mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

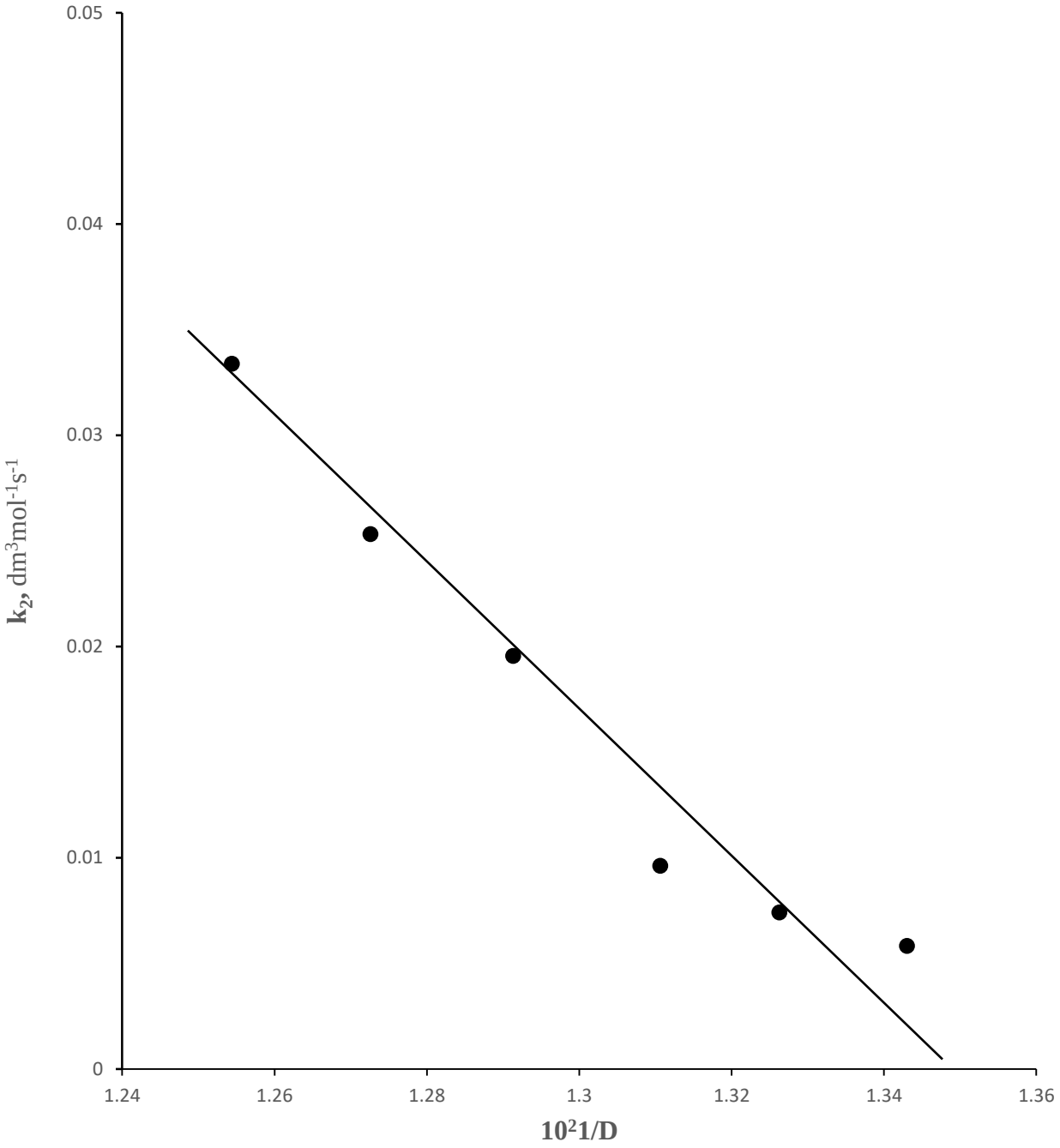


Figure 4.15: Plot of k_2 versus 1/D for the reduction of 2,6-dichlorophenol indophenol by hydrazine in aqueous medium at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3}, [N_2H_4] = 4.0 × 10^{-2} mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

Table 4.9: Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of 2,6-dichlorophenol indophenol with metabisulphite ions at [DCPIP] = 1.0 × 10^{-4} mol dm^{-3} , [$S_2O_5^{2-}$]= 1.0 × 10^{-3} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

X	10^3[X], mol dm^{-3}	k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
NO_3^-	0	16.21	16.21
	10	5.77	5.77
	20	5.48	5.48
	30	5.16	5.16
	40	4.96	4.96
	50	4.58	4.58
	60	4.51	4.51
CH_3COO^-	0	16.21	16.21
	10	7.09	7.09
	20	6.25	6.25
	30	5.54	5.54
	40	5.43	5.43
	50	5.11	5.11
	60	4.81	4.81

Table 4.10: Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of 2,6-dichlorophenol indophenol with sulphite ions at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [SO_3^{2-}]= 3.0×10^{-2} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

X	10^3[X], mol dm^{-3}	k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
NO_3^-	0	1.78	1.78
	10	1.86	1.86
	20	1.92	1.92
	30	1.96	1.96
	40	1.98	1.98
	50	2.02	2.02
	60	2.08	2.08
CH_3COO^-	0	1.78	1.78
	10	1.83	1.83
	20	1.89	1.89
	30	1.92	1.92
	40	1.97	1.97
	50	2.05	2.05
	60	2.11	2.11

Table 4.11: Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of 2,6-dichlorophenol indophenol with hydrazine at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [N_2H_4]= 4.0×10^{-2} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

X	10^3[X], mol dm^{-3}	10^2k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
NO_3^-	0	0.54	0.14
	10	0.54	0.13
	20	0.53	0.13
	30	0.54	0.13
	40	0.54	0.13
	50	0.54	0.14
	60	0.54	0.14
CH_3COO^-	0	0.54	0.14
	10	0.54	0.13
	20	0.54	0.13
	30	0.53	0.13
	40	0.54	0.13
	50	0.54	0.14
	60	0.55	0.14

Table 4.12: Pseudo-first order and second order rate constants for the effect of added anions on the redox reaction of 2,6-dichlorophenol indophenol with hydrogen peroxide at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [H_2O_2]= 2.0×10^{-3} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

X	10^3[X], mol dm^{-3}	10^3k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
NO_3^-	0	6.03	3.01
	10	6.31	3.16
	20	6.95	3.48
	30	7.21	3.60
	40	8.03	4.01
	50	8.42	4.21
	60	8.87	4.44
CH_3COO^-	0	6.03	3.01
	10	6.63	3.32
	20	6.94	3.48
	30	7.37	3.68
	40	8.16	4.08
	50	8.35	4.17
	60	9.0	4.50

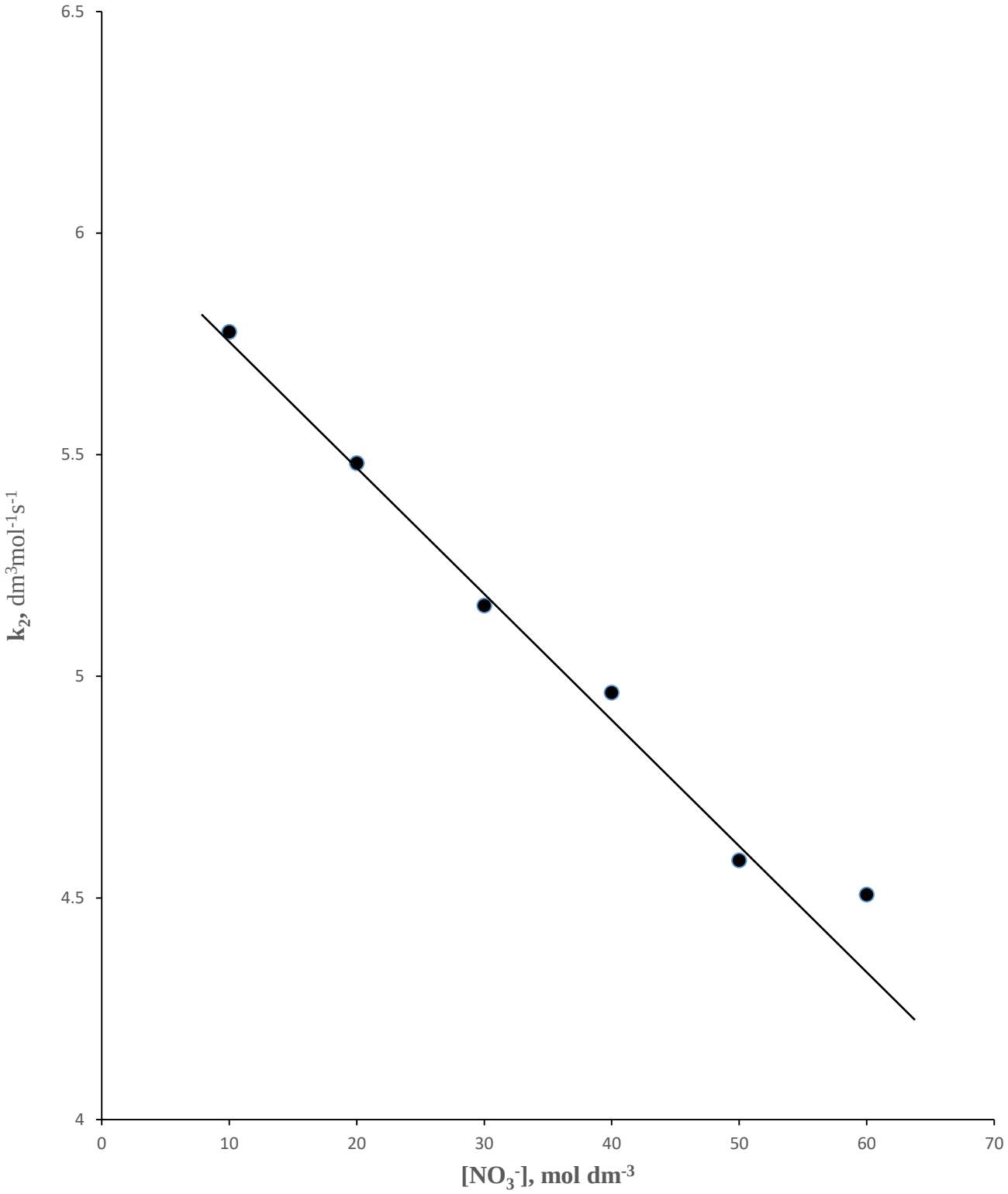


Figure 4.16: Plot of k_2 versus $[NO_3^-]$ for the reduction of 2,6-dichlorophenol indophenol by metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[S_2O_5^{2-}] = 1.0 \times 10^{-3}$ mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

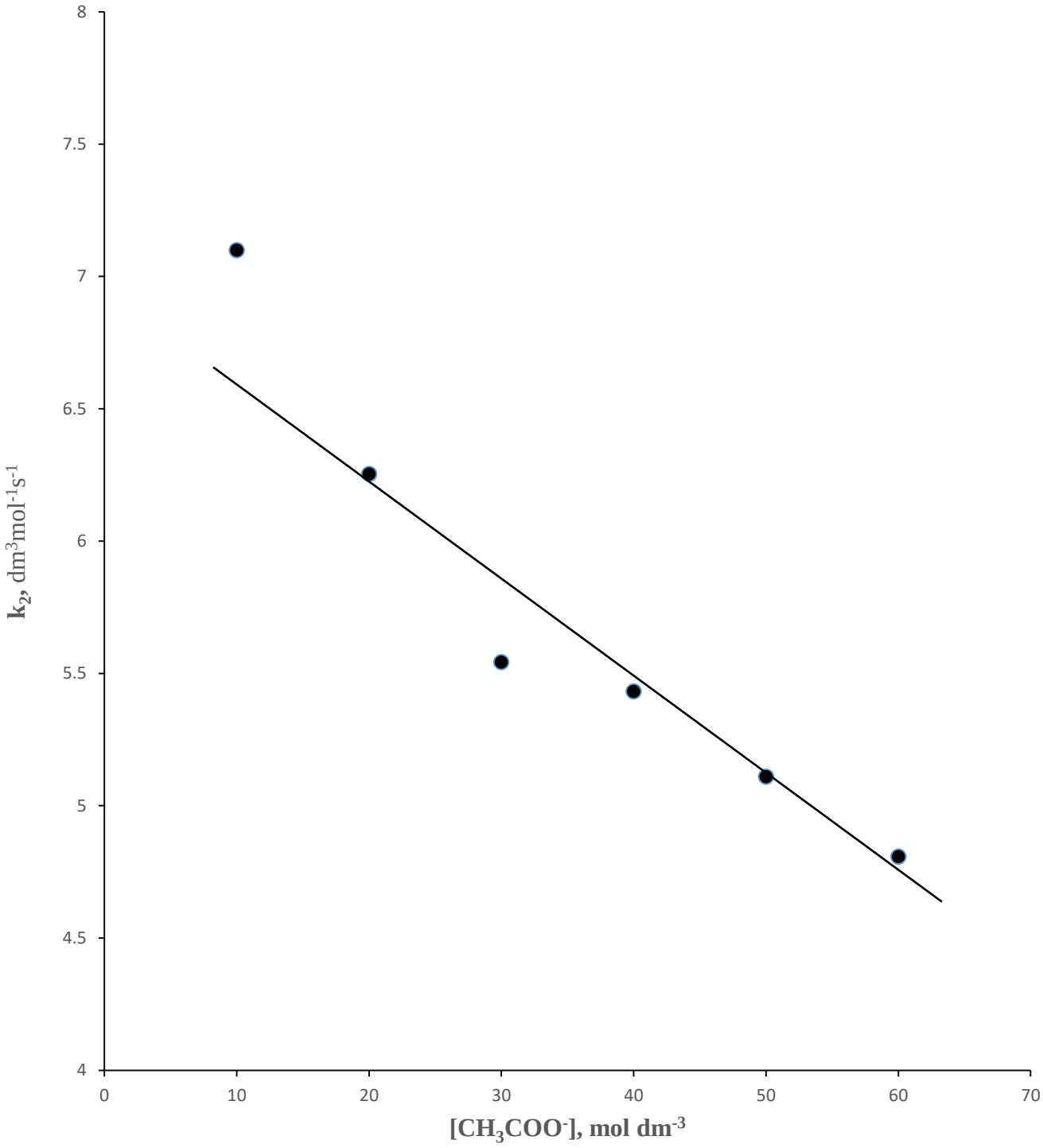


Figure 4.17: Plot of k_2 versus $[CH_3COO^-]$ for the reduction of 2,6-dichlorophenol indophenol by metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[S_2O_5^{2-}] = 1.0 \times 10^{-3}$ mol dm^{-3} T= 28 ± 1°C and λ_{max}= 600 nm

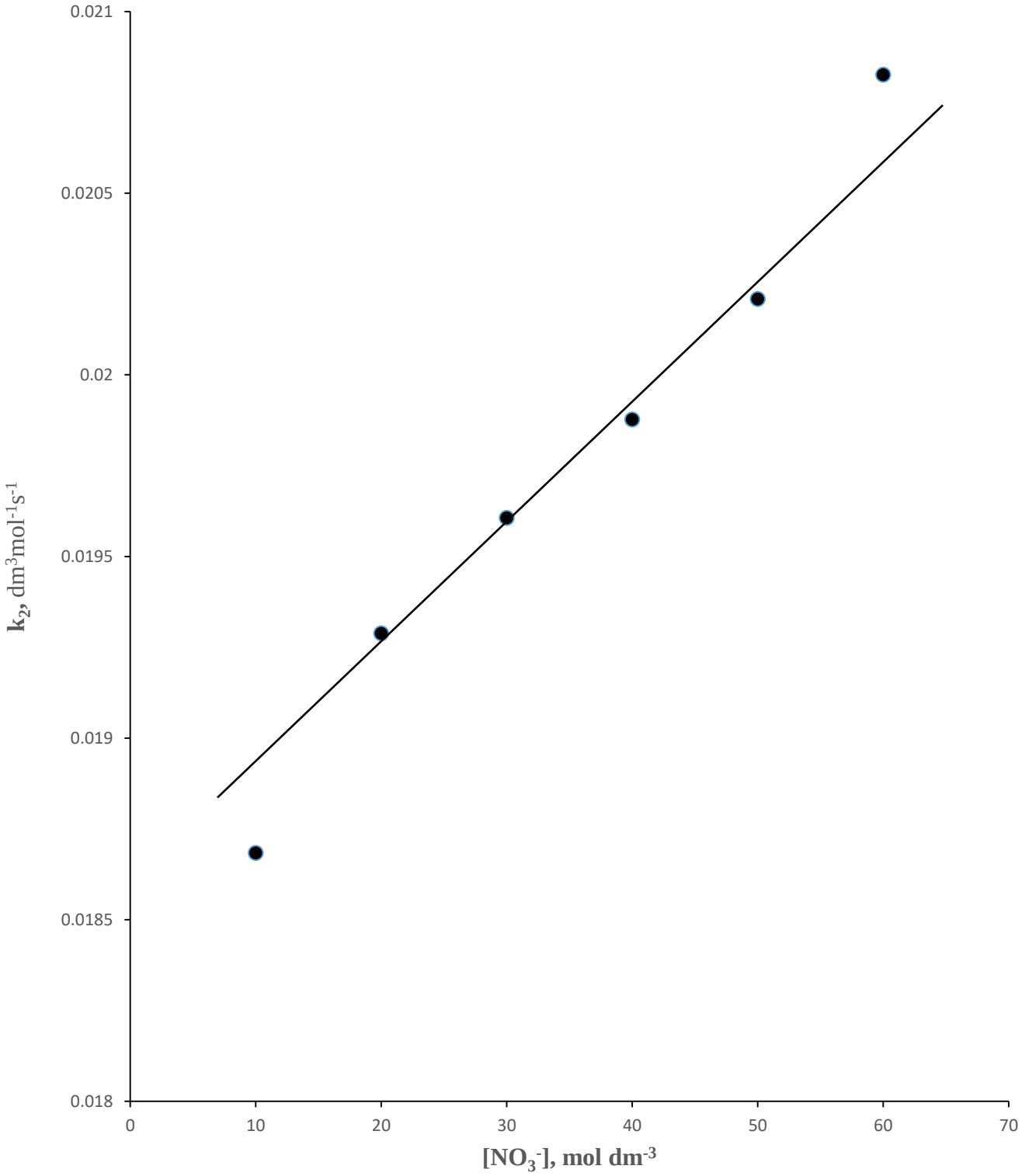


Figure 4.18: Plot of k_2 versus $[NO_3^-]$ for the reduction of 2,6-dichlorophenol indophenol by sulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[SO_3^{2-}] = 3.0 \times 10^{-2}$ mol dm^{-3} T= 28 ± 1°C and λ_{max}= 600 nm

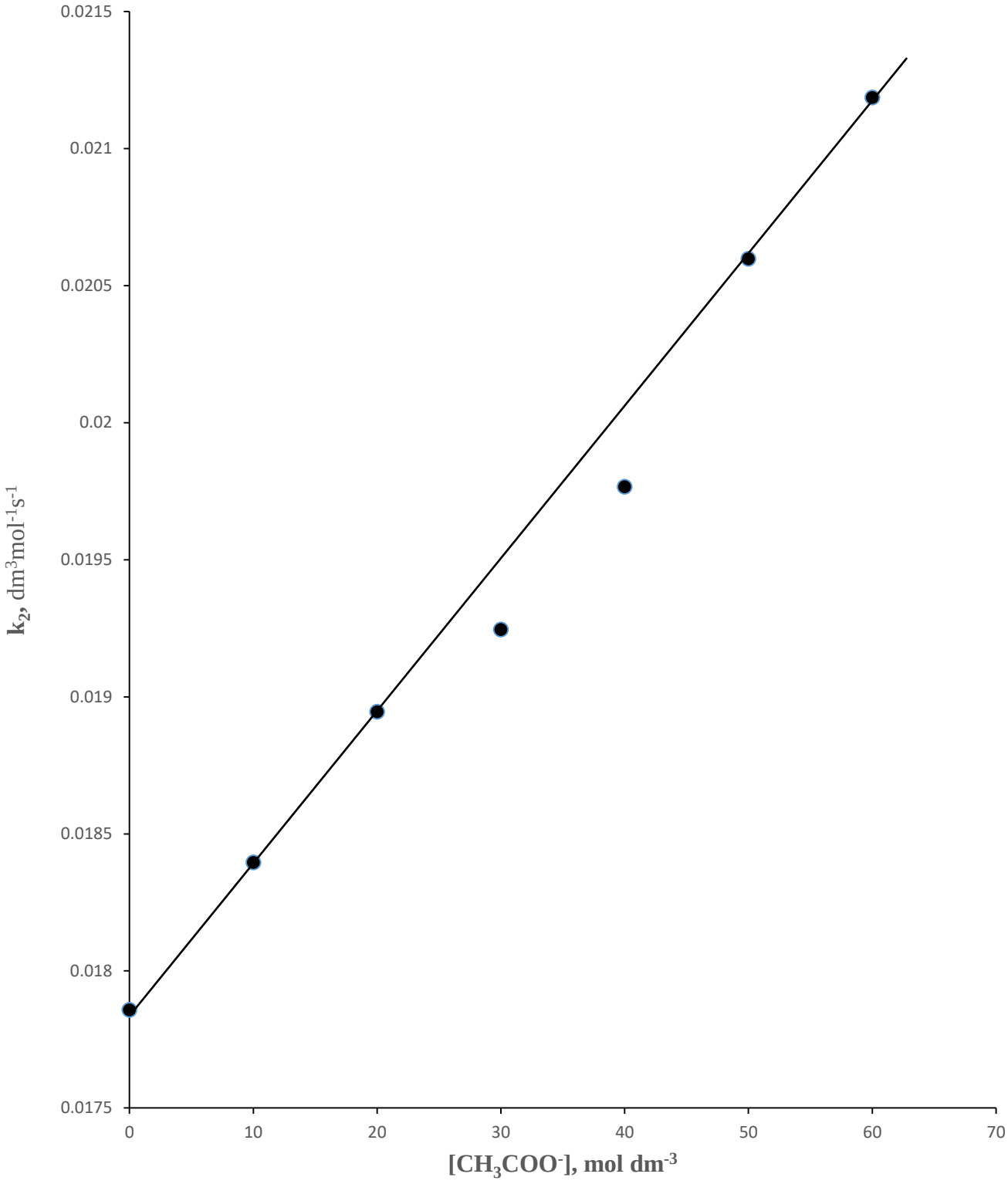


Figure 4.19: Plot of k_2 versus $[CH_3COO^-]$ for the reduction of 2,6-dichlorophenol indophenol by sulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[SO_3^{2-}] = 3.0 \times 10^{-2}$ mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

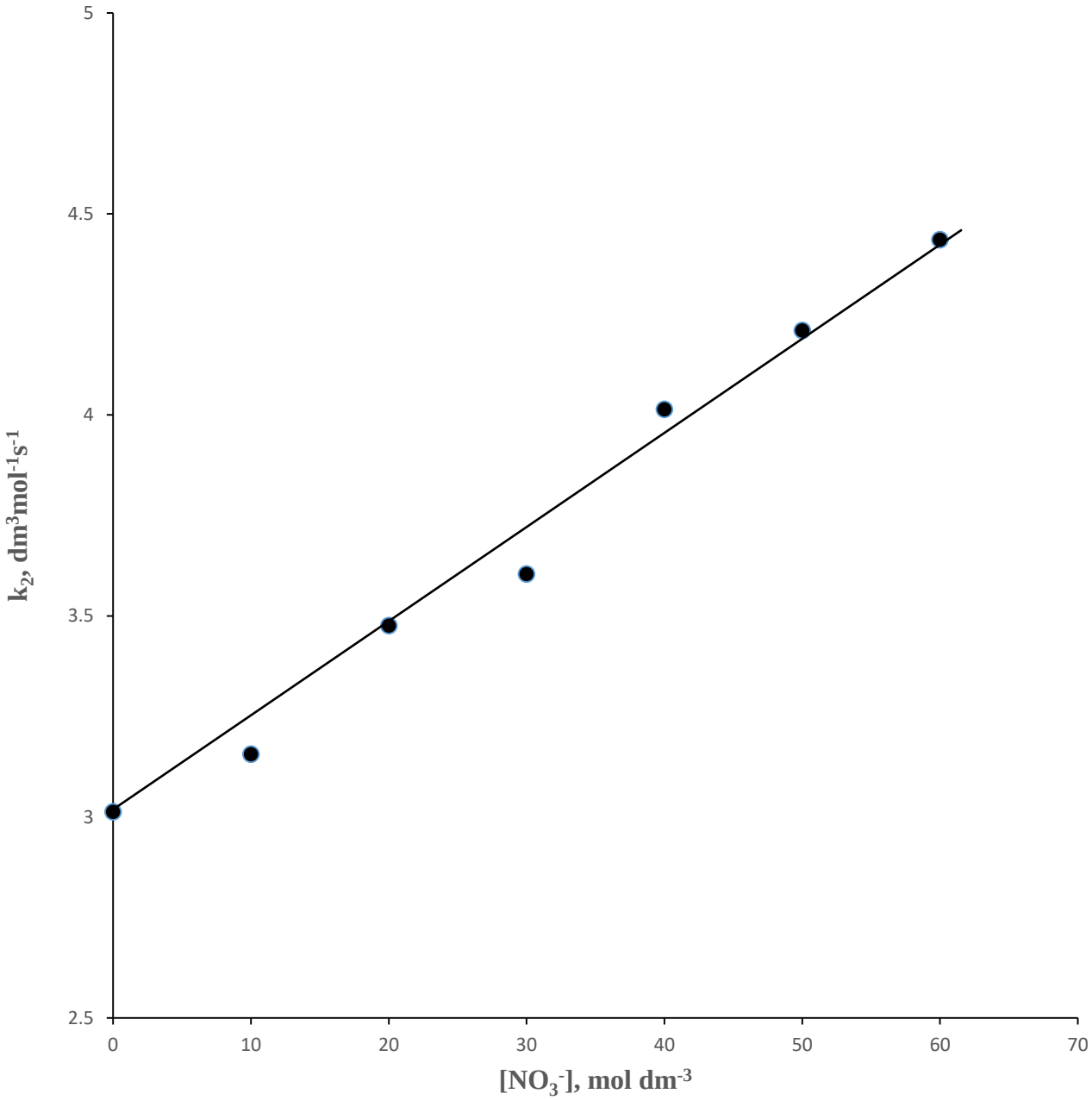


Figure 4.20: Plot of k_2 versus $[NO_3^-]$ for the reduction of 2,6-dichlorophenol indophenol by hydrogen peroxide in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[H_2O_2]$ = 2.0×10^{-3} mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

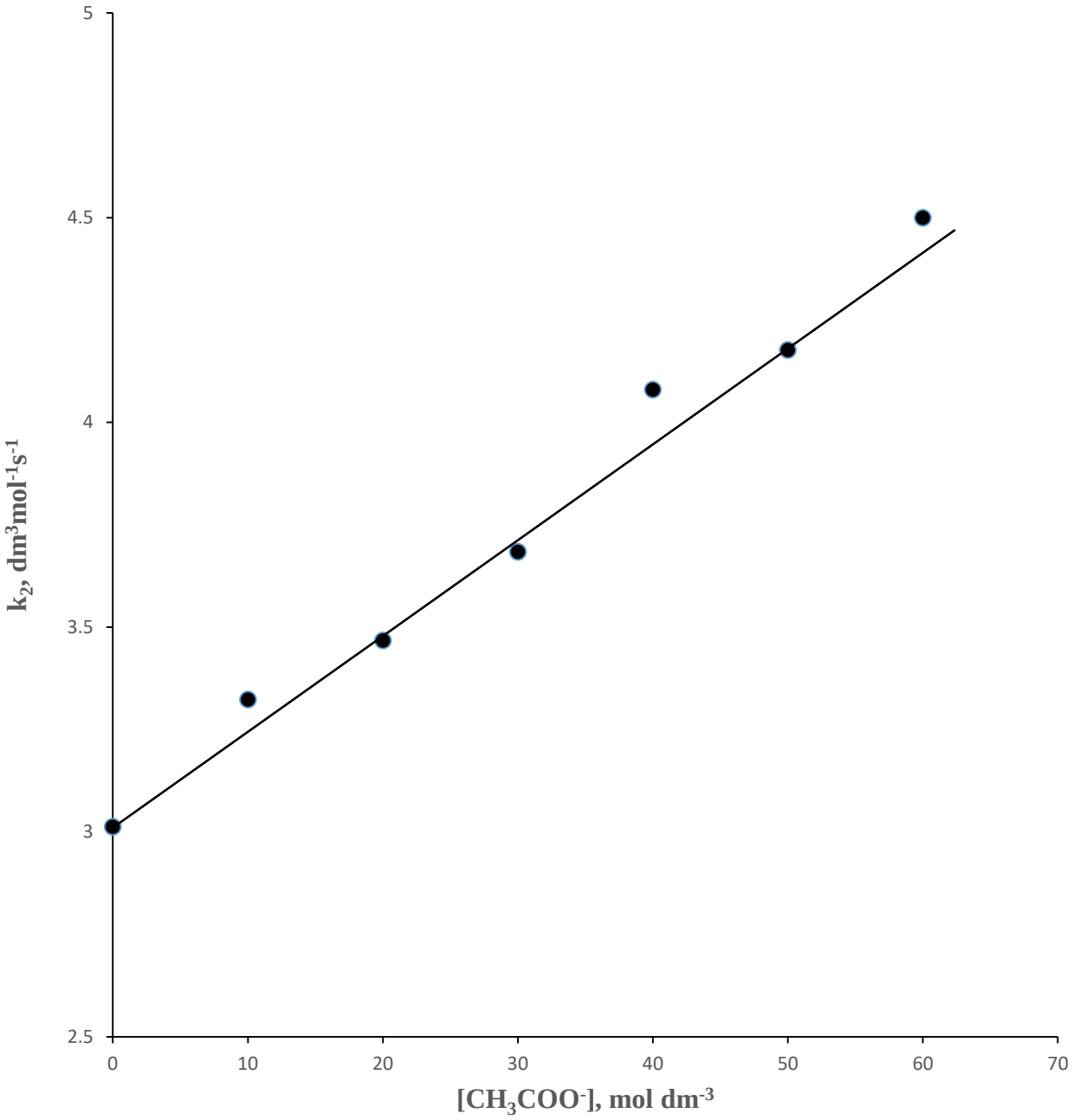


Figure 4.21: Plot of k_2 versus $[CH_3COO^-]$ for the reduction of 2,6-dichlorophenol indophenol by hydrogen peroxide in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[H_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3} T= 28 ± 1°C and λ_{max}= 600 nm

Table 4.13: Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of 2,6-dichlorophenol indophenol with metabisulphite ions at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , $[S_2O_5^{2-}] = 1.0 \times 10^{-3}$ mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

X	10^3[X], mol dm^{-3}	k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
Mg^{2+}	0	16.21	16.21
	10	6.73	6.73
	20	6.33	6.33
	30	6.04	6.04
	40	5.92	5.92
	50	5.64	5.64
	60	5.26	5.26
Ca^{2+}	0	16.21	16.21
	10	4.42	4.42
	20	3.87	3.87
	30	3.77	3.77
	40	3.54	3.54
	50	3.38	3.38
	60	3.17	3.17

Table 4.14: Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of 2,6-dichlorophenol indophenol with sulphite ions at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [SO_3^{2-}]= 3.0×10^{-2} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

X	10^3[X], mol dm^{-3}	k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
Mg^{2+}	0	1.78	1.78
	10	1.79	1.79
	20	1.79	1.79
	30	1.79	1.79
	40	1.78	1.78
	50	1.78	1.78
	60	1.78	1.78
Ca^{2+}	0	1.78	1.78
	10	1.78	1.78
	20	1.79	1.79
	30	1.79	1.79
	40	1.78	1.78
	50	1.78	1.78
	60	1.78	1.78

Table 4.15: Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of 2,6-dichlorophenol indophenol with hydrazine at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [N_2H_4]= 4.0×10^{-2} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

X	10^3[X], mol dm^{-3}	10^2k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
Mg^{2+}	0	0.54	0.13
	10	0.55	0.14
	20	0.54	0.13
	30	0.55	0.14
	40	0.54	0.13
	50	0.54	0.13
	60	0.54	0.13
Ca^{2+}	0	0.54	0.13
	10	0.54	0.13
	20	0.54	0.13
	30	0.54	0.13
	40	0.53	0.14
	50	0.53	0.13
	60	0.54	0.13

Table 4.16: Pseudo-first order and second order rate constants for the effect of added cations on the redox reaction of 2,6-dichlorophenol indophenol with hydrogen peroxide at [DCPIP] = 1.0×10^{-4} mol dm^{-3} , [H_2O_2]= 2.0×10^{-3} mol dm^{-3}, I= 0.2 mol dm^{-3} and T= 28 ± 1˚C

X	10^3[X], mol dm^{-3}	10^3k_1, s^{-1}	k_2, $dm^3mol^{-1}s^{-1}$
Mg^{2+}	0	6.03	3.01
	10	6.04	3.02
	20	6.05	3.03
	30	6.03	3.01
	40	6.03	3.01
	50	6.03	3.01
	60	6.03	3.01
Ca^{2+}	0	6.03	3.01
	10	6.03	3.01
	20	6.05	3.03
	30	6.03	3.01
	40	6.03	3.01
	50	6.03	3.01
	60	6.03	3.01

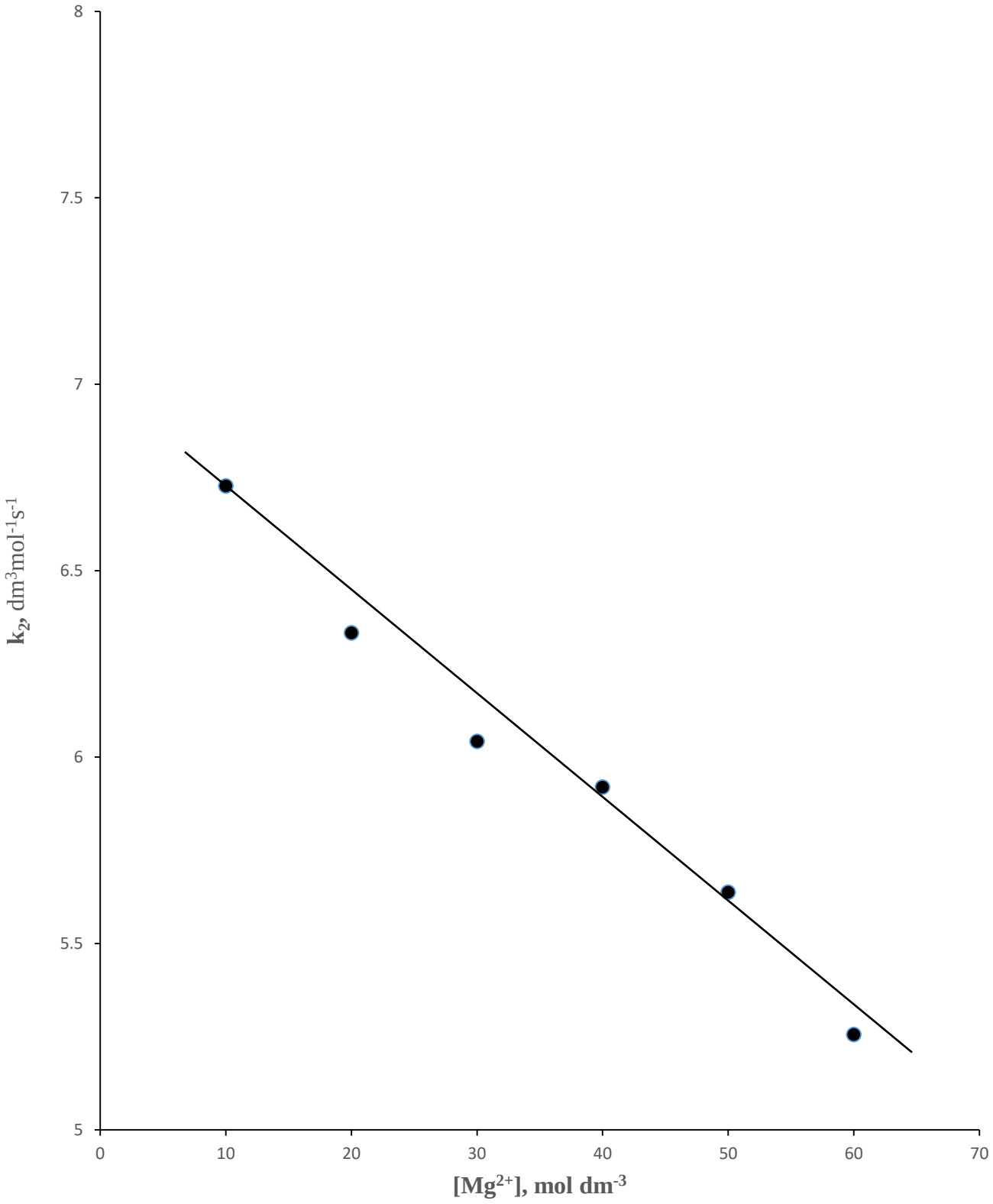


Figure 4.22: Plot of k_2 versus $[Mg^{2+}]$ for the reduction of 2,6-dichlorophenol indophenol by metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[S_2O_5^{2-}]$ = 1.0×10^{-3} mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

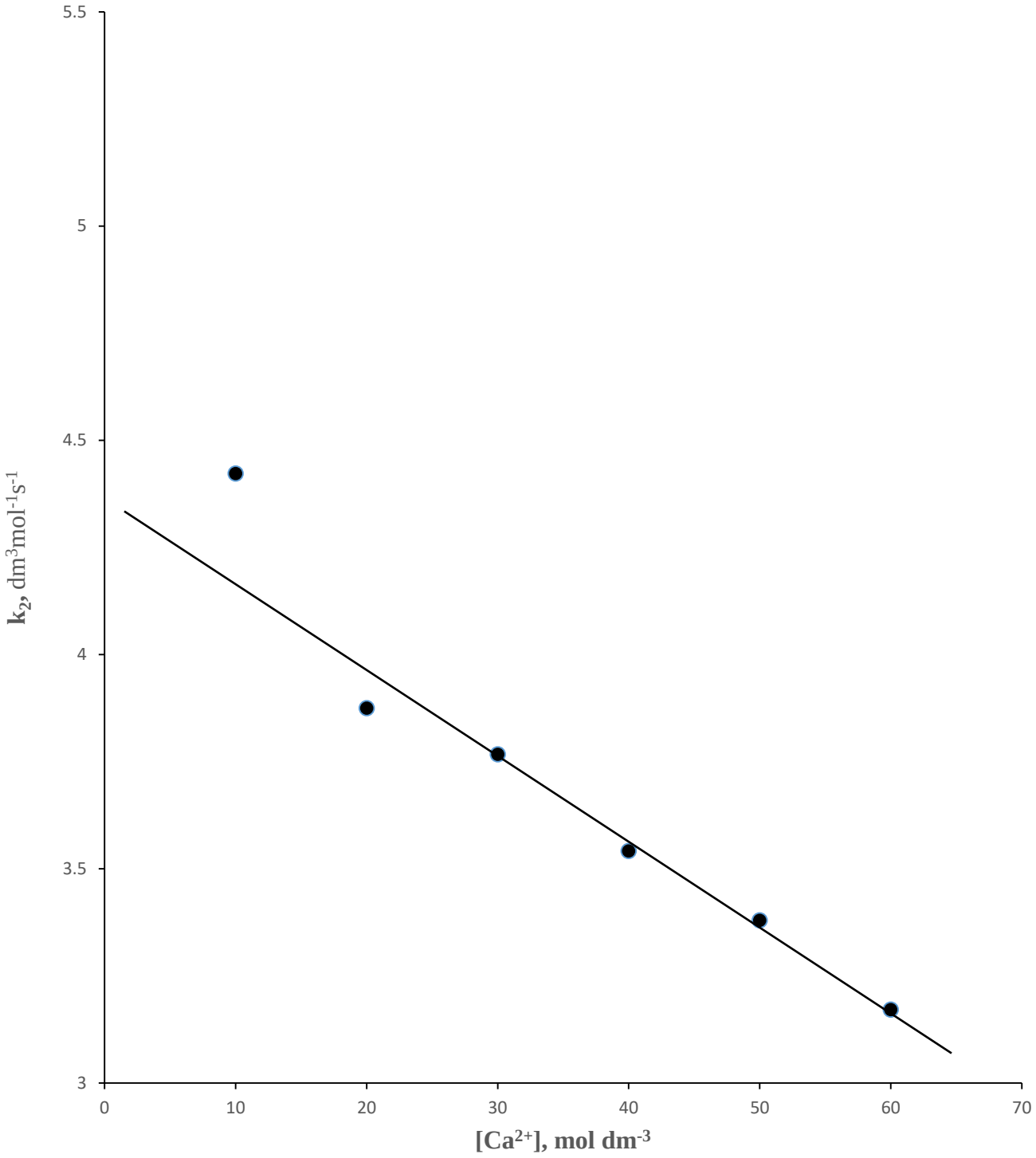


Figure 4.23: Plot of k_2 versus $[Ca^{2+}]$ for the reduction of 2,6-dichlorophenol indophenol by metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[S_2O_5^{2-}]$ = 1.0×10^{-3} mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

4.6 Test for Intermediate Complex

4.6.1 Michaelis-Menten plot

The Michaelis-Menten's plots of $1/k_1$ versus 1/[reductant] for DCPIP - $S_2O_5^{2-}$ and DCPIP – H_2O_2 systems were linear with zero intercept while for the DCPIP – N_2H_4 system, the plot gave intercept (Figures 4.24 – 4.26).

4.6.2 Test for free radicals

Acrylamide was added to the partially oxidized reaction mixtures for the DCPIP – $S_2O_5^{2-}$, DCPIP – SO_3^{2-} , DCPIP – N_2H_4 and DCPIP – H_2O_2 to initiate free radical polymerization, then followed by addition of excess methanol. For all the systems investigated, there was no formation of gelatinous precipitate which would have indicated the presence of free radical in the reaction mixtures.

4.6.3 Spectrophotometric test

Spectrophotometric test was carried out to detect the presence of any intermediate complex of significant stability in the reactions. These tests were performed by comparing the electronic spectra of the reaction mixtures taken after two minutes of the commencement of the reactions, with that of 2,6-dichlorophenol indophenol solution within the wavelength range of 400 -700 nm to check for any appearance of new peak or shift in the λ_{max} of 600 nm characteristic of 2,6-dichlorophenol indophenol. No new peak or shift in the λ_{max} was observed. The spectra are shown in Figures (4.27 - 4.30).

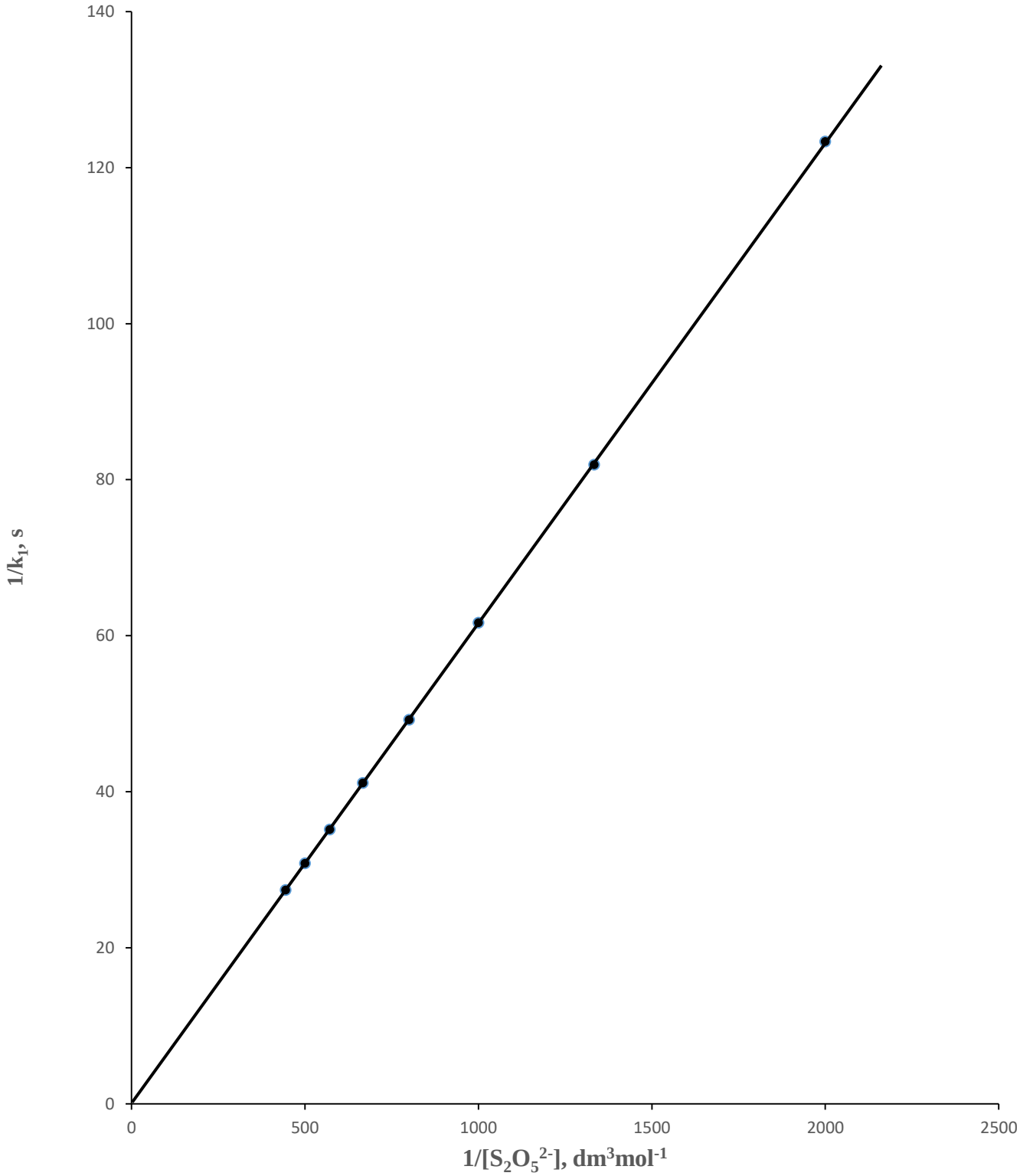


Figure 4.24: Michaelis-Menten plot of $1/k_1$ versus $1/[S_2O_5^{2-}]$ for the reduction of 2,6-dichlorophenol indophenol by metabisulphite ions in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[S_2O_5^{2-}] = 1.0 \times 10^{-3}$ mol dm^{-3} T= 28 ± 1°C and λ_{max}= 600 nm

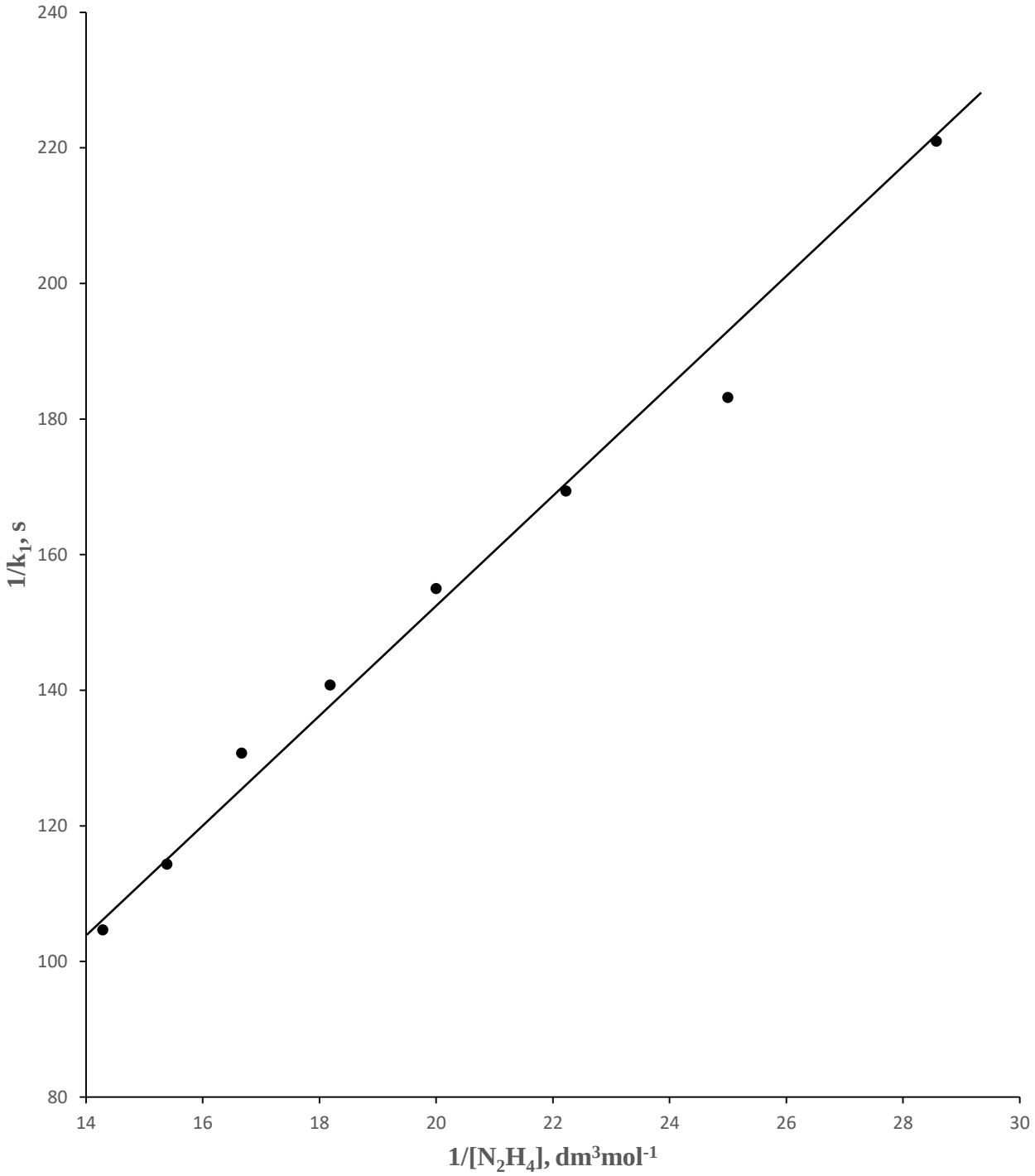


Figure 4.25: Michaelis-Menten plot of $1/k_1$ versus $1/[N_2H_4]$ for the reduction of 2,6-dichlorophenol indophenol by hydrazine in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[N_2H_4] = 4.0 \times 10^{-2}$ mol dm^{-3} T= 28 ± 1°C and λ_{max}= 600 nm

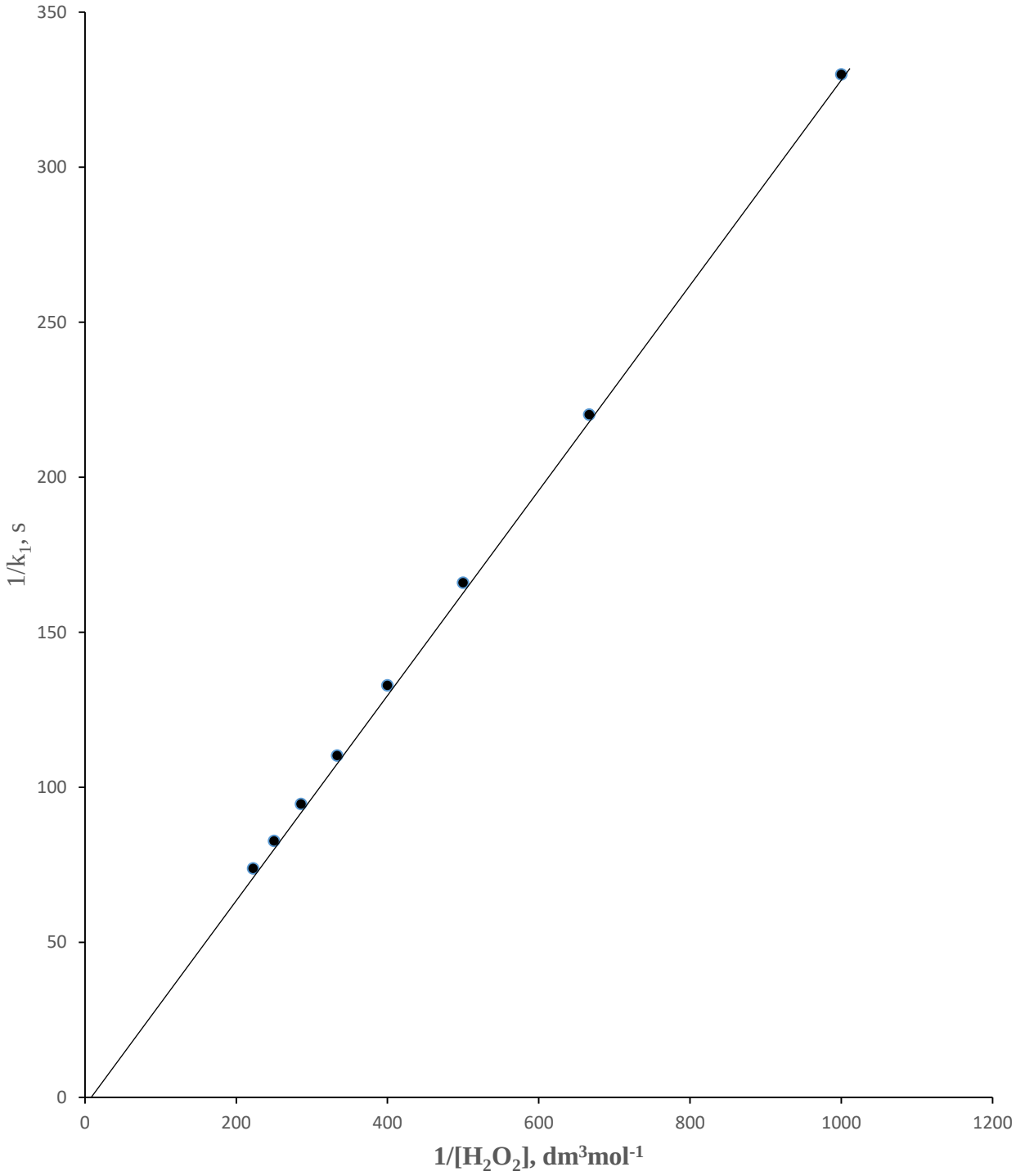


Figure 4.26: Michaelis-Menten plot of $1/k_1$ versus $1/[H_2O_2]$ for the reduction of 2,6-dichlorophenol indophenol by hydrogen peroxide in aqueous medium at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[H_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

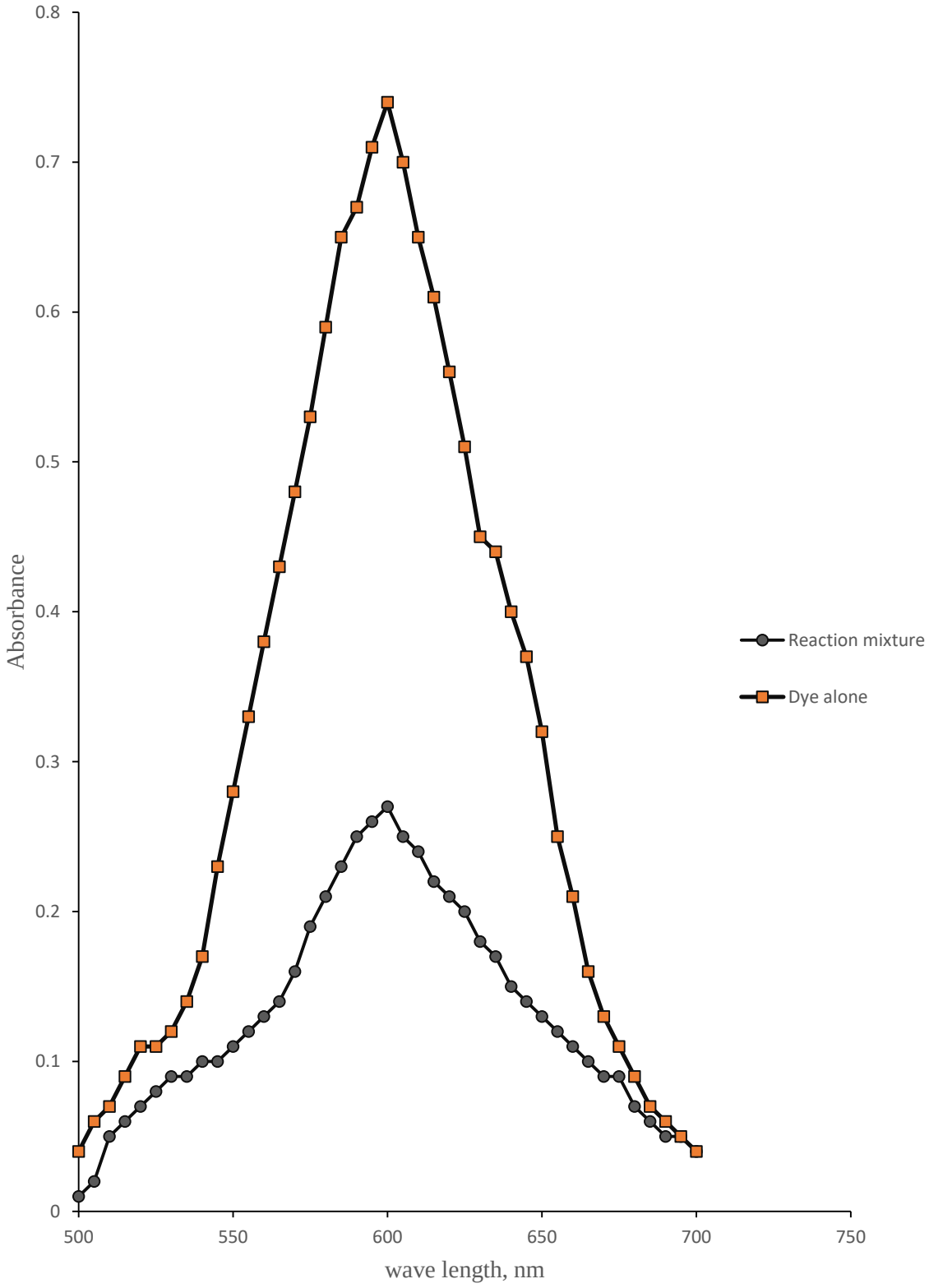


Figure 4.27: Spectrum of 2,6-dichlorophenol indophenol and that of the partial oxidized reaction of 2,6- dichlorophenol indophenol [DCPIP] with metabisulphite ions at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[S_2O_5^{2-}] = 1.0 \times 10^{-3}$ mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

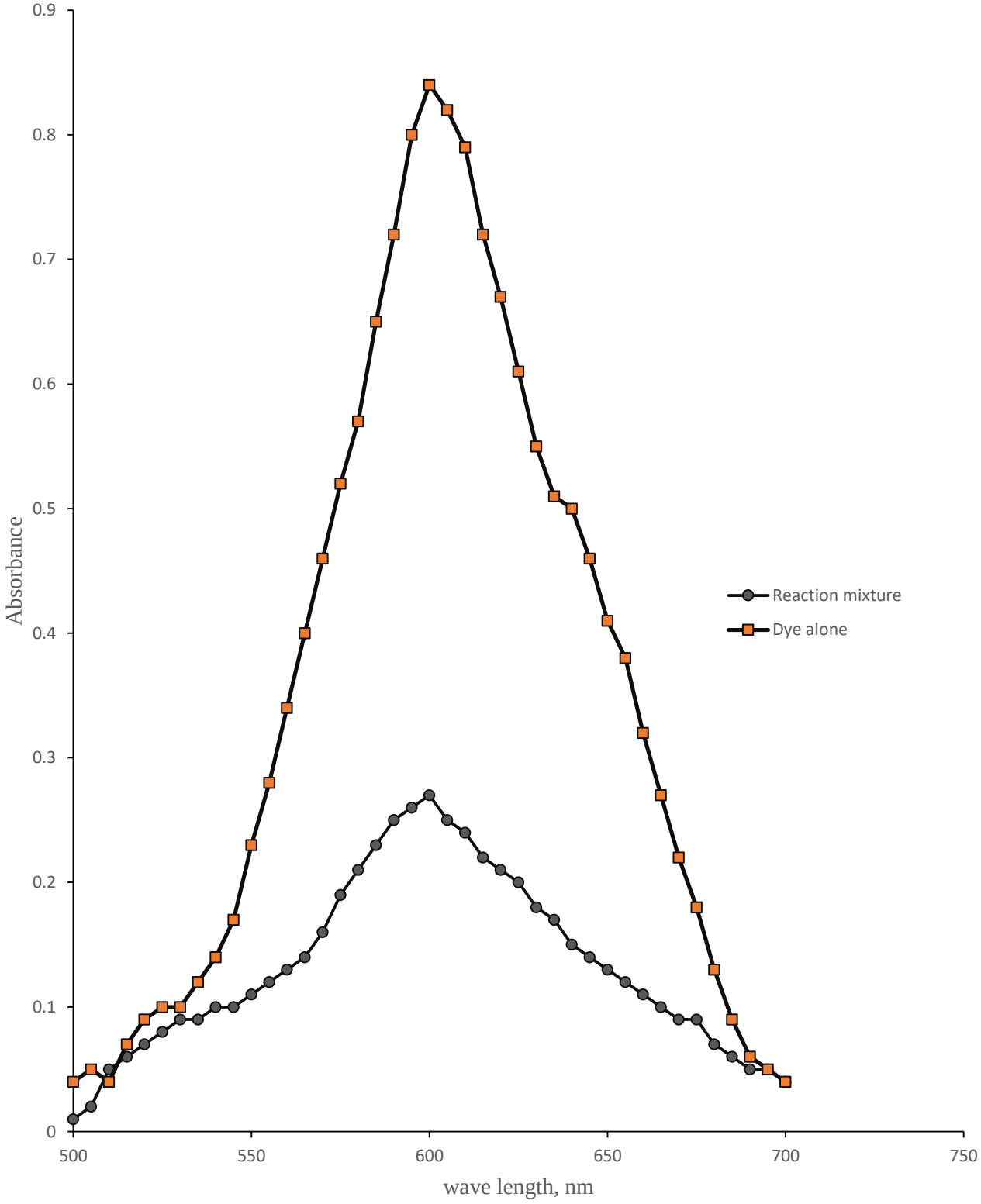


Figure 4.28: Spectrum of 2,6-dichlorophenol indophenol and that of the partial oxidized reaction of 2,6- dichlorophenol indophenol [DCPIP] with sulphite ion at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[SO_3^{2-}] = 3.0 \times 10^{-2}$ mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

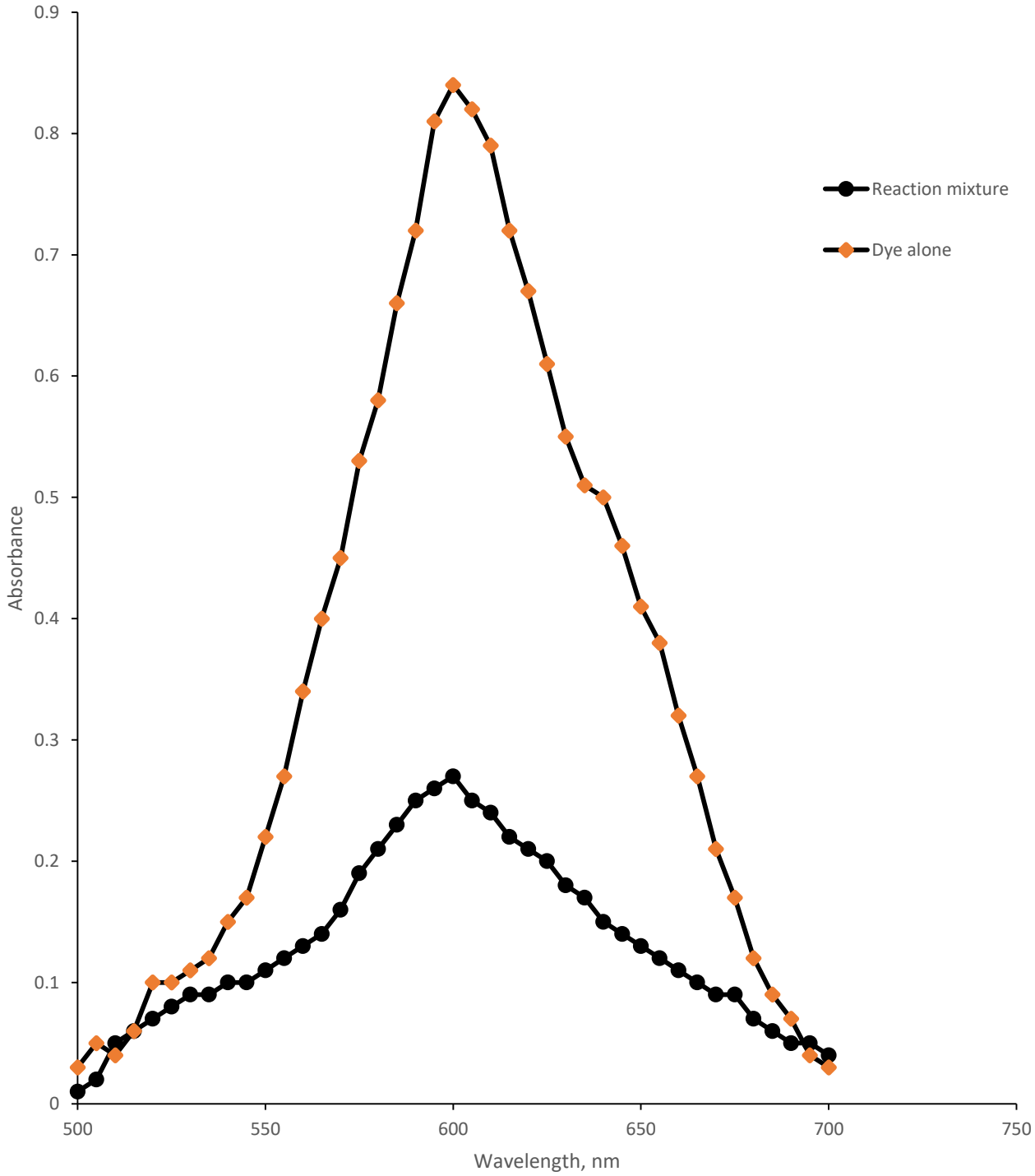


Figure 4.29: Spectrum of 2,6-dichlorophenol indophenol and that of the partial oxidized reaction of 2,6- dichlorophenol indophenol [DCPIP] with hydrazine at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, [N_2H_4] = 4.0×10^{-2} mol dm^{-3} T= 28 ± 1°C and λ_{max}= 600 nm

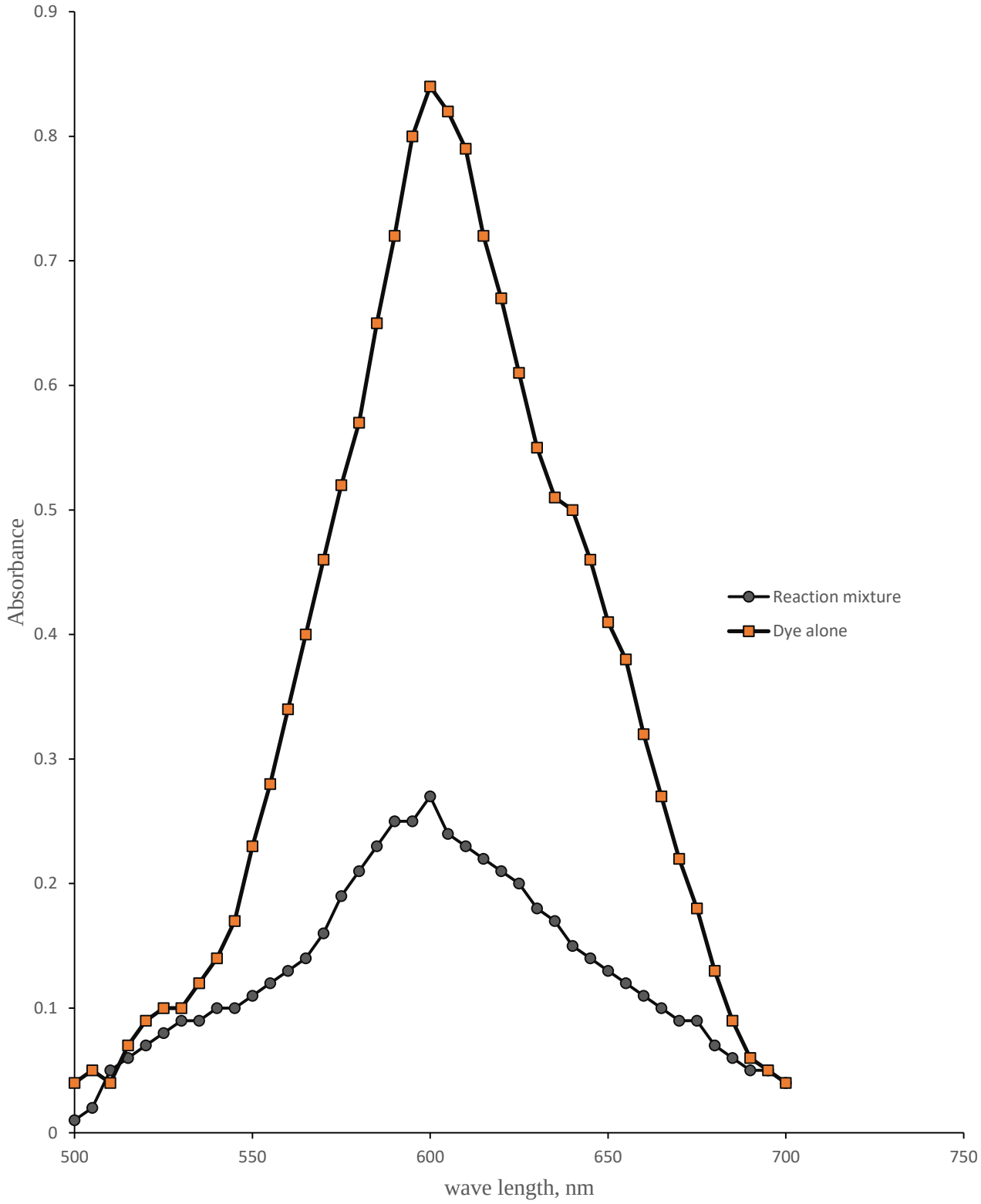


Figure 4.30: Spectrum of 2,6-dichlorophenol indophenol and that of the partial oxidized reaction of 2,6- dichlorophenol indophenol [DCPIP] with hydrogen peroxide at [DCPIP] = 1.0×10^{-4} mol dm^{-3}, $[H_2O_2] = 2.0 \times 10^{-3}$ mol dm^{-3} T= 28 ± 1˚C and λ_{max}= 600 nm

4.7 Products Analysis

The SO_4^{2-} ion product of DCPIP-$S_2O_5^{2-}$ and DCPIP – SO_3^{2-} reactions was confirmed by the formation of white precipitate insoluble in excess dilute HCl when $BaCl_2$ was added to each solution.

A distinctive “pop” sound that slightly ignite the flame on a splint held near the opening of the reaction mixture confirmed the presence of H_2 for DCPIP – N_2H_4 reaction. For DCPIP – H_2O_2 reaction, O_2 was confirmed when a glowing hot splint held near the opening of the reaction mixture re-ignite.

CHAPTER FIVE

5.0 DISCUSSIONS

5.1 2,6-Dichlorophenol Indophenol – Metabisulphite System

The stoichiometry study showed a mole ratio of 2:1 for the DCPIP-$S_2O_5^{2-}$ system, as given by equation (4.1). Similar stoichiometry has been reported for the reaction of DCPIP with D-amino acid oxidase (Christian *et al.,* 2005). However, stoichiometry of 1:1 has been observed for the reactions of metabisulphite ions with crystal violet (Abdulsalam, 2015), rosaniline (Onu and Iyun, 2001) and basic fuchsin (Lawal, 1997).

The kinetic study of the reaction showed a first order dependence on both reactants and second order overall. The observed first order dependence in the reaction of $S_2O_5^{2-}$ is a common feature of the reactions of $S_2O_5^{2-}$ (Abdulsalam, 2015; Onu and Iyun, 2001; Babatunde *et al*., 2013). Similarly, first order dependence in the reaction of DCPIP has been reported (Hamad *et al*., 2015; Brezova *et al.,* 1991; Konidari and Karayannis, 1988).

The rate constants of the reaction decreased with increase in ionic strength of the reaction medium, suggesting a negative Brønsted-Debye salt effect (Ibrahim, 2016). These results was supported by the observed decrease in the reaction rate as the dielectric constant of the medium was decreased. This suggests that the activated complex is formed from ions of opposite charges (Hamza, 2012). Similar results have been reported for the reactions of metabisulphite ions (Abdulsalam, 2015; Onu and Iyun, 2001). Addition of acrylamide to the partially oxidized reaction mixture followed by excess methanol did not lead to formation of gelatinous precipitate, indicating likely absence of free radicals.

Increasing the concentration of NO_3^- and CH_3COO^- decreased the rate of reaction. The effect of the added anions could be described in terms of columbic forces of repulsion, as the

activated complex of the reaction is made up of oppositely charged species, introducing negative charged species would lead to overall repulsion that will lead to decrease in the reaction rate. The inhibitive effect of these ions is quite useful as it suggests that the reactant species are not joined by any bridging group in the activated complex (Babatunde and Iyun, 2009). Likewise, increasing the concentration of Mg^{2+} and Ca^{2+} decreased the rate of reaction, it is also due to the fact that the activated complex is made up of oppositely charged species, which lead to overall repulsion as positively charged species were introduced (Abdulsalam, 2015).

The electronic spectrum of the reaction mixture was taken over the range of 400 – 700 nm after two minutes of initiating the reaction. The spectrum obtained showed no shift from the λ_{max} of 600 nm for DCPIP. This suggests that there is no detectable intermediate complex formation prior to the electron transfer, signifying that the reaction occur through outersphere mechanism.

Michaelis-Menten's plot of $1/k_1$ versus $1/S_2O_5^{2-}$ gave a straight line with zero intercept (Figure 4.26). This suggest the absence of the formation of an intermediate complex of significant stability

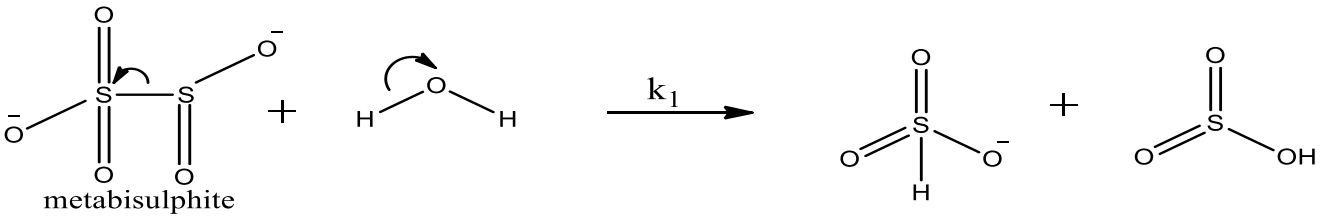
SO_4^{2-} was confirmed qualitatively by the observation of white insoluble precipitate (Vogel, 1996) on addition of $BaCl_2$ solution followed by dilute HCl to the solution at the end of the reaction involving stoichiometric amount of the reactants. DCPIP lost its dark blue colour to colourless due to electron transfer between DCPIP and $S_2O_5^{2-}$ ion that led to disruption of the conjugated double bond of the quinoid ring, C=O and C=N on the DCPIP, causing the electron to become localized and the ring to cease being chromophore (Fessenden and Fessenden, 1990).

At this juncture, the point of interest is whether this reaction occurs via the inner- or outer-sphere mechanism. Mechanism for the reaction of DCPIP and $S_2O_5^{2-}$ ion can be addressed as follows:

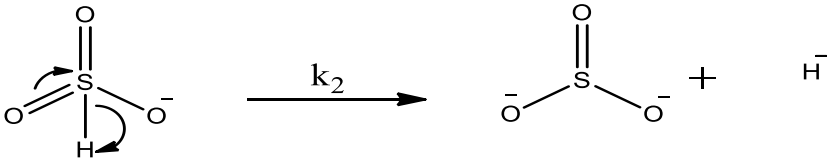
(a) The rate of the reaction decreased in the presence of both added cations and anions, this is characteristic of reactions occurring via the outer-sphere mechanism.

(b) Spectroscopic evidence indicated no shift in λ_{max} suggesting that there was no inner-sphere complex formation. This observation suggests the occurrence of the outer-sphere mechanism. (c) Michaelis – Menten's plot of $1/k_1$ versus $1/ S_2O_5^{2-}$ gave a straight line which passed through the origin. The zero intercept of the Michaelis - Menten plot suggests the absence of an intermediate in the rate determining step, an observation which further support outer-sphere mechanism.

Based on the spectroscopic and kinetic result obtained the following mechanism has been proposed



5.1



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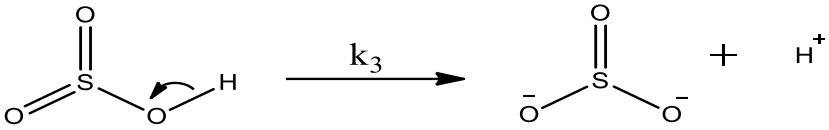

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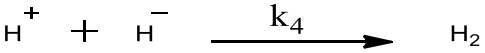

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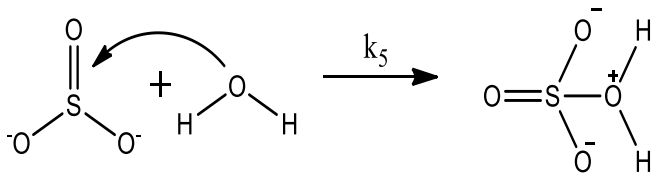

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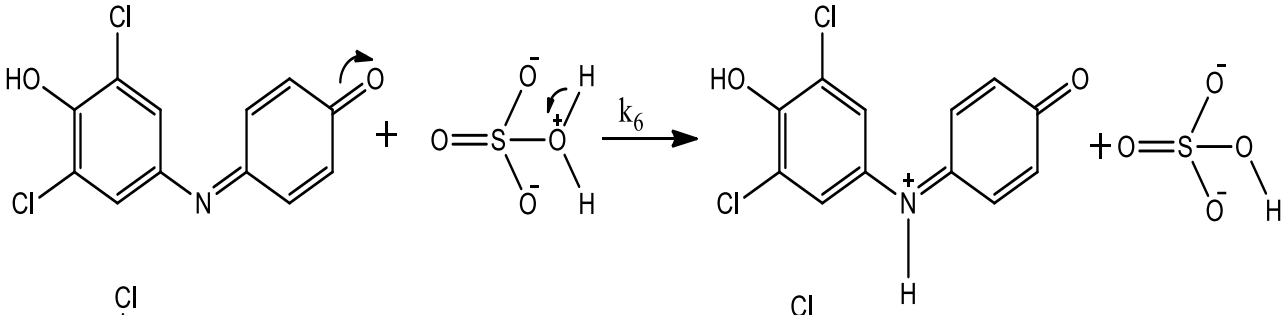

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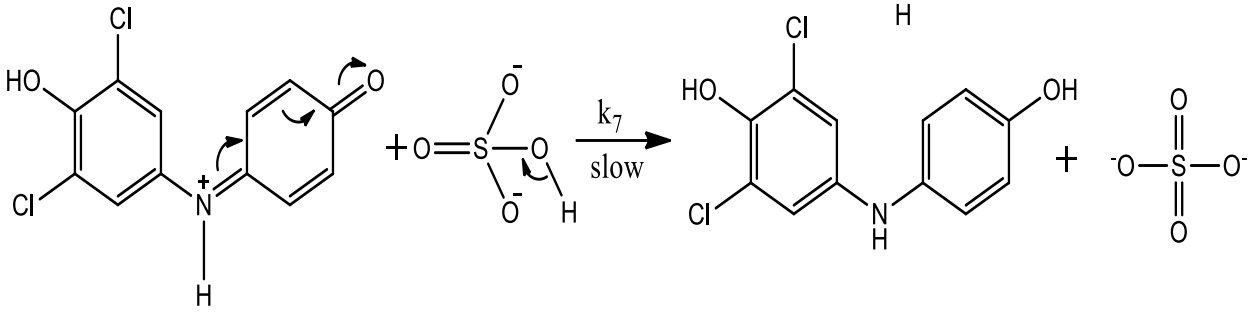


5.7

$$rate = k_7[DCPIPH^+][HSO_4^{2-}] \quad 5.8$$

Applying steady state approximation

$$\frac{d[DCPIPH^+]}{dt} = k_6[DCPIP][SO_4H_2^-] - k_7[DCPIPH^+][HSO_4^{2-}] = 0$$

$$[DCPIPH^+] = \frac{k_6[DCPIP][SO_4H_2^-]}{k_7[HSO_4^{2-}]} \quad 5.9$$

Substituting equation 5.9 in equation 5.8

$$rate = k_7 \frac{k_6[DCPIP][SO_4H_2^-]}{k_7[HSO_4^{2-}]}[HSO_4^{2-}] \quad 5.10$$

$$rate = k_6[DCPIP][SO_4H_2^-] \quad 5.11$$

$$\frac{d[SO_4H_2^-]}{dt} = k_5[SO_3^{2-}][H_2O] - k_6[DCPIP][SO_4H_2^-]$$

$$[SO_4H_2^-] = \frac{k_5[SO_3^{2-}][H_2O]}{k_6[DCPIP]}$$

5.12

[DCPIP] is in excess. Therefore [DCPIP] ≈ 1

$$[SO_4H_2^-] = k_5[SO_3^{2-}][H_2O] \quad 5.13$$

$$\frac{d[SO_3^{2-}]}{dt} = k_2[SO_3H^-] + k_3[SO_2OH] - k_5[SO_3^{2-}][H_2O]$$

$$[SO_3^{2-}] = \frac{k_2[SO_3H^-] + k_3[SO_2OH]}{k_5[H_2O]} \quad 5.14$$

$$[SO_3H^-] = \frac{k_1[S_2O_5^{2-}]}{k_2} \quad 5.15$$

$$[SO_2OH] = \frac{k_1[S_2O_5^{2-}]}{k_3} \quad 5.16$$

Substituting equation 5.15 and 5.16 in 5.14

$$[SO_3^{2-}] = \frac{2k_1[S_2O_5^{2-}]}{k_5[H_2O]} \quad 5.17$$

Substituting equation 5.17 in 5.13

$$[SO_4H_2^-] = 2k_1[S_2O_5^{2-}] \quad 5.18$$

Substituting equation 5.18 in 5.11

$$rate = 2k_6k_1[DCPIP][S_2O_5^{2-}] \quad 5.19$$

$$rate = k'[DCPIP][S_2O_5^{2-}] \quad 5.20$$

$$where\ k' = 2k_6k_1 \quad 5.21$$

Both spectroscopic and kinetic data generated are in support of outer-sphere mechanism and is hereby proposed for the reaction.

5.2 2,6-Dichlorophenol Indophenol – Sulphite System

The stoichiometry study showed that the mole ratio for the DCPIP-SO_3^{2-} reaction is 1:1. Equation (4.2) gives the stoichiometric equation for the reaction. The stoichiometry obtained in this reaction agrees with the 1:1 stoichiometries observed in the electron transfer reactions of sulphite with cobalamin (Ilia *et al.*, 2013), methylene blue (Busari, 2007), hydrogen peroxide (Hoffmann and Edward, 1975) and hydrogen sulphite (George 1976).

The linearity of the pseudo-first order plots suggests first order dependence in the reaction of DCPIP under the experimental condition in this study. The order of the reaction with respect to [SO_3^{2-}] was found to be zero, making the reaction first order overall. The observed zero order

dependence in the reaction of SO_3^{2-} is common with the reactions of SO_3^{2-} (Zhao *et al*., 2007; Jonnalagadda and Gollapalli, 2000; Girish and Rameshwar, 1976). However, first order dependence in the reaction of SO_3^{2-} with methylene blue was reported (Busari, 2007).

Increase in ionic strength of the reaction medium has no effect on the rate of the reaction. log k_2 vs $\sqrt{I}$ gives a straight line with a slope of 0.006. Ionic strength dependence of this nature suggests that the activated complex consist of neutral reactant species (Onu *et al.*, 2015). Similarly, the dielectric constant of the medium had no significant effect on the reaction rate. However, negative salt effect has been reported for the reaction of sulphite with methylene blue (Busari, 2007). Addition of acrylamide to the partially oxidized reaction mixture of DCPIP and SO_3^{2-} did not form gel even with addition of large excess of methanol, this indicates that the involvement of free radicals in the reaction is unlikely.

Increase in concentration of the added anions NO_3^- and CH_3COO^- increased the rate of reaction. this could be related to characteristics of reaction occurring via outersphere mechanism (Hamza, 2012). Added cations Mg^{2+} and Ca^{2+} did not affect the rate of reaction.

Spectroscopic studies indicate there was no clear shift from 600 nm (Figure 4.27), the wavelength of maximum absorption of DCPIP studied. This indicates the absence of formation of intermediate complex during the course of the reaction.

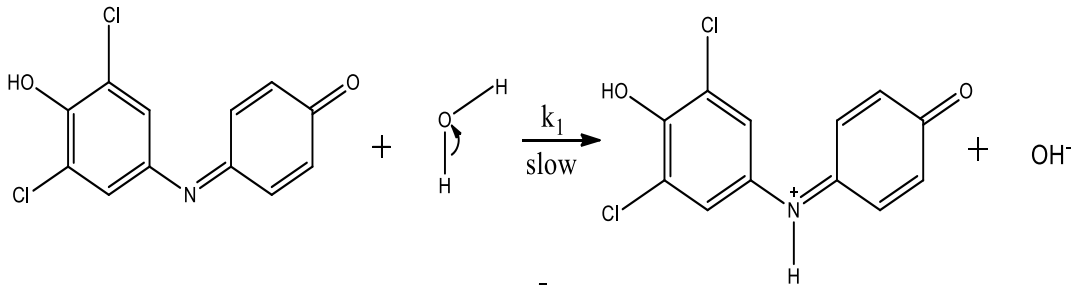
SO_4^{2-} ion was confirmed from the product analysis by observation of white insoluble precipitate (Vogel, 1996) on addition of $BaCl_2$ solution followed by dilute HCl to the solution at the end of the reaction involving stoichiometric amount of the reactants. The dye change from dark blue to colourless due to disruption of chromophores of quinoid ring, C=O and C=N by the SO_3^{2-} ion, making the DCPIP to absorb light outside visible region (Fessenden and Fessenden, 1990).

To ascertain the mechanism for the reaction of DCPIP and SO_3^{2-} ion. The following observations has been drawn:

(a) Added anions increased the rate of the reaction. This is characteristic of reactions occurring via the outer-sphere mechanism.

(b) Spectroscopic studies indicated no shift from the λ_{max} suggesting that there was no inner-sphere complex formation. This observation suggests the occurrence of the outer-sphere mechanism.

Based on the result obtained the following mechanism has been proposed



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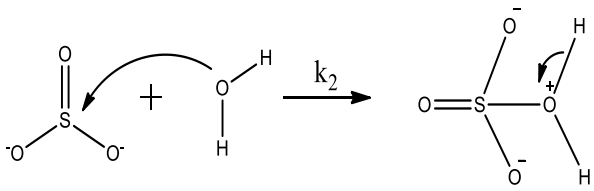

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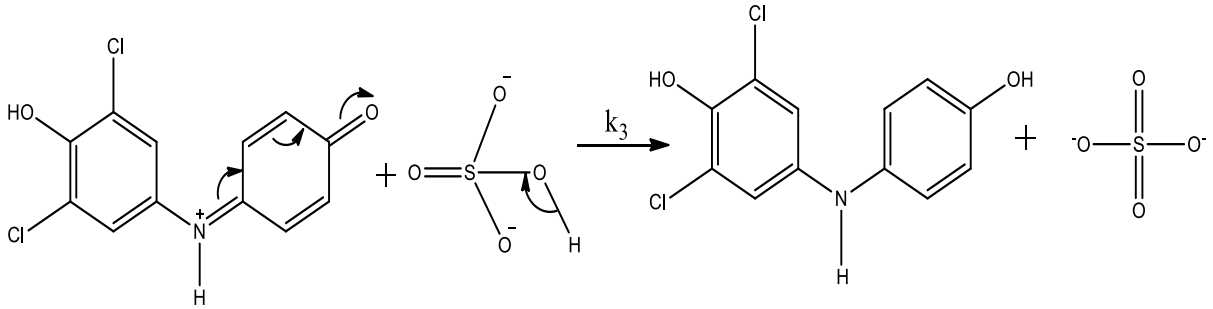

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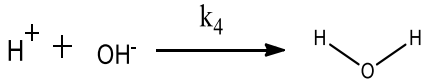


5.25

$$rate = k_1[DCPIP][H_2O] \quad 5.26$$

$$rate = k_1[DCPIP] \quad 5.27$$

Spectroscopic and kinetic evidence are in support of the occurrence of outer-sphere mechanism and is hereby proposed for the reaction.

5.3 2,6-Dichlorophenol Indophenol – Hydrazine System

The stoichiometry study gave 1:1 mole ratio for the reaction of DCPIP-N_2H_4 system. Equation (4.3) gives the stoichiometric equation for the reaction. Similar stoichiometry has been reported for the electron transfer reaction of hydrazine with platinum (Ananiev *et al*., 2000). However, stoichiometry of 4:1 has been observed for the reaction of hydrazine with cobalt (III) (Amit and Rupendranath, 2009). As part of the product of the reaction, H_2 was confirmed by burning splint test, a splint was lit and held near the opening of a closed tube of the reacting mixture, a distinctive "pop" sound that slightly ignite the flame was heard, the sound and slight ignition of the flame confirmed the presence of H_2 gas (Emil *et al.,* 2011). The DCPIP change from dark blue to colourless due to disruption of it chromophores of quinoid ring, C=O and C=N by the N_2H_4, making the delocalized electron cloud to localized and the DCPIP to absorb light outside visible region (Fessenden and Fessenden, 1990)

The kinetic study of the reaction showed a first order dependence on [DCPIP] and [N_2H_4]. Thus, second order overall. Earlier workers (Myek, 2012; Beck and Durham, 1970) observed first order dependence also on [N_2H_4] for reactions of N_2H_4.

The rate constant of the reaction increased with increase in ionic strength of the reaction medium, the plot of log k_2 versus $\sqrt{I}$ gave a straight line with a slope of 0.93, suggesting a positive Brønsted-Debye salt effect. This suggest that the activated complex is formed from two ions of like charges (Hamza *et al.,* 2012), Ionic dependence of this nature has been reported for reactions of hydrazine (Myek, 2012; Bartlomiej *et al.,* 2014). Also, Increase in dielectric constant of the reaction medium decreased the reaction rate.

Addition of acrylamide to the partially oxidized reaction mixture followed by excess methanol didn't lead to formation of gelatinous precipitate, indicating involvement of free radicals in the reaction is unlikely.

Addition of varying concentration of anions and cations had no significant effect on the rate of reaction. Non catalysis by the added ions suggest that the reaction is occurring through innersphere mechanism. Non catalysis of reaction rates by added ions is a characteristic of innersphere pathway (Imam, 2016).

The electronic spectrum of the reaction mixture was taken over the range of 400 – 700 nm after two minutes of initiating the reaction. The spectrum obtained showed no shift from the λ_{max} of 600 nm for DCPIP. Lack of significant shift in λ_{max} could indicate absence of intermediate complex. However, it is known that detection of intermediate is a function of the instrument and stability of the intermediate. So the lack of shift in λ_{max} obtained from the spectrum of the partially initiated reaction mixture may not necessary rule out the presence of intermediate.

Michaelis-Menten's plot of $1/k_1$ versus $1/N_2H_4$ gave a straight line with an intercept (Figure 4.27). This suggest the formation of an intermediate complex of significant stability (Abdulsalam, 2015).

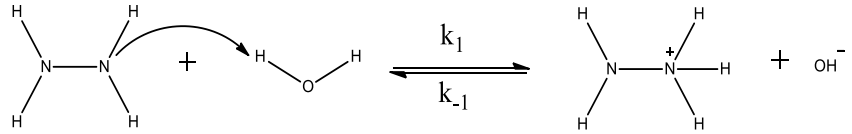
A key point of interest in this discussion is whether this reaction occurs via inner- or outer-sphere or a combination of both. Mechanism for the reaction of DCPIP and N_2H_4 can be addressed as follow;

(a) The rate of the reaction was not altered in the presence of both added cations and anions, this is characteristic of reactions occurring via the inner-sphere mechanism.

(b) Spectroscopic evidence showed no shift in λ_{max} suggesting that there was no inner-sphere complex formation. This observation suggests the occurrence of the outer-sphere mechanism. But can be overruled if we look at the transient nature of some intermediate when reaction is occurring via inner-sphere mechanism.

(c) Michaelis – Menten's plot of $1/k_1$ versus $1/ N_2H_4$ gave a straight line that did not passed through the origin. This suggests the presence of an intermediate in the rate determining step. This observation further support inner-sphere mechanism.

Based on the result obtained the following mechanism has been proposed



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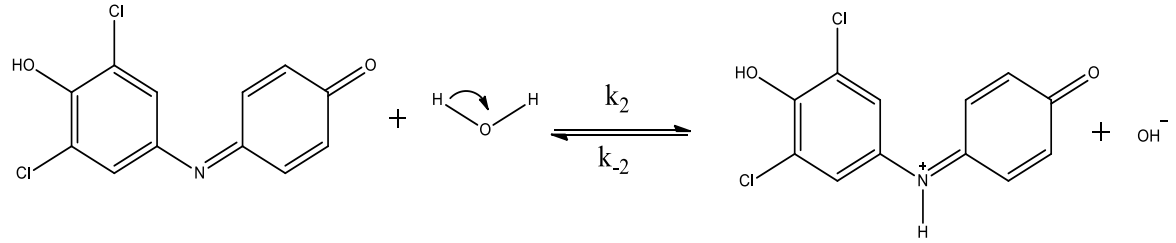

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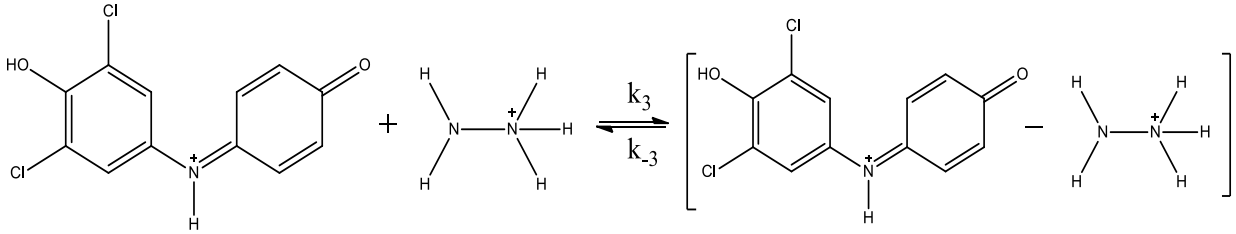

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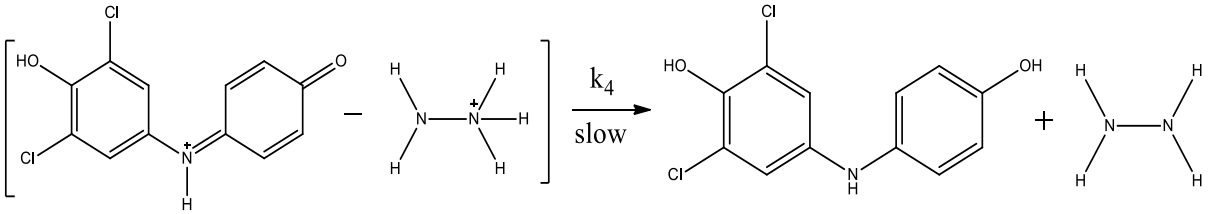

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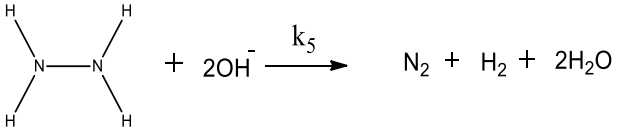


5.32

$$rate = k_4\,[DCPIPH^+\text{-}\,N_2H_5^+] \tag{5.33}$$

$$but\ [DCPIPH^+ - N_2H_5^+] = K_3[DCPIPH^+][N_2H_5^+] \tag{5.34}$$

Substituting equation 5.34 in equation 5.33

$$rate = K_3k_4[DCPIPH^+][N_2H_5^+] \tag{5.35}$$

$$but\ [DCPIPH^+] = \frac{K_2[DCPIP][H_2O]}{[OH^-]} \tag{5.36}$$

$$also\ [N_2H_5^+] = \frac{K_1[N_2H_4][H_2O]}{[OH^-]} \tag{5.37}$$

Substituting equation 5.36 and 5.37 in equation 5.35

$$rate = K_3K_2K_1k_4 \frac{[DCPIP][H_2O]}{OH^-} . \frac{[N_2H_4][H_2O]}{OH^-} \quad 5.38$$

$[H_2O] \approx 1$. pH of the solution was 8.3, $[OH^-]$ is in excess. Therefore, $[OH^-] \approx 1$

$$rate = K_3K_2K_1k_4 [DCPIP][N_2H_4] \quad 5.39$$

$$rate = k' [DCPIP][N_2H_4] \quad 5.40$$

$$where\ k' = K_3K_2K_1k_4 \quad 5.41$$

Both spectroscopic and kinetic data generated are in support of inner-sphere mechanism and is hereby proposed for the reaction.

5.4 2,6-Dichlorophenol Indophenol – Hydrogen Peroxide System

The stoichiometry study showed that the mole ratio for the DCPIP- H_2O_2 is 1:1. Equation (4.4) gives the stoichiometry equation for the reaction. Similar stoichiometry of 1:1 has been reported for the redox reaction of hydrogen peroxide with sulphite (Hoffmann and Edward, 1975). However, Onu *et al.*, (2015, 2016) reported a stoichiometry of 2:1 for the reactions of ethylenediaminetetraacetatocobaltate(II) and aminocaboxylactocobaltate(II) complex with hydrogen peroxide, both $[CoEDTA]^{2-}$ and $[CoHEDTAOH_2]^-$ are known as one electron reductant and exhibit such stoichiometry to a two electron reactant like H_2O_2. DCPIP is known as two-electron acceptor (Christian *et al.,* 2005). As part of the product of the reaction, O_2 was confirmed by burning splint, a burning splint was blown out by shaking whilst the amber at the tip is still glowing hot, exposing the amber to a trapped gas in a tube re-ignite the splint which indicate the presence of O_2 gas. The dye change from dark blue to colourless due to disruption of it chromophores of quinoid ring, C=O and C=N by the H_2O_2, making the delocalized electron cloud to localized and the dye to absorb light outside visible region (Fessenden and Fessenden, 1990).

The kinetic study of the reaction showed a first order dependence in both [DCPIP] and $[H_2O_2]$. Thus, second order overall. The observed first order dependence in the reaction of H_2O_2

has been reported by earlier researchers (Onu *et al.,* 2015; Quentel *et al.,* 2004). However, Onu *et al.,* (2016) reported half order dependence in the reaction of H_2O_2.

Increase in ionic strength has no effect on the rate constant of the reaction medium. log k_2 vs $\sqrt{I}$ gives a straight line with a slope of 0.002. Ionic dependence of this nature suggest that the activated complex consist of either neutral reactant species (Ibrahim, 2016). Furthermore, change in dielectric constant of the medium had no significant effect on the reaction rate. Similar result has been reported for the neutral salt effect of hydrogen peroxide (Onu *et al.,* 2015).

Addition of acrylamide to the partially oxidized reaction mixture of DCPIP and H_2O_2 did not form gel even when a large excess of methanol was added to the reaction mixture, this indicates that free radicals were not formed.

Increasing the concentration of NO_3^- and CH_3COO^- enhanced the rate of reaction. This is a characteristic of reactions occurring via outer-sphere mechanism (Ibrahim, 2016). However, the addition of varying concentrations of Mg^{2+} and Ca^{2+} have no significant effect on the rate of reaction.

Spectroscopic studies indicate that there was no clear shift of λ_{max} of 600 nm for DCPIP (Figure 4.32) when the reaction mixture was taken over the range of 400 – 700 nm after two minutes of initiating the reaction. This indicates the absence of formation of intermediate complex during the course of the reaction.

Michaelis-Menten's plot of $1/k_1$ versus $1/H_2O_2$ gave a straight line which passed through the origin (Figure 4.28). This suggests the absence of the formation of an intermediate complex of significant stability (Idris *et al.,* 2015).

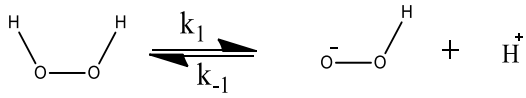
A key point of interest in this discussion is whether the reaction occurs via inner-sphere or outer-sphere. This issue for the reaction of DCPIP and H_2O_2 can be addressed as follows;

(a) The rate of the reaction was increased in the presence of added anions, this is characteristic of reactions occurring via the outer-sphere mechanism.

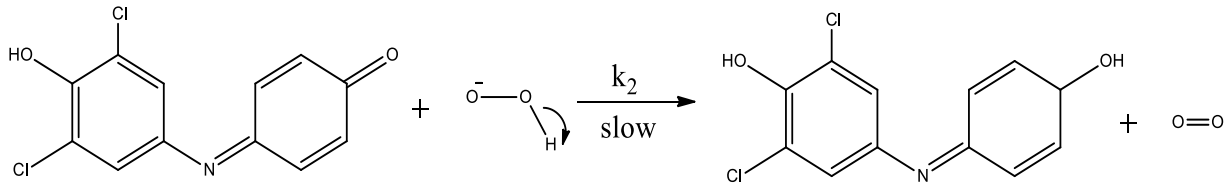
(b) Spectroscopic evidence indicated no shift in λ_{max} suggesting that there was no intermediate complex formation. This observation suggests the occurrence of the outer-sphere mechanism.

(c) Michaelis – Menten's plot of $1/k_1$ versus $1/ H_2O_2$ gave a zero intercept. This suggests the absence of an intermediate in the rate determining step. This observation further support outer-sphere mechanism.

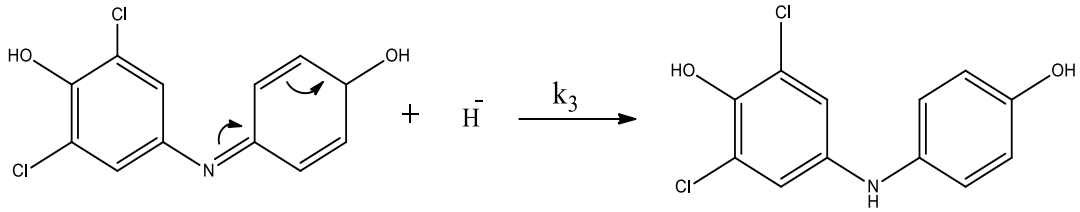
Based on the result obtained the following mechanism has been proposed



5.42



5.43



5.44

$$rate = k_2[DCPIP][O_2H^-] \quad 5.45$$

$$but\ [O_2H^-][H^+] = K_1[H_2O_2] \quad 5.46$$

$$[O_2H^-] = \frac{K_1[H_2O_2]}{[H^+]} \quad 5.47$$

pH of the solution was 8.3, $[H^+]$ is negligible.

$$[O_2H^-] = K_1[H_2O_2] \quad 5.48$$

Substituting equation 5.48 in equation 5.45

$$rate = K_1k_2[DCPIP][H_2O_2] \quad 5.49$$

$$rate = k'[DCPIP][H_2O_2] \quad 5.50$$

where $k' = K_1k_2$ 5.51

Spectroscopic and kinetic evidence are in support of the occurrence of outer-sphere mechanism and is hereby proposed for the reaction.

CHAPTER SIX

6.0 SUMMARY, CONCLUSION AND RECOMMENDATION

6. 1 Summary and Conclusion

The kinetic studies of redox reactions of 2,6-dichlorophenol indophenol with some oxyanions ($S_2O_5^{2-}$ and SO_3^{2-}), hydrazine (N_2H_4) and hydrogen peroxide (H_2O_2) in aqueous medium were carried out. The stoichiometric studies showed a 1:1 mole ratio for [DCPIP]-[SO_3^{2-}], [DCPIP]-[N_2H_4] and [DCPIP]-[H_2O_2] systems and 2:1 for [DCPIP]-[$S_2O_5^{2-}$] system.

The kinetic study showed a first order dependence with respect to [$S_2O_5^{2-}$], [N_2H_4], [H_2O_2] and zero order dependence with respect to [SO_3^{2-}].

The reactions are therefore in conformity with the following rate equations:

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

2,6-dichlorophenol indophenol – $S_2O_5^{2-}$- reaction, $(16.24 \pm 0.03)\ dm^3\ mol^{-1}\ s^{-1}$

2,6-dichlorophenol indophenol – SO_3^{2-}- reaction, $(1.79 \pm 0.02)\ dm^3\ mol^{-1}\ s^{-1}$

2,6-dichlorophenol indophenol – N_2H_4 reaction, $(0.13 \pm 0.02)\ dm^3\ mol^{-1}\ s^{-1}$

2,6-dichlorophenol indophenol – H_2O_2 reaction, $(3.01 \pm 0.02)\ dm^3\ mol^{-1}\ s^{-1}$

Increase in concentrations of ionic strength inhibited the reaction for [DCPIP]-[$S_2O_5^{2-}$] and enhanced [DCPIP]-[N_2H_4] system while it had no effect for [DCPIP]-[SO_3^{2-}] and [DCPIP]-[H_2O_2] systems.

Spectroscopic evidence showed no shift in λ_{max} and Michaelis – Menten plot of $1/k_1$ versus 1/[oxidant] or 1/[reactant] had no intercept for all the reaction systems except for [N_2H_4], where intercept was obtained.

From the results, the outer-sphere mechanism was proposed as the probable plausible mechanism for [DCPIP]-[$S_2O_5^{2-}$], [DCPIP]-[SO_3^{2-}] and [DCPIP]-[H_2O_2] systems while the inner-sphere mechanism is proposed for [DCPIP]-[N_2H_4] system.

6.2 Recommendation

It is recommended that:

1. Further studies should be carried out on the activation parameters of these reactions.
2. Computational chemistry programs should be used to study kinetic reactions of the dye.

REFERENCES

Abbas, A.E. and Nabeel, H.K. (2010). Kinetics of the reduction of hexacyanoferrate (III) 3,7-bis(dimethylamino)phenothionium chloride by metabisulphite ion in acidic medium. *Pelagia Research Library* **4**(3): 69-78.

Abdulsalam. S. (2015). Kinetics and mechanisms of the redox reactions of crystal violet with some oxyanions in aqueous acidic medium. Ms.c thesis, Ahmadu Bello University, zaria. Nigeria.

Amit, M. and Rupendranath, B. (2009). Kinetics and mechanism of uncatalyzed oxidation of hydrazine with superoxide coordinated to cobalt(III). *Indian Journal of Chemistry.* **48**:645-649.

Ananiev, A.V., Tananaev, I.G. Brossard, H. and Broudic, J.C. (2000). The platinum catalyzed decomposition of hydrazine in acidic media. *Institute of physical chemistry.* **2**:02.

Babatunde, O.A and Iyun, J.F. (2009). Kinetics and mechanism of the reaction of di-μ-oxo-tetrakis (1,10-phenanthroline)-dimaganese(III,IV) perchlorate by sulphite ion in acidic solution. *European Journal of Scientific Reseach,* **26**: 406.

Babatunde, O.A., Faruruwa, M.D. and Umoru, P.E. (2013). Mechanism of the reduction of 3,7-bis(dimethylamino)phenothionium chloride by metabisulphite ion in acidic medium. *Pelagia Reseach Library* **4**(3): 69-78.

Banerjee, R., Mondal, B. and Kundu, S. (1997). Kinetics of oxidation of hydrogen peroxide by dioxo-bridged manganese (III, IV) complexes. *J. chem. Soc. Dalton Trans.*, 4341-4344

Bartlomiej, S., Wiktor, J., Konrad, S. and Krzysztof, P. (2014). Kinetics and Mechanism of Redox Reaction between Tetrachloroaurate(III) Ions and Hydrazine. *International journal of chemical kinetics,* **46**(6):328-337

Beck, M.T. and Durham, D.A. (1970). The oxidation of hydrazine by chromium (VI). *Journal of Inorganic and Nuclear Chemistry,* **32**(6):1971-1977.

Booth, G. (2000). *Dyes, General Survey.* Wiley-VCH. Retrieved from http://dyes-pigments.standardcon.com/what-is-dye.html

Brezová, V., Čeppan, M., Veselý, M. and Lapčík, L. (1991). Photocatalytic oxidation of 2,6-Dichloroindophenol in the titanium dioxide aqueous suspension. *Chem. Papers, **45*** (2): 233-24.

Bronsted, J.N. (1922) Theory of chemical reaction velocity. *Z. Phys. Chem.,* **102**:160.

Busari, A. (2007). The electron transfer reactions of 3,7 bis(dimethylamine)phenothionium chloride (methylene blue) with oxyanions in aqueous acidic medium. Ms.c thesis, Ahmadu Bello University, zaria. Nigeria.

Cabello, C.M., Bair W.B., Bause A.S. and Wondrak G.T.(2009). Antimelanoma activity of the redox dye DCPIP (2,6-dichlorophenolindophenol) is antagonized by NQO1**.** *Biochem Pharmacol* 2009, **78**(4):344-54.

Catherine, E.H. and Alan G.S. (2008). *Inorganic Chemistry,* (3rd ed.). Pearson.UK. Pp. 520.

Christian, T., Anita, S., Waander, R. and Bernd, N. (2005). Reaction of *Trigonopsis variabilis* d-amino acid oxidase with 2,6-dichloroindophenol: kinetic characterisation and developmentof an oxygen-independent assay of the enzyme activity. *Journal of Molecular Catalysis B: Enzymatic* **32**: 271–278.

Cox, P.A. (2004). *Inorganic Chemistry,* (2nd ed.). BIOS Scientific publisher, Oxford. UK. p. ix.

Cui, S., Wang, L., Hao, S. and Du L. (2012). Oxidation rate of sodium sulfite in presence of inhibitors. *energy procedia **16**:*2060 – 2066.

Dupuy, C., Kaniewski, J., Ohayon, R., Deme, D., Virion, A., and Pommier, J. (1990). Nonenzymatic NADPH-Dependent Reduction of 2,6-Dichlorophenol-lndophenol. *Analytical Biochemistry* **191**:16-20.

Emil, S., Wayne, W. and Robert, R. (2011). *Chemical principle in the laboratory.* Cengage learning. Boston, U.S.A. p. 133.

Emine, A. and Duygu, G. (2015). The influences of drying method and metabisulfite pre-treatment on the color, functional properties and phenolic acids contents and bioaccessibility of pumpkin flour. *LWT - Food Science and Technology,* **60**: 385-392.

Erling, S. and Tor, H. (2007). Kinetics and mechanism of sulphite oxidation on a rotating platinum disc electrode in an alkaline solution. Electrochimica Acta. **5**(11):3510-3517.

Espenson, J. H. (2002). *Chemical kinetics and reaction mechanisms* (2nd ed.). McGraw-Hill. New York, U.S.A. p. 6.

Fadee, G.M., Sivapriya, P., Janita, G., Courtney, H., Shrikant, A., Panayotis, P. and Rama, P.R., (2010). "Inhibition of angiogenesis- and inflammation-inducing factors in human colon cancer cells *in vitro* and *in ovo* by free and nanoparticle-encapsulated redox dye, DCPIP". *Journal of Nanobiotechnology*. **8**:17.

Fessenden, R.J. and Fessenden J.S. (1990). *Organic Chemistry* (4th ed.). Brooks/Cole Publishing Company, Pacific Grove, California.

Fry, F. H., Holme, A. L., Giles, N.M., Giles, G.I., Collins, C., Holt, K., Pariagh, S., Gelbrich, T., Hursthouse, M.B., Gutowski, N.J. and Jacob, C. (2005). Multifunctional redox catalysts as selective enhancers of oxidative stress. *Org Biomol Chem*. **3**:2579 - 2587.

Gennady, E.Z., Artur J.M. and Alexei L.L. (2013). Advance in kinetic and mechanism of chemical reactions, Apple Acedemic Press, New jersey. pp. xviii

George, W.H. (1976). Stoichiometry of the Reaction of sulfite with hydrogen sulfide ion. *Inorganic. Chem.,* **16**(6): 1411–1413.

Girish, C.M. and Rameshwar, D.S. (1976). Kinetics of heterogeneous oxidation of ammonium sulphite. *Journal of Chemical Technology and Biotechnology.* **26**(1): 401-405.

Goor, G., Glenneberg, J. and Jacobi S. (2007). Hydrogen Peroxide. *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim.

Hamza, S.A., Iyun J.F. and Idris S.O. (2012). Kinetics and mechanism of the redox reaction of toluidine blue and nitrite ions in aqueous acidic medium. *Scholars Research Library* Archives of Applied Science Research. **4**(1): 10-18.

Hamad, H.A., Sadik, W.A., Abd El-latif, M.M., Kashyout, A.B. and feteha, M.Y. (2015). Photocatalytic parameters and kinetic study for degradation of dichlorophenol-indophenol (DCPIP) dye using highly active active mesoporous TiO_2 nanoparticles. *Journal of Environmental Science.* **8**(5): 11 – 14.

Hamza, S.A. (2012). Kinetics and mechanisms of the redox reactions of toluidine blue with some oxyanions and ascorbic acid in aqueous acidic medium. Ms.c thesis, Ahmadu Bello University, zaria. Nigeria.

Hassan, V. and Neil L.A. (2012). Adverse reaction to the sulphite additives. *Gastroenterol hepatol bed bench winter* **5**(1): 16-23.

Hill, C.N. (2001). *A Vertical Empire: The History of the UK Rocket launch and Space Programme,* Imperial College Press. London.

Hoffmann, M.R. and Edwards, T.O. (1975). Kinetics of the oxidation of sulfite by hydrogen peroxide in acidic solution. *J. phy. chem.,* **79**(20): 2096-2098.

Ibrahin. I. (2016). Kinetics and mechanisms of the redox reactions of neutral red by some oxyanions and hypophosphorus acid in aqueous acidic medium. Ms.c thesis, Ahmadu Bello University, zaria. Nigeria.

Idris, S.O., Tanimu, A., Iyun, J.F. and Mohammed, Y. (2015). Kinetics and mechanism of malachite green oxidation by hypochlorite ion in aqueous acidic medium. *American Chemical Science Journal*, **5**(2): 185-193.

Ilia, A.D., Denis, S.S., Sergei, V.M., Gerry, R.B. and Oskar, I.K. (2013). Kinetics and mechanism of oxidation of super-reduced cobalamin and cobinamide species by thiosulfate, sulfite and dithionite. *Dalton trans.* **21**(43): 42.

Imam, M. (2016). Kinetics and mechanisms of the redox reactions of malachite green with some oxyanions in aqueous acidic medium. Ms.c thesis, Ahmadu Bello University, zaria. Nigeria.

Ivana, M., Ana, A., Alisson, F., Danilo, L., Francisco, C., Francisco, M. and Juliana, S. (2011). Environmental mutagenicity and toxicity caused by sodium metabisulfite in sea shrimp harvesting in Piauí, Brazil. *Chemosphere,* **82**: 1056–1061.

Jagannadham, V. (2012). Electron Transfer Reactions: a Treatise. *American Journal of Chemistry*, **2**(2): 57-82.

Jean-Pierre, S. and Paul, B. (2002). Hydrazine. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim.

Jeffery, G.H., Bassett, J., Mendham, J. and Denny R.C. (1991). *Vogel's Textbook of qualitative chemical analysis,* (5th ed.). Longman, England. p. 391.

John, W.L., Micheal, F., Kwang, Y.K., Matthew, S. and John, L.S. (2000). Mechanism of the carbon catalyzed reduction of nitrobenzene by hydrazine. *Carbon.* **38**:5. Pp 655 - 661

John, S.H., and Phil, S. (2001). *Chemistry*. Nelson thornes. UK. p. 26.

Jonnalagadda, S.B. and Gollapalli N.R. (2000). Kinetics of Reduction of Toluidine Blue with Sulfite; Kinetic Salt Effect in Elucidation of Mechanism. *J. Chem. Educ.*, **77** (4): 506.

Konidari, C.N. and Karayannis, M.I. (1988). Kinetic and mechanistic study of the reduction of 2,6-Dichlorophenol Indophenol by dithionites. *Analytica Chzmica* Acta, **224**:199-210.

Kumar, S. and Acharya, S. K. (1999). 2,6-Dichloro-phenol indophenol prevents switch-over of electrons between the cyanide-sensitive and -insensitive pathway of the mitochondrial electron transport chain in the presence of inhibitors. *Anal Biochem*. **268**:89 - 93.

Lawal, H.M. (1997). The electron transfer reactions of pararosaniline chloride (Basic fuchsin) and trisoxalatocobaltate(III) iron in acidic medium. Ph.D Thesis, Abubakar Tafawa Balewa University, Bauchi, Nigeria.

Luis, F.G. (2016). Sulfites in beer: reviewing regulation, analysis and role. *Sci. agric. (Piracicaba, Braz.)* **73**: 2.

Miessler, G.L. and Tarr, A.D. (2003). *Inorganic Chemistry.* (3rd ed.). Prentice Hall publisher, USA.

Miline, G.W.A. (2005).*Gardner's commercially important chemicals: synonyms, trade names and properties.* Wiley interscience, New York, U.S.A. p. 568.

Moore, W.J. (1999). *Physical Chemistry.* (5th ed.). Prentice-Hall. New York, U.S.A. p. 574.

Myek, B. (2012). Kinetics and mechanism of the redox reactions of Napthol B with some oxy-anions and hydrazine dihydrochloride in aqueous acidic medium. Ms.c thesis, Ahmadu Bello University, zaria. Nigeria.

Olajire, A.A. and Olajide, A.J. (2014). Kinetic Study of Decolorization of Methylene Blue with Sodium Sulphite in Aqueous Media: Influence of Transition Metal Ions. *Journal of Physical Chemistry and Biophysics.* **4**:2.

Onu, A.D. and Iyun, J.F. (2001). Kinetics and mechanism of the oxidation of rosaniline monochloride with sodium metabisulphite in aqueous acid medium. *Journal of Chemical Society of Nigeria,* **28**: 156-159.

Onu, A.D., Iyun, J.F. and Idris, O.S. (2015). Kinetics and Stoichiometry of the Reduction of Hydrogen Peroxide by an Aminocarboxylactocobaltate(II) Complex in Aqueous Medium. Open Journal of Inorganic Chemistry, **5**: 75-82.

Onu, A.D., Iyun, J.F. and Idris, O.S. (2016). Oxidation of ethylenediaminetetraacetatocobalt(II) complex by Hydrogen Peroxide in Aqueous acidic Medium. Journal of Chemical Society of Nigeria, **2**: 81-86.

Quanxi, Z., Yunlong, B., Zhenhua, Y., Jingjing, T. and Ziqiang, M. (2015). The molecular mechanisms of sodium metabisulfite on the expression of K_{ATP} and L-Ca^{2+} channels in rat hearts. *Regulatory Toxicology and Pharmacology,* **72**: 440–446.

Quentel, F., Filell, M., Elleouet, E. and Madee, C.L. (2004). Kinetic studies of Sb(III) oxidation by hydrogen peroxide in aqueous solution. *Environ Sci. Technol*. **38**(10): 2843-1848.

Tiwari, R.K. and Mishra, K.K. (1991). Kinetics and mechanism of oxidation of 2-mercaptobenzathiazole by 2,6 – dichlrophenol indophenol in aqueous acetone medium. *Indian journal of chemistry*. **3**: 140–143.

Vogel, A.I. (1996). *Vogel's Qualitative Inorganic Analysis* (Seventh Edition). Prentice Hall, New Jersey. ISBN-10: 0582218667.

Wondrak, G. T. (2009). Redox-directed cancer therapeutics: molecular mechanisms and opportunities. *Antioxid Redox Signal*. **11**:3013 - 3069

Zhao, B., Li, Y., Zhuo, Y., Tong, H., Zhang, X. and Chen, C. (2007). Mass transfer and kinetics study on the sulfite forced oxidation with manganese ion catalyst. *Korean journal of chemical engineering.* **24**: (3), pp. 471-476.