THE EFFECT OF pH ON THE KINETICS OF SYNTHESIS OF METHYL ORANGE

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BY

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SEPTEMBER, 2014

DECLARATION

I declare that the work in this Thesis titled "**THE EFFECTS OF pH ON THE KINETICS OF SYNTHESIS OF METHYL ORANGE"** has been carried out by me in the Department of Textile Science and Technology. All information used in the literature has been duly acknowledged in the text and a list of references provided.

Nuhu Lawal **……** **……**

CERTIFICATION

This thesis titled "**THE EFFECT OF pH ON THE KINETICS OF SYNTHESIS OF METHYL ORANGE"** meets the regulations governing the award of the degree of Master of Science of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Dean, School of Postgraduate Studies	**(Signature)**	**Date**

DEDICATION

This research work is dedicated to Almighty God (S.W) in memory of my late father, Alh. Lawal Aliyu Baba. May Allah (S.W.) grant him his mercy and Jannat Firdaus Amin.

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All praises be to Almighty Allah, the Most Supreme, Most Sublime, Most Beneficent and the Most merciful who give health and strength to go through this course of study successfully.

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ABSTRACT

The optimization of the synthesis of methyl orange was investigated at different pH (3-8) with sulphanilic acid as diazo component and N,N- dimethylaniline as coupling component. The dye was purified by recrystallization, the purity was confirmed by melting point and TLC analysis, then characterized by FTIR and GCMS spectroscopy. Pseudo order method was utilized to study the kinetics of the above reaction where the concentration of reactant [A] (diazo component) was kept constant and that of reactant [B] coupling component was varied and about 20 fold greater than that of [A]. The yield was found to be increasing with decrease in pH values i.e highest yield was obtained at pH 3 followed by 4,5,6,7 and 8. A kinetic model was established according to the order of the reaction with respect to both [A] and [B] at each pH and tested. Theoretical values were calculated using this model and compared with actual (experimental) values using SPSS window.

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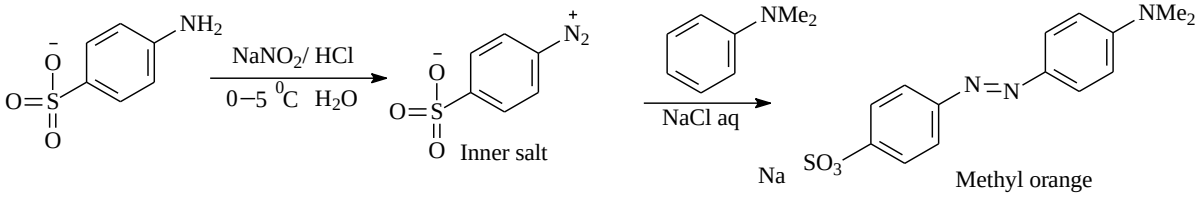
CHAPTER ONE

1.0 INTRODUCTION

Dyes are used to give colour to substances, especially fabrics. Chromophore, functional group that absorbs light, gives colour to the dyes. The most common chromophores are azo, nitro, nitroso, and carbonyl groups. Auxochromes are functional groups that increase the intensity of the colour, also important part of dyes. The most common Auxochromes are hydroxyl, amino, carboxylate and sulfonate groups. Azo dyes have a nitrogen to nitrogen double bond as their chromophore. These dyes are created by taking a diazonium salt and adding it to a strongly activated aromatic system (Gary, 2007).

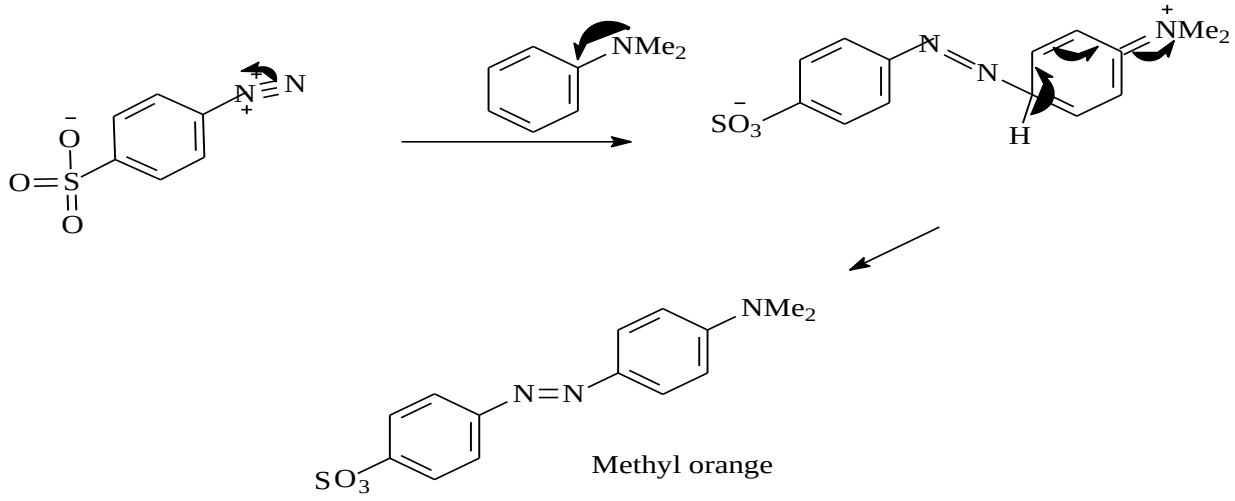
The practice of using dyes is perhaps the most ancient art of chemistry. Dyeing substances from plant, animal, or mineral sources have been known before written history. The accidental discovery of the purple dye, *mauve,* by W.H. Perkin in 1856 is generally considered to be the birth of the modern chemical industry. Several other synthetic dyes followed. One important group is known as the azo dyes, which are named after their unusual N=N, (*azo),* functional group. Methyl orange 4-(4-dimethylaminophenylazobenzene sulfonic acid) is an azo dye that forms orange crystals and is an intensely coloured mono azo compound commonly used as an indicator, but can be used in dyeing and printing textiles. It is also known as C.I. Acid orange 52, C.I.13025, helianthine B, Orange III, Gold orange, and Tropacolin D, *p*-dimethylamino-Azobenzenesulfonic acid. Methyl Orange is synthesized by diazotization and coupling (electrophilic substitution) reaction between aromatic primary amines (sulfanilic acid) and coupling component (N,N-dimethylaniline) (Rahway and Gettermann, 1998).

The first product obtained from coupling is the bright red acid form of methyl orange, called helianthin. In base Helinthin is converted to the orange sodium salt called methyl orange. Diazotization of the salt of sulfanilic acid, which is made by sulfonation of aniline (amine) leads to the formation of inner salt that combine with N,N-dimethylaniline to form the water soluble dye, methyl orange (Warren *et. al.,* 2007).



Scheme1·1 : Diazotization and coupling

The electrophilic substitution is straight forward, occurring in the para position on the activated hindered dialkylamine. It is also noted that nucleophilic attack must occur on the end nitrogen atom of the diazonium salt to avoid forming pentavalent nitrogen.

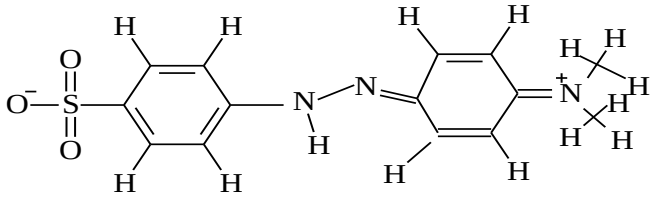


Scheme 1·2 : Mechanism of methyl orange formation

Chemists use methyl orange as pH indicator in titrations due to its very clear colour change. Methyl orange changes colour at a pH of a mid-strength acid and unlike a so called universal indicators methyl orange does not have a full spectrum of colour change, but has a sharper end point (Warren *et al.*, 2007).

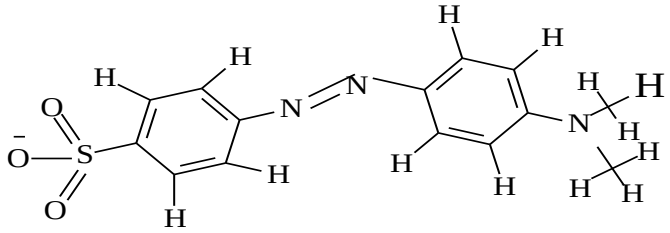
Methyl orange is used in the titration of weak bases with strong acids. It changes from red (at pH 3.1) to orange-yellow (at pH 4.4).

pH related colour changes result from changes in the way electrons are confined in a molecule when hydrogen ions are attached or detached (Gettemann,1961; Rahway, 1998).



Methyl orange in acidic solution

In a solution less acidic, methyl orange moves from red to orange and finally to yellow with the reverse occurring for a solution increasing in acidity. The entire colour change occurs in acidic conditions. In an acid, it is reddish and in alkali it is yellow. Methyl orange has a pKa of 3.47 in water at 25^0C (Rahway, 1998). The molecule absorbs blue-green light, which makes its solution appear red. Nitrogen bearing the positive charge is involved in a double bond. In the basic form of methyl orange, hydrogen ion is lost from the –NN- bridge between the rings, and the electrons formally used to bind the hydrogen neutralize the positive charge on the terminal nitrogen. Solutions of the methyl orange appear yellow in alkaline solution (Rahway, 1998).



Methyl orange in basic solutions

Methyl orange can be used for many different purposes most commonly as an indicator for acid base titration. Other uses include various complex stains to differentiate collagen fibres red.

It is also used in oil field industry for alkalinity test of mud filtrate. Methyl orange can also be used for dyeing and printing of textiles (Smith, 2008). There is not much research work done on the optimization of methyl orange production neither from kinetics nor thermodynamic studies. The first comprehensive study of the kinetics of diazo-coupling was carried out by Paul and Zollinger (1972) using phenol as the coupling component. The rate was represented as proportional to [ArN_2 OH] [Ar-OH], and thought the process is bimolecular reaction between the molecules. However, since active mass of the solvent (water) is constant, the kinetic laws are still satisfied if one molecule is removed from the transition state, the rate being set proportional to [$Ar\text{-}N_2^+$][$Ar'\text{-}O^-$], as an expression of the view that bimolecular reaction occurs between diazonium ion and aryl oxide ion. Wister and Barlett (1941) earlier studied the kinetics of primary amines as coupling components. It was shown that the only generally constant picture of the coupling process is that indicated by assuming [ArN_2^+][$Ar'\text{-}O^-$] to be the appropriate concentration product for coupling with phenol and [ArN_2^+][$Ar'NR_2$] for coupling with amines. Most diazonium ions were thermodynamically stable relative to non ionized dihydroxide, in weakly acidic and mild alkaline media.

Over this range the rate of diazo-coupling increase with pH, but at high pH the equilibrium moves appreciably to the left, reducing the active mass of the diazonium ion, and therefore reducing the accelerating effect of alkalinity on diazo-coupling (Paul and Zollinger, 1972).

$$Ar.N{:}N.OH \rightleftharpoons Ar'N{:}N + OH \qquad 1.1$$

Haight (2008) also used pseudo-order method to study reaction of Sn^{II} + with methyl orange, in which the concentration of methyl orange was found to decrease with time (because methyl orange has a strong absorbance in the visible region of the spectrum and this was used to monitor its disappearance.

1.1 Statement of research problem

Kinetics studies of the synthesis of methyl orange have been taken for granted, despite its very wide usage all over the world.

1.2 Objectives of the research

The objectives of this research are:

a) to examine the kinetics of the coupling reaction between diazotized sulphanilic acid and N, N-dimethylaniline as coupling component.
b) to investigate the effect of pH on the rate equillibria.
c) to develop a model.

1.3 Justification for the work

The use of methyl orange as an indicator, medical stain and also as a dye, make it important enough to investigate the optimization of its production through a study of the kinetics of coupling reaction between diazotized sulphanilic acid and N, N-dimethylaniline as coupling component at different pH values.

1.4 Scope of the work

The scope of this research covers the following:

a) to study the effect of pH on the kinetics of the coupling reaction in the synthesis of methyl orange by using pseudo order method at pH range of 3-8 only.
b) to establish a suitable kinetics.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Dyes

Dyes are coloured compounds or mixtures capable of imparting their colour on a substrate such as leather, cloth, plastic paper etc. in a reasonably permanent fashion, or a coloured substance that has an affinity for the fabric to which it is being applied. The dye is generally applied from an aqueous solution and some dyes require a mordant to improve their fastness on the fibre. Dyes appear to be coloured due to their ability to absorb some wavelengths in the visible spectrum of light more than others. In contrast to dyes, pigments are generally insoluble and have no affinity for the substrates. Furthermore, not all coloured substances are dyes. However, the requisites of a true dye are;

a) it must be able to attach itself to material from solution or to be capable of being fixed on it.

b) it must be soluble in water or other medium, or form a stable and good dispersion in water.

c) the substrate to be dyed must have an affinity for an appropriate dye and must be able to absorb it from solution or aqueous dispersion, in the presence of auxiliary substance under suitable conditions of concentration, pH and temperature.

d) the dye must be fast to washing, dry cleaning, perspiration, light, heat and other agencies when fixed on the substrate. It must also be resistant to the action of water, acid or alkalis in particular (Chatwal, 1990).

2.1.1 History of dyes

Dyeing is one of the ancient crafts and its history can be traced at least about four thousand years back. Until the middle of 19th Century all dyes were obtained from natural sources for example Alizarin was extracted from root of madder and has been used in India since the beginning of recorded history and indigo obtained from the plant indigofera tinctoria. In most cases dyes were extracted from a variety of plants, but also from a few animal sources (Paul and Zollinger, 1972). The root, stems, leaves, flowers and fruits of various plants supplied yellow, brown, blues, blacks and some reds; and from animals sources are reds obtained from extracts of certain dried insects. The famous Tyrian purple was produced from mollusks found on the shore of Mediterranean sea (Paul and Zollinger, 1972).

Perkins was arguably regarded to be the founder of synthetic organic dye industry with the primitive means then at his disposal, he was able to prepare a relatively pure and technically interesting product and was able to develop its synthesis so that it could be used in large scale production (Paul and Zollinger, 1972).

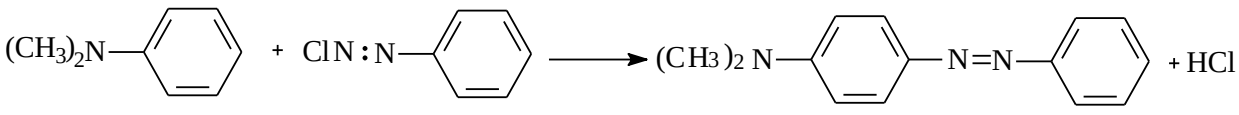
A Chemist named Verguin (1859), in Lyon discovered fuchsin which he prepared by oxidizing a mixture of one molecular equivalent of paratoluidine with two molecular equivalents of aniline with stannic chloride.This was the first of the triphenylmethane group, which are basic dyes and all of which possess intense brilliance of colour. Medlock and Nicholson in 1860 obtained fuchsine by a more effective route, using arsenic oxide as the oxidizing agent, and called the product Magenta. This was soon followed by the production of a dyestuff which was at that time known as Violet Imperial or Bleu de Lyons. It was prepared by heating the magenta with aniline. In 1863, Lightfoot discovered the first successful method of dyeing a good black base on

oxidizing cotton impregnated with aniline. The process gave what was known as aniline black, and was probably used for about sixty years before it was superseded by better method. Hoffmann, methylated or ethylated the amino group in the magenta molecule, and obtained a series of dyes called the Hoffmann violet. The two which survived were the pentermethyl derivative of magenta, which later became known as methyl violet, and the hexamethyl substitution product called crystal violet (David and Geoffery, 1994). The discovery of azo compounds by Peter Griess (1858) in England laid the foundation for the development of the currently largest class of synthetic dyes, namely "azo compounds". He brought to light what is known as the diazo reaction. When aromatic primary amines are treated with nitrous acid (produced by the action of hydrochloric acid and sodium nitrite), they form diazonium salt as illustrated in the equation.

$$C_6H_5NH_2 + HCl + HNO_2 \longrightarrow C_6H_5N{:}\,NCl + 2H_2O \qquad 2.1$$

These compounds are capable of coupling with aromatic amines or hydroxyl to form highly coloured product which when rendered soluble by sulphonation, gives rise to a range of dye stuff known as azo dyes (David and Geoffery, 1994).

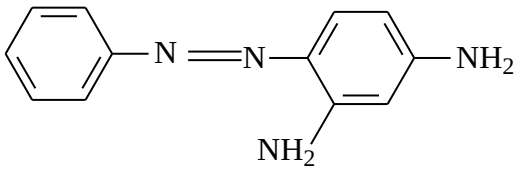
A simple example of a coupling reaction is shown in the following equations



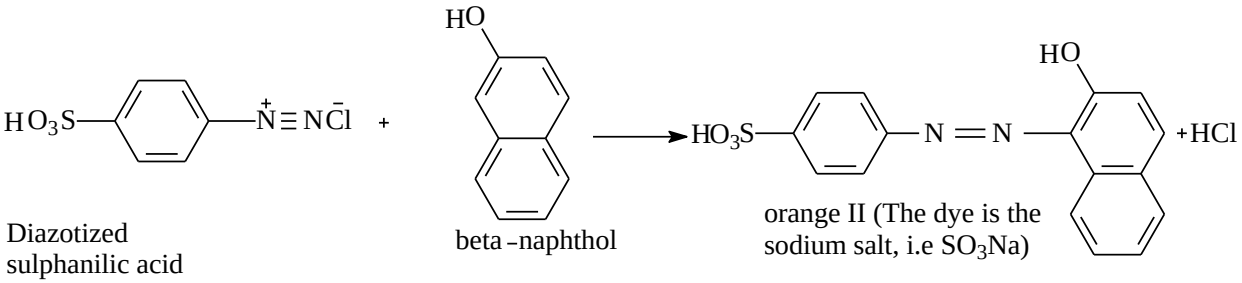
The historic structure given to the diazonium salt was used in the above equation. The weight of evidence points to the fact that ionization occurs in aqueous solutions, it is now considered that their structure is akin to that of an ammonium salt as shown below:

$$[R.N{\equiv}N]^{+}\,Cl^{-} \qquad 2.2$$

Some of the earliest dyes prepared by this reaction were Bismarck Brown in 1865, and Crysoidine G. in 1876. The latter is very simple in structure and was obtained by coupling diazotized aniline with m-phenylenediamine.



Orange II made its appearance in 1876 and was obtained by coupling diazotized sulphanilic acid with beta naphthol.



Diazotized sulphanilic acid

beta –naphthol

orange II (The dye is the sodium salt, i.e SO_3Na)

Orange IV was made by coupling diazotized sulphanilic acid with diphenyl amine. In 1877 Roccelling, the product of coupling diazotized alpha naphthylamine with 4-sulphonic acid of beta naphthol, was added to the family of azo dyes. These were some of the early azo acid dyes with a direct affinity for wool and silk. Perkins, a student of celebrated German chemist, Hofmann produced the first synthetic dye at the age of 18. In the course of his experiments he oxidized aniline with potassium dichromate, and obtained a black precipitate. When this was extracted with ethyl alcohol, a brilliant purple solution was produced which he named "mauvine". Hence he started manufacturing the dye himself with great success (David and Geoffery, 1994). This brilliant work of perkins (producing violet hue on silk) immediately attracted much attention and stimulated other chemists to carry out similar experiments (Chatwal, 1990). In 1868 the first success was achieved in this direction for the elucidation as well as the synthetis of alizarin from anthracene by Graebe and Liebermann in Germany and W.H. Perkin in Britain almost simultaneously (David and Geoffery, 1994).

Until 1884 all the synthetic dyes which had appeared had no affinity for cotton. They could be applied after the fiber had been mordanted. This was lengthy and complicated operation not suitable for quick and cheap dyeing of the mass-produced cloth. It was, therefore, a very welcome event when in 1884 Bottiger prepared congo red and found that it would dye unmordanted cotton by an extreamly simple method, by merely boiling the material in a solution of the dye. The urgent need to simplify the dyeing of cotton was a great incentive to follow up Bottiger's work, and it was not long before an adequate range of analogous dyes became available (David and Geoffery, 1994).

The so-called direct dyes which arose out of Bottiger's discovery were extremely useful and still find very extensive application. Their weakness, however, is lack of fastness to washing and other wet processes. Ever since 1884 there has therefore been a constant search for some means of producing colours on cotton which will stand up better to washing. The approach, until recently, has been to build up an insoluble colour within the fibre by successive application of two soluble components capable of combining in situ.This idea was first given practical expression by A. G. Green, who synthesized a yellow direct dyes named Primuline which itself was of no importance because its fastness was very poor. It did, however, contain within its molecule a primary amino group. Green demonstrated that it was possible to dye cotton with Primuline, then cause it to react with nitrous acid, and subsequently couple the diazotized product with beta naphthol to give a red of much greater wet-fastness. This principle has been extended to quite a number of dyes and is still in use for blacks and navies were adequate fastness at a comparatively low cost is required (David and Geoffery, 1994).

An analogous method of obtaining colours on cotton of satisfactory wet fastness consist of synthesizing an insoluble azo colour within the fibre. In 1880 Read Holliday showed that it was possible to dye cotton by padding it with beta naphthol and subsequently passing it through a solution of diazotized beta naphthylamine. This was called the Vscanceine Red process, but it never found much favour. In 1889 Meister, Lucius, and Bruning with the Badische Co. introduce Para Red, in which the fiber was first padded with beta naphthol and then coupled with the diazotized paranitroniline. This was very successful and in a short time entirely replaced the use of Alizarin for dyeing fast red shades on cotton. In 1893 a French chemist, Raymond Vidal, obtained a product which would dye cotton greenish black by heating together a mixture of sodium sulphide and sulphur with either paranitrophenol or aminophenol.This was the first of a

group known as the sulphur dyes, and was followed by the discovery of sulphur blues, green, yellows, browns, and oranges (David and Geoffery, 1994).

It was the excellent work by Kekule on the Quadra valence of carbon in 1858, and on the constitution of benzene in 1865 that the work started for the planned preparation of purely synthetic dyes, and also for the artificial production of natural dyes. The chemical structure for indigo was established by Von Baeyer in 1880, and this was followed by the synthesis of a number of substituted indigos, some of which became established as successful vat dyes. A new era in the development of vat dyes arrived in 1901 when Rene Bohn, by fusing beta aminoanthraquinone with caustic potash, obtained an insoluble blue substance resembling indigo both in appearance and in the fact that it was rendered soluble by the action of a reducing agent in the presence of alkali. Before leaving cotton dyeing there is one more recent development of profound importance, this is called reactive dyes which contained a cyanuryl chloride group which made them capable of entering into true chemical combination with the fibre (David and Geoffery, 1994). In the beginning of 20^{th} Century, Engi and Friedlander developed indigo dyes. They succeeded in synthesizing Ciba Blue 4B and Thioindigo respectively. In 1901, Bohn synthesized Indanthrone, which is the first anthraquinoid vat dye. Neolan dye (1915), phthalocyanine (1836) and 1,2-metal compex dye, ingrain dyes (1949) were also synthesized. In 1920, Clavel and Dreyfuss also introduced disperse dyes which solved the problem of dyeing hydrophobic fibres.

Cellulose acetate yarn, when it appeared on the market in 1921, presented a new problem because it had no affinity for any of the existing dyestuffs. The first satisfactory method of colouration was due to Holland Ellis who observed that many simple insoluble azo dyes would

be absorbed by cellulose acetate from an aqueous dispersion, stabilized with sulphated fatty alcohols or similar surface active compounds. A large number of dyes whose application depends on this principle have now made their appearance and are known as the disperse dyes. The demand for this group has increased very significantly with the advent of the truly synthetic man-made fibres. After the second world war, certain pigments were also synthesized which achieved importance for colouring plastics e.g Quinoacridone (1948). Later, reactive dyes for wool (1951/1952), Remalan and Cibalan Brilliant dyes and especially reactive dyes for cellulose fibers (procion dyes, 1956,) were also synthesized (Chatwal, 1990).

Reactive dyes, for example, clearly show the general tendency of dyestuff research to move away from purely empirical synthesis of coloured molecules to the study of mechanism and of interaction of substrate and dye with already known chromogenes (e.g.azo, anthraquinone as cyclic azo compounds). Nowadays, thousands of dyes of different constitutions are commercially available and this clearly shows that a thorough knowledge of synthetic organic chemistry (leading to the preparation of new dyes, the discovery of new reactive group etc.) of the reaction mechanism (leading to the optimization process) and of the techniques of applying the results of dye research can ultimately bring success (Paul and Zollinger, 1972). All the early dyes were discovered as a result of purely empirical experiments. They were all derivatives of benzene and it was not until 1865, and this model provided a satisfactory frame work for the interpretation of chemistry of benzene. Before the first world war almost the whole world's requirement of synthetic dyes was manufactured by Germany (apart from Germany, only Switzerland contributed significant portion of world's production), nowadays manufacturing is spread over large number of countries. Yet Germany is still the largest exporter of dyestuffs. Switzerland

produces partially high grade dyes, and the production of markedly cheap dyes is concentrated in countries like China, Japan and Italy (David and Geoffery, 1994).

2.1.2 Classification of dyes

Dyes can be classified either according to their chemical constitution or method of application. There is hardly any chemical class of the dye which occurs solely in one colourist group and vice-versa. In some way, colourist group can be applied to two or more substrates whilst others are specific to a single substrate (Paul and Zollinge, 1972).

2.1.3 Chemical constitution

This is the classification of dyes according to their chemical constitution the most common ones are azo, nitro, nitroso, anthraquinone, phthalocyanine, e.t.c. It is the way of classifying dye based on their chemical structure (constitution), particularly considering the chromophoric group present in the dye molecule (Chatwal, 1990). The chemical constitutions of dyes so varied that it is not possible to classify all the dyes into proper groups. However, the main classes of dyes according to chemical constitutions are given in table below;

Table 2.1: Classification of dyes according to their chemical constitution

Class	Sub-class	Example
Nitro		Naphthol Yellow S
Nitroso		Fast Green O
Azo	Mono azo	Methyl Orange
	Disazo	Congo Red
	Tris-azo	Direct Blue Ew
	Mordant azo	Erichcrome Black T
	Stilbene azo	Chrysophenine G
	Pyrazalone	Tetrazine
Diphenylmethane		Auramine O
Triphenylmethane		Malachite Green
Xanthene		Fluorescein
Acridine		Acridine Orange NO
Thiazole		Basic Yellow T
Indamine and Indophenols		Tolvylene Blue
Azine		Safranine T
Oxazine		Capri Blue GN
Thiazine		Methylene Blue
Cyanine	Methine	Astrafloxine FF
	Quinoline	Kryptocyanine
Sulphur		Sulphur Black T
Lactone		Resofavine W
Amino Ketone		Helindon Brown CR
Hydroxy Ketone		Alizarin Dark Green W
Anthraquinonoid		Erlon Fast Green 3B
Indigoid		Indigo
Sulphurized Vat Dye		Hydron Blue R
Phthalocyanine		Monostral Fast Blue BS

2.1.4 Classification of dyes according to application

Dyes are also classified according to their methods of application for the convenience of dyers (Chatwal, 1990).

I) Acid dyes

These are dyes usually sodium salts of the coloured acid s which may contain sulphonic acid or phenolic group. These dyes give very bright hues and have a wide range of fastness properties from very poor to very good. They are used to dye fibres having basic groups such as wool, silk and polyamides. The application is generally made under acidic conditions which cause protonation of the basic group e.g. Picric acid, Metanil Yellow, Orange II, Naphthol Yellow etc (Paul and Zollinger, 1972).

The dyeing process can be represented as follows:

$$Dye^{-} + H + Fibre \longrightarrow Dye^{-}H^{+}\text{----}Fibre \qquad 2.3$$

II) Basic dyes

These are dyes having amino groups which are protonated under acidic conditions of the fibre by the formation of salt linkages with anionic or acidic groups in the fibre. They generally give intense and brilliant shades but have poor fastness. They are used for dyeing silk and wool directly but not unmordanted cotton (vegetable fibres). Hence, for dyeing cotton, they need mordant such as tannic acid and tartar emetic or some synthetic organic substances, examples of basic dyes include Magenta, Rhodamine, Methylene Blue, Methyl Violent, Crystal Violet etc. (Paul and Zollinger, 1972).

III) Direct dyes

These are dyes that are strongly adsorbed on cellulose. They usually bear sulphonic acid groups. However, these are not considered acid dyes because these group is not used as means of attachment to the fibre. They have poor fastness to washing but are mainly used because they are cheap and easy to apply e.g. Direct Black 17, (Zambezi Black D) (Paul and Zollinger, 1972).

IV) Mordant dyes

These are dyes having a group which can hold the metal in stable combination or chelate groups. The mordant dyes require a pre-treatment of the fibre with a mordant material designed to bind the dye. They get attached to the fibre and then combine with the dye to form insoluble complex called a" lake". Mordants such as aluminium, chromium and iron salts are used, depending upon the fibre and the nature of the dye e.g Alizarin (Paul and Zollinger, 1972).

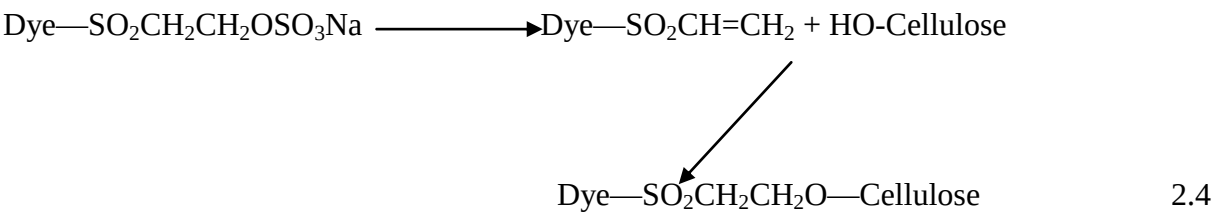
V) Vat dyes

These dyes are insoluble in water, due to the presence of carbonyl group C=O but their reduced forms are soluble. Therefore they are applied in their reduced forms which are obtained by treating the compounds with some reducing agents such as alkaline sodium hydrosulphite in a large wood vat. These dyes are fast to washing and in most cases; they are designed to be fast to light and bleaching as well, e.g. Indigo and Anthraquinone vat dyes. Due to their excellent fastness, they are most often used on cotton fabrics which are subject to severe conditions of washing and bleaching. They are applied on cotton, acetate and wool (Paul and Zollinger, 1972).

VI) Reactive dyes

These are the dyes having suitable groups capable of forming a covalent bond with a Nitrogen, oxygen and sulphur of amino, hydroxyl and mercaptor groups of the substrate. The chlorine atom(s) of reactive dye will react with the hydroxyl group of the fibre in the precence of alkali, e.g. cyanuric chloride (trichloro-triazinyl) (Paul and Zollinger, 1972).

A reactive group may have an activated vinyl group which can react with a cellulose hydroxyl group in the precence of alkali according to the following scheme:



2.4

2.1.5 Azo dye

These are the largest group of industrial dyes having at least one azo chromophoric group (-N=N-) in association with one or more aromatic system (Chatwal, 1990).

Azo dyes also defined as compounds containing azo group (-N=N-) which are linkaged to SP^2 – hybridized carbon atoms. In accordance with the number of such groups, dyes are described as mono, dis, tris, tetrakis etc azo dyes. The azo groups are mainly bound to benzene or naphthaline rings, but in some cases, they are also attached to the aromatic hetrocyclic (e.g Pyrazole) or enolizable aliphatic groups e.g. aceto-acetic acid derivatives. Azo compounds are also defined as dyes and pigments having chromophoric group (-N=N-) in association with one or more aromatic systems. There may be one, two, three or four groups present in a dye or pigment molecule (Chatwal, 1990).

2.1.6 Type of azo dyes

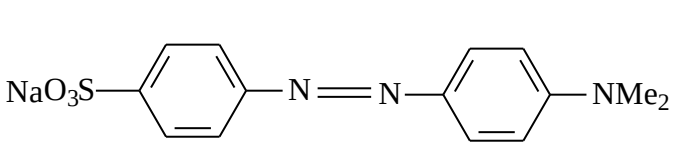
Azo dyes are grouped into various sub-classes these include:

I) Monoazo dyes

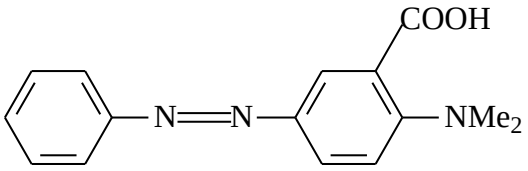
These are considered to be the largest group of dyes belonging to many application classes, they are of A-E type coupling is done in either acidic or alkaline medium.

Monoazo dyes cut across many classes of dyes such as;

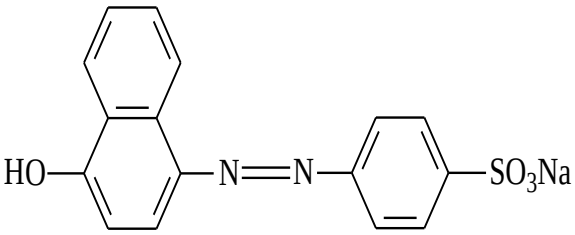
a) Monazo acid dyes have been characterized by the presence of an acid group such as SO_3H, COOH,or phenolic (-OH). It is this acid group that makes the dye more soluble and is also used as reactive group point for fixing the dye. Hence the acid acts as auxochromes in these dyes example of monoazo dyes are Methyl orange, Methyl red, Orange I, Orange II, Orange IV, etc.



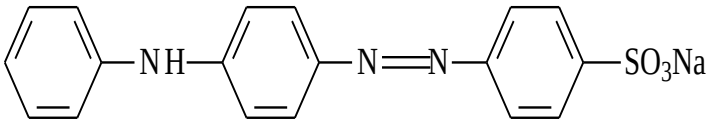
(a) Methyl orange (orange III)



(b) Methyl red

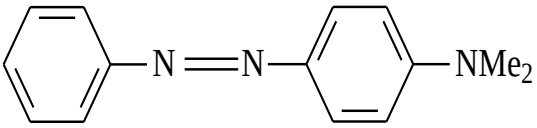


(c) Orange I

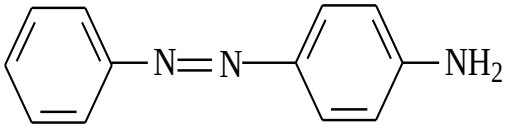


(d) Orange IV

b) Monoazo basic are dyes having $–NH_2$ groups as the auxochrome. The chromophoric group is present as cation. These dyes are not much used and they are therefore not of much significance industrially. So only few of basic dyes are known examples of these dyes are Butter Yellow, Aniline Yellow etc.



(a) Butter Yellow

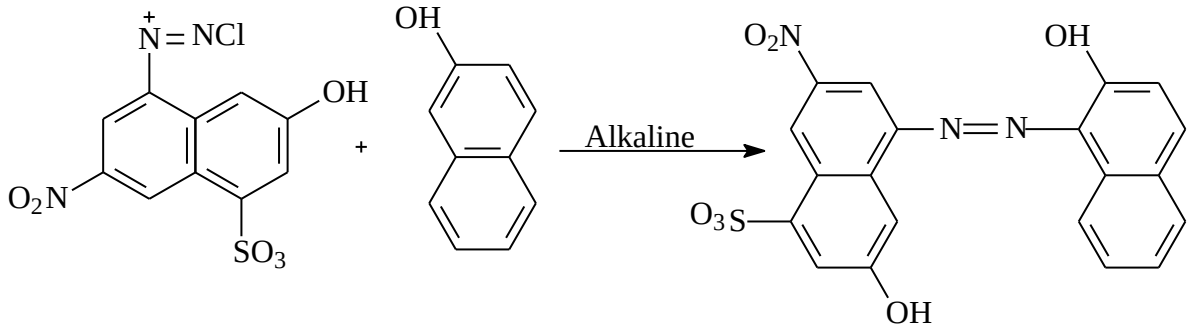


(b) Aniline Yellow

The molecular geometry also played an important role in their application. The fastness of the dye increases with the increase in molecular weights of the dye. However the

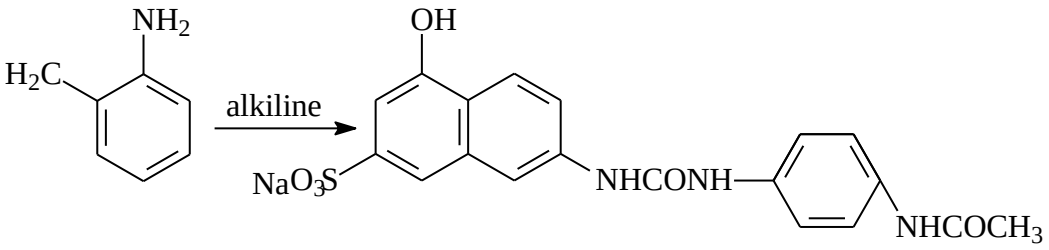
broader the molecule in comparison with its length the higher the fastness, so those molecules that are broad and have high molecular weight are used for dyeing fibres.

c) Monoazo mordant dyes involved many important members of dyes with various characteristic grouping under mordant dyes example of this is Eriochrome Black A.



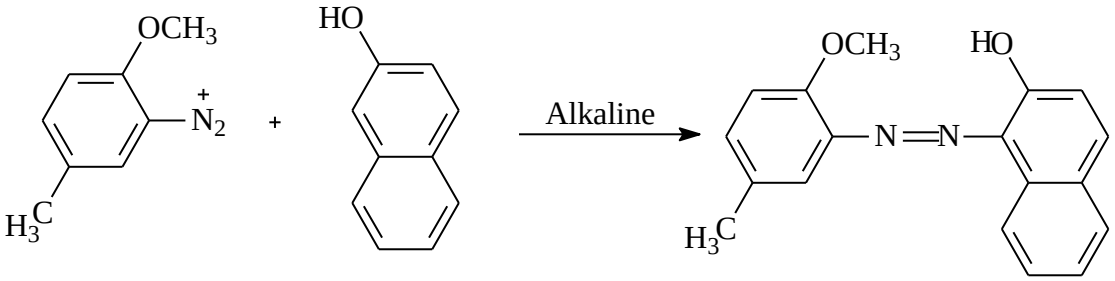
Eriochrome Black A

d) Monoazo direct dyes: Only few direct dyes from monoazo subclass have been used commercially. Only useful dyes of this type have been derived from J-acid derivatives as coupling component example of this dye is C.I Direct Red 65.



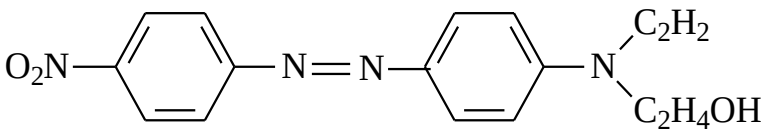
C.I Direct Red 65

e) Monoazo solvent dyes contained no solubilising groups. Example Sudan Red R.



Sudan Red R

f) Monoazo disperse dyes: These are dyes that impart yellow to blue shades on polyester and other hydrophobic fibres example of this dye is Celliton Scarlet B (Chatwal, 1990).



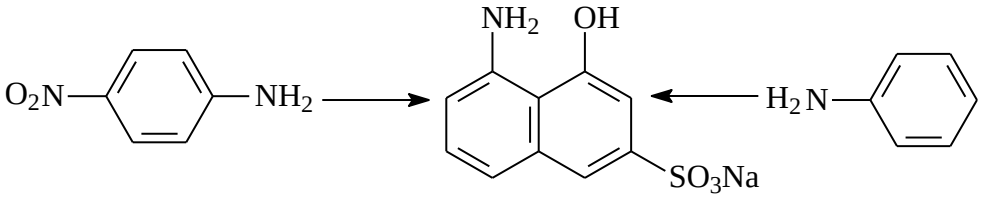
Celliton Scarlet B

II) Disazo dyes

These are dyes that have two azo-groups (chromophoric groups) in a molecule, and are subdivided into (4) four, according to their coupling position(s).

a) Disazo dyes of the type A → Z ← A_1

Various coupling components (Z) such as Resorcinol, Metaphenylene diamine, H-acid etc are used for the manufacture of such dyes. For example Naphthol Blue Black as shown below;



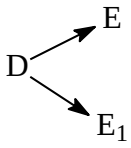
Naphthol Blue Black

A = Paranitroaniline

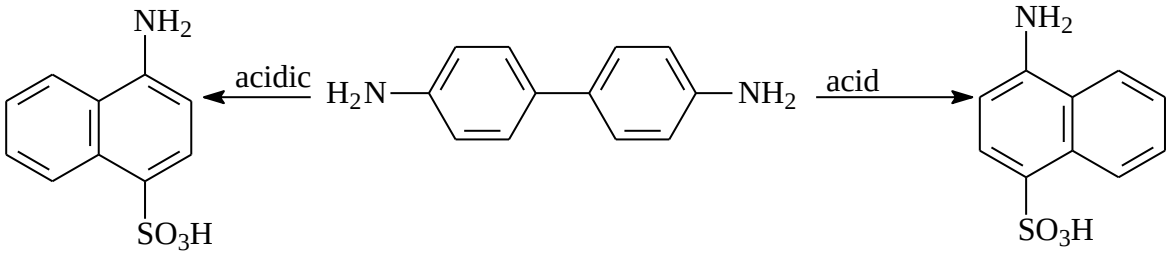
A1 = Aniline

Z = H-acid

b) Disazo dyes of type



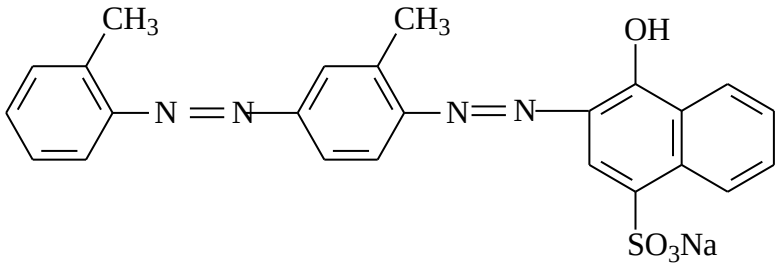
These are obtained when diazonium components having two amino groups (D) are used. In such case the process of getting double diazonium group are known as tetradiazotisation, e.g Congo Red.



Congo Red

c) Disazo dyes of type A → M → E

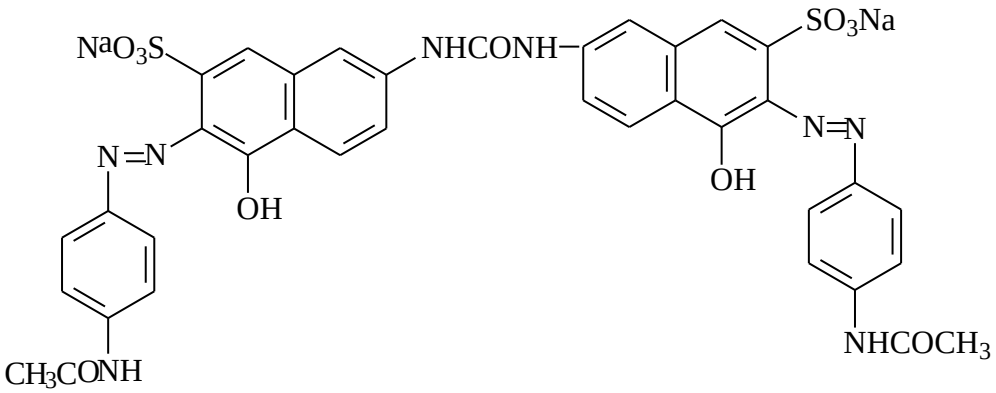
In this case, the middle component M, has been an arylamino group which is capable of diazotization and coupling with suitable end components, for example Cloth Red B.



Cloth Red B

d) Disazo dyes of the type: A → Z → L → A_1

In this case, L is the linkage bridge which can be made by using a condensing agent like phosgene ($COCl_2$) and cyanuric chloride example Chlorazol Scarlet 4 BS.



Chlorazol Scarlet $_4$ BS

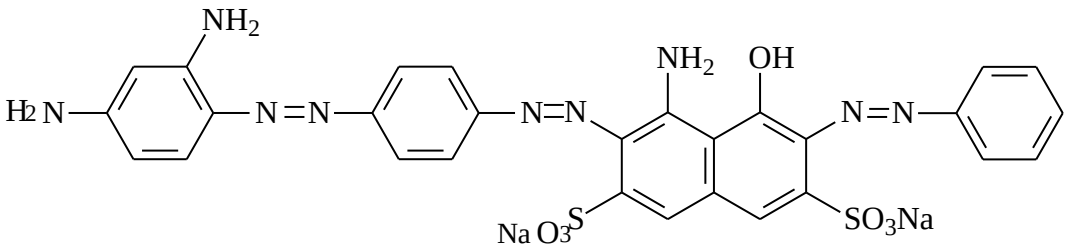
In general, many direct dyes, acid dyes mordant dyes disperse dyes, reactive dyes, solvent dyes, and food colours belong to this diazo dyes depending upon the specific structural requirements. However for the sake of simplicity these classes by application have not been described individually (Chatwal, 1990).

III) Trisazo dyes

These dyes include less number of commercially important members compared to monoazo and diazo dyes. They are produced by combination and permutation of diazonium components and coupling componenets. Hence, they are of three types as follows:

a) Trisazo dyes of the type: E → D → Z → A.

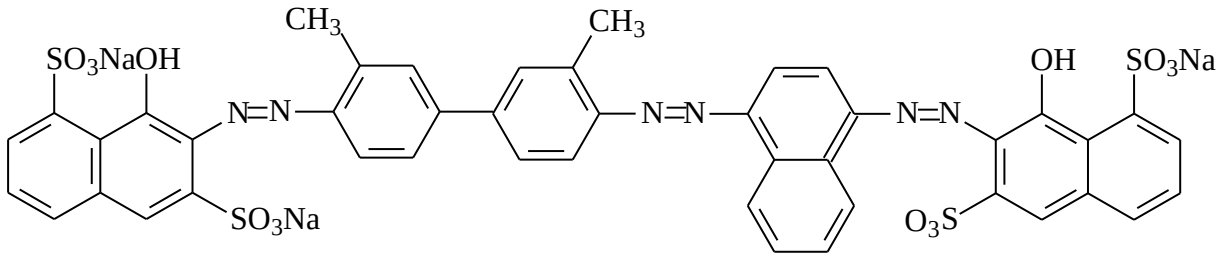
Here an example is Direct Black EW.



Direct Black EW

b) Trisazo dyes of the type: E → D → M → E_1

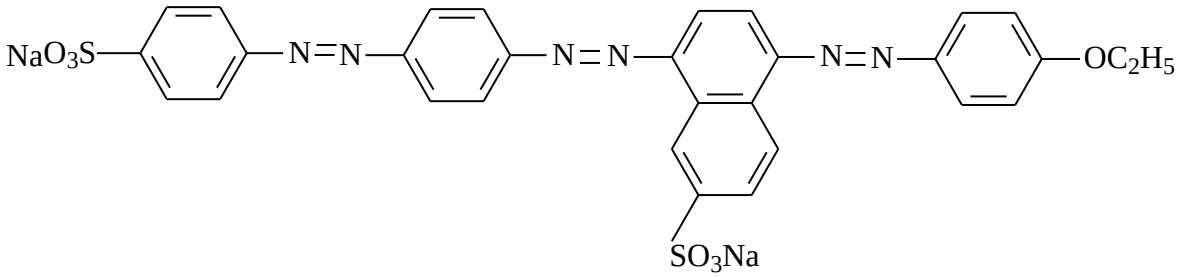
A number of brown, blue and black dyes are prepared following the above scheme Example Benzo Fast Blue R.



Benzo Fast Blue R

c) Trisazo dyes of type: A ⟶ M ⟶ M_1 ⟶ E_1

This type includes a good number of blue, green, brown and grey direct dyes having good fastness to light. Example of this dye is Sirius Supra Brown RL and other type they are bright, fast and give level dyeing on cotton.



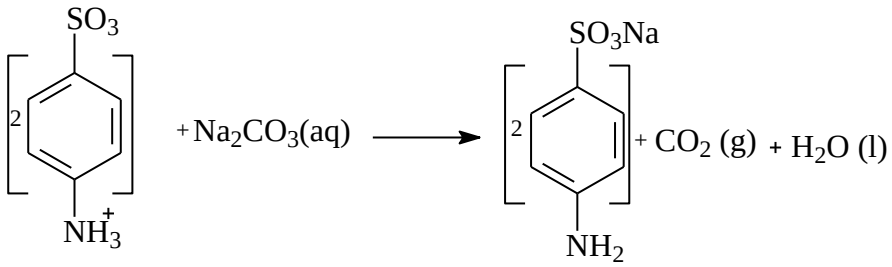
Siriusn Supra Brown RL

2.2 Formation of azo compounds

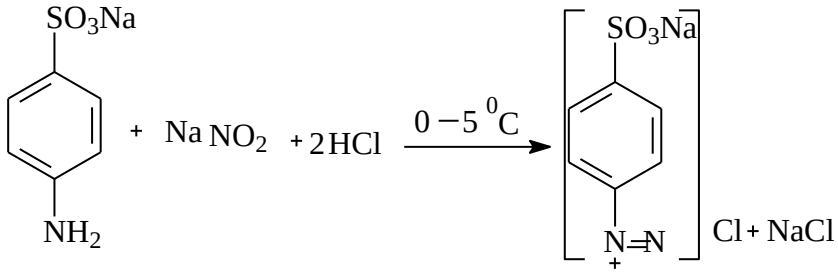
Practically all azo compounds are produced from diazo and coupling components by means of azo-coupling reaction.

2.2.1 Diazotization

Normally an aqueous solution of primary aromatic amine is converted into the diazonium ion at temperature of about 0-5^{0}C by action of sodium nitrite in the presence of mineral acid e.g. HCl, H_2SO_4. At least two (usually 2.5) equivalents of the acid is necessary for smooth reaction (i.e to stabilize the diazonium ion produced and prevent self coupling) (Tewari, 1979).

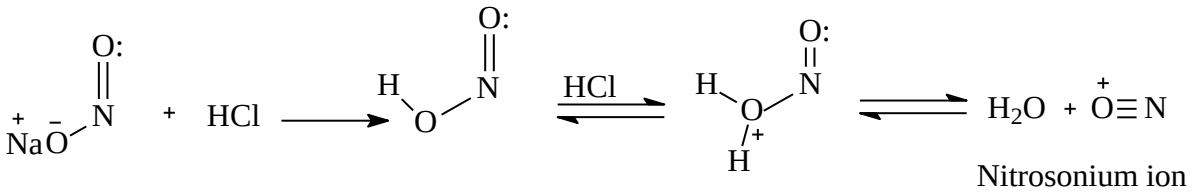


(a) Dissolution of Sulphanilic acid.



(a) Formation of Diazonium salt

Tewari (1979) described how nitrous acid formed by the reaction of sodium nitrite and mineral acid takes up a proton from the acid and undergoes hetrolysis to form nitrosonium ion NO^+.



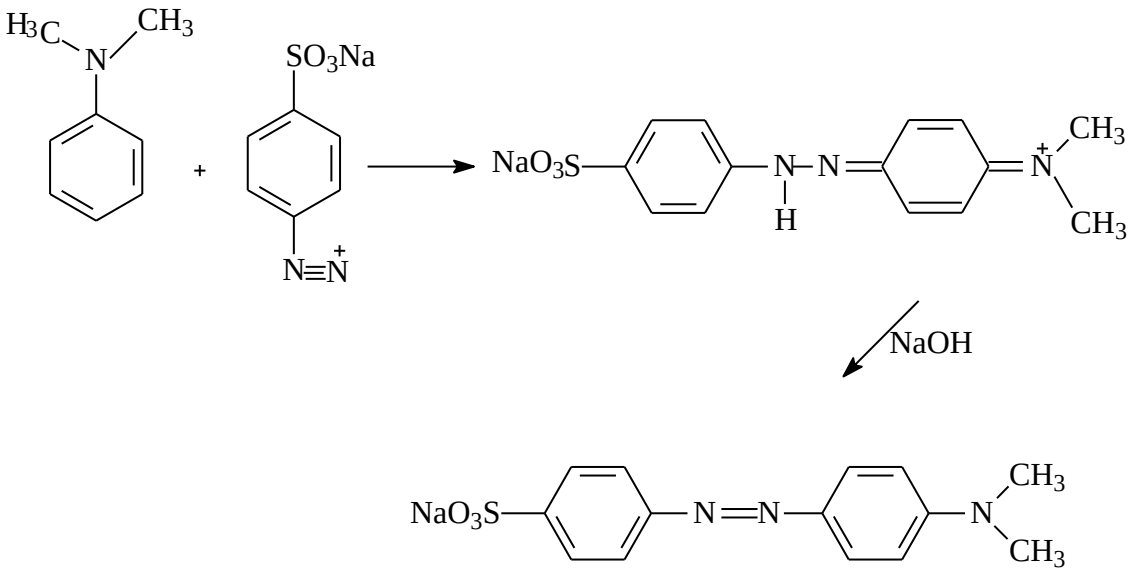
Scheme 2:1 Generation of nitrosonium ion

The electrophilic nitrosonium ion in a slow rate determining step reacts with the nitrogen of the amine and combines with the lone-pairs of electrons of nigrogen to form N-nitroso derivative which by prototropic shift rearrangement forms diazohydroxide. In acidic solution, this diazohydroxide takes up proton by elimination of water molecule to form diazonium ion. This diazonium ion may take up acid anion X to form diazonium salt.

2.2.2 Coupling reaction

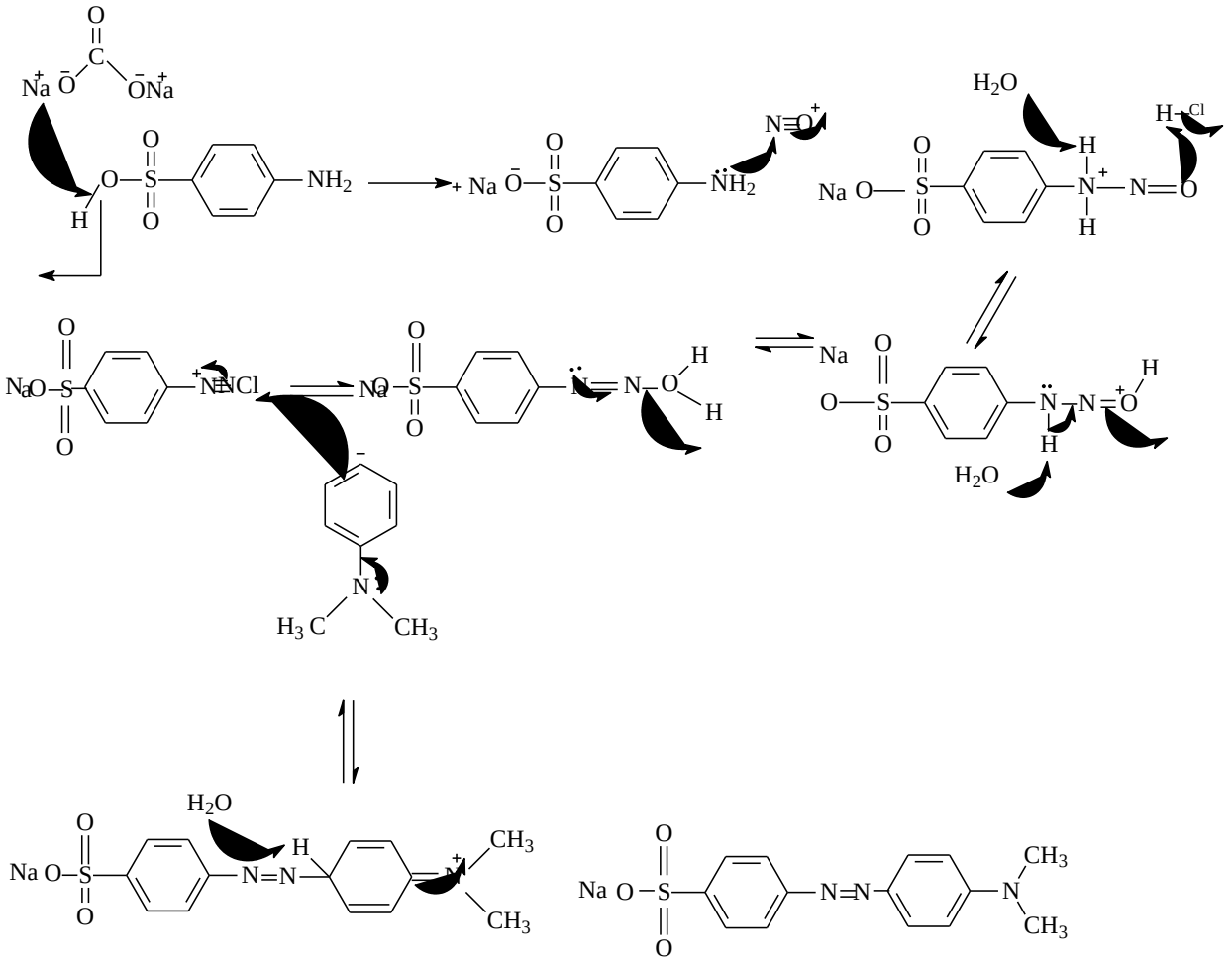
This is an electrophilic substitution reaction between diazonium salt and aromatic primary amines to give azo-compounds having the general formula:

$$Ar—N=N—Ar' \qquad 2.5$$



Scheme 2.2: Coupling Reaction

This reaction is known as coupling reaction, and thousands of azo-compounds have been synthesized by this method for use as dyes.



Scheme 2.3: Mechanism for Methyl Orange formation

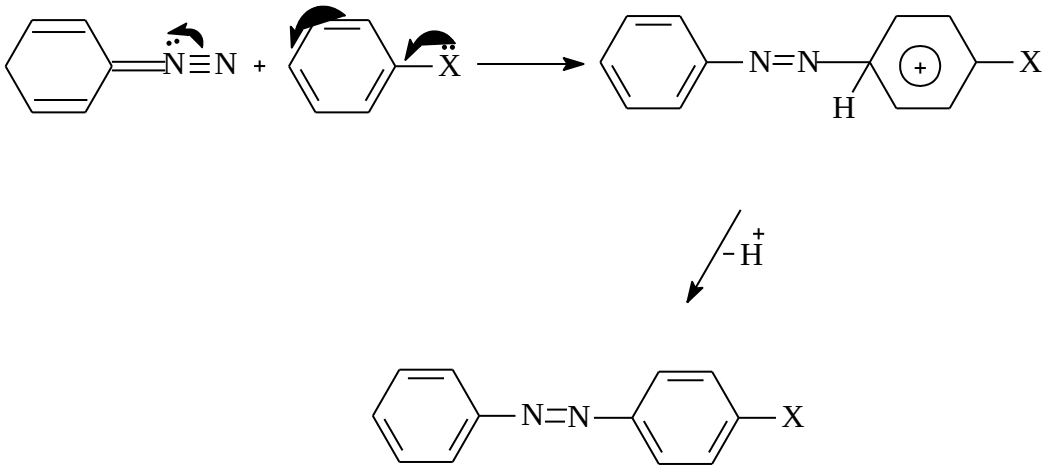
In this reaction, the aromatic compound Ar-H must contain strongly electron releasing groups such as –OH, -NH_2, -OR, -NHR, -NR_2 etc. The coupling usually occurs at Para-position with respect to activating group. If the para-position is occupied, and then the coupling may occur at ortho-position. If both *O*- and *P*- position are occupied, then generally the coupling does not occur but sometimes the subtituent in para-position is knocked off the molecule and coupling occurs at this position (Tewari *et al.*, 1979).

It was clearly stated that in carrying out azo-coupling, it is therefore necessary to take into account, not only this pre-equillibria of the azo compound, but also those of the coupling components. In accordance with the above mentioned rule, i.e the reactivity of the nucleophilic substrate increases with rising bacisity, the phenolate ion ($Ar\text{-}O^-$) and the free amine ($Ar\text{-}NH_2$) must react readily as coupling coupling components than the free phenol (Ar-OH) and ammonium ion ($Ar\text{-}NH_3^+$). So the coupling with phenol is carried out in mild alkaline solution and with amine in weakly acidic medium. This means it is important that the alkalinity or acidity of the medium should be properly adjusted in order to avoid side reactions. If the diazonium salt is present in excess, more than one azo group may be introduced in *O*- or *P*- positions with respect to activating group. There must also be an electrophilic aromatic substitution that are base-catalysed and those that are not affected by the concentration and type of added bases as long as we can disregard the pre-equillibria (hence, general base catalysis has no effect on the pre-equillibria), as specific base catalyses and influences the reaction rate.

Paul and Zollinger, (1972) also re-iterated that coupling reaction must be carried out in a medium in which the pre-equilibria of the diazo and coupling components lie as far as possible towards the diazonium, the phenolate ion, the enolate anion or the free amine, depending on weather coupling is performed with phenol (Naphthol etc) and enol(acetoacetanilide malanonitrile parazolines etc) or with an aromatic amine . This results in an optimum coupling pH region for each combination of diazo and coupling components. This region lies approximately between pH 7 and pH 9 for phenol (pH 9-12 with o-diazophenol as diazo compound).

Murray, (1987) explained that the positive nitrogen atom of diazonium ion is attached to *pi*-system of activated ring and usually bond to the para-position (unhindered) forming a

carbocation followed by fast loss of proton (H^+). Aromatic amines are coupled under slightly acidic medium. This provides an optimum stability of diazonium salt without deactivating the nucleophile, while hydroxyl compound such as phenols are coupled under alkaline medium.



Scheme 2.4: Mechanism of coupling reaction

Schwander, 1982 also stated that the great success of azo dyes is mainly due to the simplicity of the coupling reaction, the possibility for structural variation and often the higher molar extinction coefficient. Of all these classes of dyes, azo dyes have attained the widest range usage.

There are some azo dyes used for dyeing natural as well as synthetics materials, for colouring of paints, vanishes, plastics, printing, inks, rubber, food, drugs and cosmetics while some are used as pH indicators for acidimetric and alkalimetry titration (Kirk-Othmer, 1978).

2.2.3 Effect of substituent on diazotization

Substituent groups can affect the stability and hence the elctrophilicity of the resulting diazonium ion as well as influencing side reactions and condition for coupling. It was observed that 2-Cyno-4-nitroaniline is less basic than 4-nitroaniline (Chatwal, 1990).

The readiness with which an aromatic amine may be diazotized has been found to depend upon the nature and position of the subsituents in the nucleus as affecting the basicity of the amine. For example, as it is to aniline, p-nitroaniline and 2,4-dinitroaniline are much less basic due to the presence of electron withdrawing group (NO_2) and therefore requires special method for their diazotization. For example, weakly basic amines, such as 1,2-dinitroaniline and 1,2-aminoanthraquinone are diazotized by using nitrosylsulphuric acid. Diazotization may give rise to difficulties through low solubility in aqueous acid, the presence of easily replaceable groups such as SO_3H, -NO_2 or the presence of easily oxidisable groups such as –OH, --CHO. A number of methods have been developed to overcome these difficulties (Chatwal, 1990).

The presence of electron acceptor group at ortho-position of diazonium ion will enhance its electrophilic character. Electron donor group on the other hand, decreases the electrophilicity of the diazonium ion as illustrated by 4-methoxybenzenediazonium ion

Thus, coupling reaction involving diazoninium ions with electron donor will be less efficient and give rise to more impurities and lower yields (Paul and Zollinger, 1981).

2.2.4 Effect of substituent on coupling

The stronger the meta-directing groups at ortho or para positions, the more vigorous and rapid is the coupling reaction.

It is also noted that the ortho or para directors group e.g. CH_3, OH, NH_2 etc increase the basicity of coupling component and meta directors such as SO_3H, NO_2 decrease the basicity of coupling component. Electron donation tends to disperse the positive charge of the anilinium ion and thus stabilizes the ion relative to aniline, while electron acceptor destabilizes the ion relative to aniline and intensifies the positive charge (Bailey and Peter, 1988).

2.2.5 Influence of diazo components on colour and λ_{max}

Introducing meta-director into diazo compound enhances the electron interaction in the azo system. If the substitution pattern results in a significant over-crowding, the observed λ_{max} is lower than that calculated from individual substituent effect (Peters and Mehta, 1981).

A dye derived from 2, 6-dichloro-4-nitroaniline has a change in λ_{max} of -22. The negative value is typically of sterically hindered dyes. This steric effect is partially compensated for by increased mobility in the dye system (Idem, 1988).

It is concluded that the conventional diazo components, 4-nitroaniline and 2-chloro-4-nitroaniline in particular are used to produce orange and red dyes, while 2, 6-dichloro-4-nitroaniline produces violet as well as brown and red dyes.

It has been found that the chlorine atom ortho to the azo-linkage causes enforced non-polarity of the phenyl ring, leading to the hypsochromic shift from red to yellow and also causes undesirable

drop in tintorial strength. Meta directors in 2,-4, 6-position of aminoazobenzene diazo component afford blue azo dispers dyes (Daveson, 1972).

2.2.6 Influence of coupling component on colour and λ_{max}

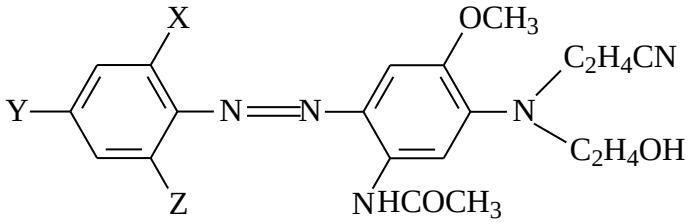
Factors that lowers the ionization potential of the donor half of azo chromogen will cause a bathochromic shift of the visible band; hence this can be achieved in aromatic ring system by;

a) Increasing the number of donor groups
b) Varying the position of attachment of the donor groups relative to the point of attachment of azo group.
c) Increasing the electron donating strength of the donor groups

(Griffith, 1976).

Introduction of ortho or para-director in the coupling components increases resonance which in turn decreases the energy gap of the ground—excited state transition, leading to bathochromic shift, while meta-director diminishes resonance often by forcing pi-orbital out of co-planarity which in turn increases the energy gap of the ground-excited state transition leading to hypsochromic shift (Chatwal, 1990).

Dyes with general formular shown below;



Have a visible absorption maximum (ʎ max) at longer wavelength (bathochromic shift) than those of the same dyes derived from N,β Cynoethyl-N,β-Hydroxyethylaniline as coupling component. Thus the presence of ortho-para director (ethylamino and methoxy group) in the coupling component residue where X=Y=Z=H ($ʎ_{max}$ 397nm) result in bathochromic shift of 32nm relative to the dye from aniline ($ʎ_{max}$ 397nm). This observation was rationalized by Gordon and Gregory (1983) in terms of inter-molecular hydrogen bonding factors rather than electronic-donation (ortho/para) character.

In the dyes based on 4-nitroaniline and N,N-diethylaniline, introduction of methoxy group at 5 position leads to bathochromic shift of 2nm and an acetylamino group at position 2 one of 25nm while conjoint substitution of the group gives a shift of 44nm. Peters in 1985 reported that alkylated amines tend to yield more bathochromic dyes than dyes derived from unalkylated amines and that the secondary substitution of alkyl group tend to have less drastic effect on the hue. Ring substitution of aniline coupling component with donor groups ortho to the azo group tends to result in more bathochromic shift, while that of meta-position to the azo group (ortho to the amine group) often results in hypsochromic shift, particularly if the amine is dealkylated as a result of steric interaction leading to the loss of planarity in the charge-separated species.In azobenzene dye model it has been found that ʎ max depends markedly on the basicity of the tertiary nitrogen atom of the coupling component. It was also testified that the intensified field effect caused by electron acceptor (meta-director) substituent varies with the basicity and hence the hue (Mathew *et al.*, 1970).

This effect is shown below:

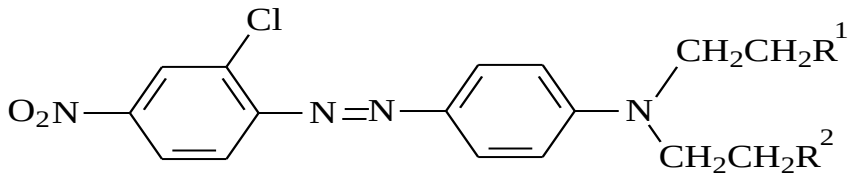


Table 2.2: The dependence of λ_{max} on basicity

R_1	R_2	Pk_b	λ_{max}
CN	**CN**		**474**
CN	**H**		**499**
Cl	**H**		**504**
OH	**H**		**525**
H	**H**	Decreasing	**525**

(Mathew *et al.*, 1970).

2.3 Kinetics

Chemical kinetics is the study of the rate of reactions, reflected in the time-dependence of the concentration of reactants and products. The rate of a chemical reaction is generally expressed as the change in the concentration of a reactant or product per unit time. For example the reaction below shows nitrogen and hydrogen reacting to form ammonia rate may be expressed in three ways as shown.

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3 \qquad 2.6$$

$$\text{Rate} = -\Delta [N_2]/\Delta t \qquad 2.7$$

$$\text{Rate} = -\Delta [H_2]/\Delta t \qquad 2.8$$

$$\text{Rate} = \Delta [NH_3]/\Delta t \qquad 2.9$$

Because by convention chemists treat reaction rate as positive quantity, negative signs are placed in front of the concentration changes for the reactants, because reactants are used up as reaction proceeds and therefore experiences negative concentration changes. Ammonia is formed as reaction proceeds, so its concentration change is positive. Other than this matter of sign, however, there is another minor problem that must be addressed. As a result of the reaction stoichiometry, the changes in concentration of the three substances in a given time period are not the same, and unless it is corrected for this somehow, the rate will be different depending on which of the substances was chosen to express it. This problem is corrected by dividing the concentration change for a species by the stoichiometric coefficient for the species (Haight, 1965).

Thus,

$$\text{Rate} = -\Delta [N2]/\Delta t = -\Delta [H2]/3\Delta t = \Delta[NH3]/2\Delta t \qquad 2.10$$

This is also expressed as the study of reaction rates, the change in concentration of reactant or products as a function of time. The goal of kinetics experiment is to measure the concentrations of species at a particular time during a reaction so that the rate law can be determined (Sparks, 2008).

Kinetics may be seen as an essential qualitative tool for calculating product yields from reactants amount, it tells nothing about the three dynamic aspects of the reaction, which are essential to understanding chemical change. These are:

a) How fast is the reaction proceeding at a given moment?
b) What will be the reactant's and product's concentrations when the reaction is complete?
c) Will the reaction proceed by itself and release energy or will it require energy to proceed? (Avery, 1993).

Likewise thermodynamics only tells how far the reaction may likely occur but quite unable to explain how fast the reaction will likely occur. So this makes thermodynamic to be a necessary but not sufficient condition for predicting reactions and their mechanisms.

2.3.1 Rate of reaction

The rate of a chemical reaction is generally expressed as the change in concentration of reactants or products per unit time. It is a total rate of a reaction and it is the rate in the rate law. Rate of reaction is proportional to the rates of change in concentration of reactants and products i.e the rate is proportional to the derivatives of concentration. The units are always M/s (Avery, 1993).

Considering the reaction below:

$$H_{2(g)} + I_{2(g)} \longrightarrow 2HI_{(g)} \qquad 2.11$$

$$\text{Rate} = \Delta [HI]/\Delta t = - ½ \Delta [H_2] /\Delta t = - ½ \Delta [I_2]/\Delta t \qquad 2.12$$

In general for the reaction below;

$$aA + bB \longrightarrow cC + dD \qquad 2.13$$

The rate is expressed as follows:

$$\text{Rate} = - 1/a \Delta[A] /\Delta t = - 1/b \Delta[B] /\Delta t = 1/c \Delta[C] / \Delta t = 1/d \Delta [D] /\Delta t \qquad 2.14$$

$$\text{Rate} = K [A]^m [B]^n \qquad 2.15$$

Rate laws can also be expressed to relate the concentration of reactants to the time of the reaction expression. This is called an integrated rate law because it is the integral of the differential rate law:

$$\text{Rate} = K [A] = - d [A] / dt \qquad 2.16$$

Rearranging this equation gives the following:

$$\text{In } [A] = -Kt + \text{In } [A]_O \qquad 2.17$$

2.3.2 Reaction order

Order of the reaction is an exponent on each concentration term of that particular reactant or product, and the overall order is the sum of individual orders.

$$\text{Rate} = K [A]^n [B]^m \quad 2.18$$

Here n and m are generally not the same as the stoichiometric coefficients from the balanced equation but some experimentally determined power which may not be equal to n and m. The power n is called the order of the reaction for reactant A, and m is the order for reactant B.

The overall order = (n + m) (Avery, 1993; Haight, 1965).

These component of the rate law: rate, reaction orders and rate constant must be found by experiment, they can't be deduced from the reaction stoichiometry, thus experimental approach is used to find these components by;

a) Using concentration measurement to find the initial rate.

b) Using initial rates from several experiments to find reaction order.

c) Using the above mentioned values to calculate rate constant.

(Avery,1993).

2.3.3 Factors that affect rate of reaction

1) Physical state of the reactants

In order to react, molecules must come in contact with each other, and the frequency of collision between molecules also depends on the nature of the reactants. The more homogeneous (i.e more uniform or similar) the mixture of reactants, the faster the molecule can react. But the more heterogeneous the mixture of the reactant, the slower the molecules reacts; in this case vigorous stirring or grinding may be required (Brown *et al.*, 2006).

2) Concentration of reactants

This is the major factor that influences the rate of reaction. As the concentration of the reactants increases, so does the likelihood that reactant molecules will collide. The more frequently they collide, the more often a reaction occurs. Thus the rate is proportional to the concentration of the reactants (Brown *et al.,* 2006).

3) Temperature

At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy. This means that raising the temperature increases the reaction rate by increasing the number and especially the collision energy (*Brown et al.,* 2006).

4) Presence of a catalyst

Catalysts are important in chemical reaction; in the presence of catalyst the reaction is speed up by changing the way the reaction happen (i.e the reaction mechanism).Catalysts they speed up both forward and reversible reactions. It doesn't increase yield but gives fast product (Brown *et al.,* 2006).

2.3.4 Reaction progress determination

Reaction progress kinetic analysis relies on the ability to accurately monitor the reaction conversion over time. This goal may be accomplished by a range of techniques, the most common of which are described below. While these techniques are categorized as differential (Monitoring reaction rate over time), simple mathematical manipulation (differential or integration) allows inter-conversion of the data obtained by either of the two. Regardless of the

techniques implemented, it is generally advantageous to confirm the validity in the system of interest by monitoring with an additional independent method (Blackmond, 2005).

2.3.5 Reaction progress NMR

NMR Spectroscopy is often the method of choice for monitoring reaction progress, where the substrate consumption and or product formation may be observed over time from the change of peak integration relative to a non-relative standard from the concentration data, the rate of reaction over time may be obtained by taking the derivative of a polynomial fit to the experimental curve. Reaction progress NMR may be classified as an integral technique as the primary data collected are proportional to concentration vs time. This technique has a drawback of requiring a homogeneous system amenable to reaction in an NMR tube (Blackmond, 2005).

2.3.6 In situ FT-IR

In situ Infrared spectroscopy may be used to monitor the course of a reaction, provided that the reagent or product shows distinctive absorbance in the IR spectral region. The rate of reactant consumption and or product formation may be abstracted from the change of absorbance over time by application of (Beer's Law). In situ IR may be classified as an integral technique as the primary data collected are proportional to concentration versus time and from these data the starting material or product concentration over time may be observed by simply taking the integral of polynomial fit to the experimental curve (Blackmond, 2005).

2.3.7 In situ UV-VIS

Analogously to the In situ IR experiments described above, In situ UV-VIS absorbance spectroscopy may be used to monitor the course of reaction, provided that the reagent or product

shows distinctive absorbance in the UV spectral region. The rate of reactant consumption and or product formation may be abstracted from the change of absorbance over time (by application of Beer's Law), again leading to classification as an integral technique (Blackmond, 2005).

2.3.8 Reaction calorimetry

Calorimetry may be used to monitor the course of reaction, since the instantaneous heat flux of the reaction which is directly related to the enthalpy change for the reaction is monitored.

Reaction calorimetry may be classified as a differential technique since the primary data collected are proportional to rate versus time. From these data, the starting material or product concentration over time may be obtained by simply taking the integral of a polynomial fit to the experimental curve (Steel and Naquvi, 1991).

2.3.9 Further technique

Gas Chromatography, HPLC, and Mass Spectrometry are all excellent techniques for distinguishing mixtures of compound (and sometimes even enantiomers).

The time resolution of this measurement is less precise than that of the techniques described above (Steel and Naquvi, 1991).

CHAPTER THREE

3.0 Materials and Methods

3.1 Chemicals

The following reagents were used:

- Sulphanilic acid
- Sodium bicarbonate
- Sodium nitrite
- Concentrated hydrochloric acid
- N, N-dimethylaniline
- Glacial acetic acid
- 20% Sodium hydroxide solution
- Citric acid
- Potassium di-hydrogen phosphate
- Di- Potassium hydrogen phosphate
- Ethanol and
- Petroleum ether

3.2 Equipment

The following equipment were also used in this research work:

- GCMS Spectrophotometer (GCMS-QP2010 PLUS SHIMADZU)
- FTIR Spectrophotometer (FTIR-8400S SHIMADZU)
- pH meter (ISTRPHEPR1 08/01 HANNA)
- Ice water bath (DK-420 GALLENKAMP)
- Hot plate (7/SS618 GALLENKAMP)

3.3 Buffer preparation

The citrate and phosphate buffers of (3, 4, 5, 6, 7 & 8) were prepared by mixing adjusters with a known volume of the primary salt solution and made up to 250ml with water as follows:

1) A= 100ml 0.1M potassium dihydrogen phosphate + mls of 0.1 M NaOH.
2) B= 100ml 0.1M potassium hydrogen phosphate + mls of 0.1M NaOH.
3) C= 100ml 0.1 M citric acid + mls of 0.1M Sodium citrate ($Na_3C_6H_5O_7$)

Table 3.1: Buffer solution

Buffer A		Buffer B		Buffer C	
pH	**Volume added**	**pH**	**Volume added**	**pH**	**Volume added**
3.00	44.6	5.00	45.2	6.00	11.2
4.00	2.0	_	_	7.00	58.2
_	_	_	_	8.00	93.4

3.4 Diazotization

Sulphanilic acid 0.1g (0.0571mol/dm^3) was dissolved in 10ml of 2% aqueous sodium bicarbonate solution in ten separate beakers. A drop of the solution was tested to make sure it is alkaline; and small amount of (2-3ml) of 2% sodium bicarbonate solution was added to each beaker and checked again.

0.2g of Sodium nitrite (0.00289 mol) were added to each of the solution of sulfanilic acid and the resulting mixture were kept in an ice water bath, 0.5ml of conc. HCl was added to each beaker a drop at a time with swirling to avoid rise in temperature. The solutions turned to red-orange at this point. The resulting solutions were kept in an ice water bath at all times (it now contained diazonium salt,) which could decompose if it becomes warm (Brown *et al.,* 2006).

3.5 Preparation of coupling component

In ten separate cleaned test tubes, the coupling component was prepared by using an adjustable pipette to combine 1ml (0.375 mol/dm^3), 1.2ml (0.446mol/dm^3), 1.4 (0.516 mol/dm^3), 1.6ml (0.584 mol/dm^3), 1.8ml (0.651 mol/dm3) and 2.0ml (0.717mol/dm^3) of N,N-dimethylaniline and 20ml of buffer solution (3, 4, 5, 6, 7 and 8) respectively (Brown *et al.*, 2006).

3.6 Coupling reactions

While the flasks labeled 0, 5, 10 15, 20, 25, 30, 35, 40, & 45min containing suspensions of diazotized sulphanilic acid (diazonium ion) was still in an ice bath, 1ml (0.375mol/dm^3)of the above solutions (coupling component) was poured to each beaker at temperature between 0 – 5^0C, golden-orange precipitate was obtained. The concentration of coupling components were varied from 1ml (0.375mol/dm^3), 1.2 (0.446mol/dm^3), 1.4ml (0.516mol/dm^3), 1.6ml (0.584mol/dm^3) and 1.8 (0.651mol/dm^3) and 2.0ml (0717mol/dm^3). The coupling times were

also varied from 0, 5, 10, 15, 20, 25, 30 35, 40 & 45. These reactions were deactivated/inhibited at interval of five minute for each (0-45min) by slowly adding $3cm^3$ of 20% sodium hydroxide solution after the specified period of time and stirred vigorously. The mixtures were removed from ice bath and the crystals formed were filtered drained and washed with little ethanol and finally small amount of petroleum ether and then air dried. The residue (orange precipitate) was scraped from the filter paper and its weight was taken. From the weight molar concentrations were calculated for each dye produced (Brown *et al.*, 2006).

3.7 Purification

The dye was purified using the following methods:

3.7.1 Recrystallization

The dye was dissolved in acetone, water was added and then boiled untill fully dissolution. The dissolved mixture was filtered and the filtrate was allowed to cool slowly at room temperature for more crystals. The crystals were filtered and the above experiment was repeated three times for more purity (multi-solvent recrystallization method) (Laurence *et al.*, 1989).

3.7.2 Thin layer chromatography

The purity of the recrystallized dye was checked using TLC procedure and the R_f value was calculated (Christopher *et al.*, 1989).

3.8 Characterization

The sample was also characterized as follows:

3.8.1 Wavelength of maximum absorption (λ_{max})

Maximum absorbance of the purified sample was measured in water, acid and alkali using ultraviolet/visible spectrophotometer (UV-Vis-2700-2800).

3.8.2 Melting point

The temperature at which the dye melt was also determined using melting point apparatus (Gallenkamp).

3.8.3 FTIR

An infrared spectroscopy was carried out using (FTIR-8400S) to investigate the functional group present in the dye this reveles whether or not there are impurities in the sample. It also justified if the compound obtained was methyl orange or not as shown in appendices (John *et al.,* 1999).

3.8.4 GCMS

The dye was analyzed using gas chromatography mass spectrophotometer (GCMS-QP2010) to explore the molecular weight of the dye and also elucidate its structure as shown in appendices (John *et al.,* 1999).

CHAPTER FOUR

4.0 RESULTS

The results obtained during this research work would be as follows:

4.1 characterization of the product

The dye synthesized was characterized by determining its M.P, Rf value and λ_{max}. It was also analyzed using FTIR and GCMS spectroscopy as the results are shown in the Table 4.1

Table 4.1: Some physical and UV-Visible spectroscopic data

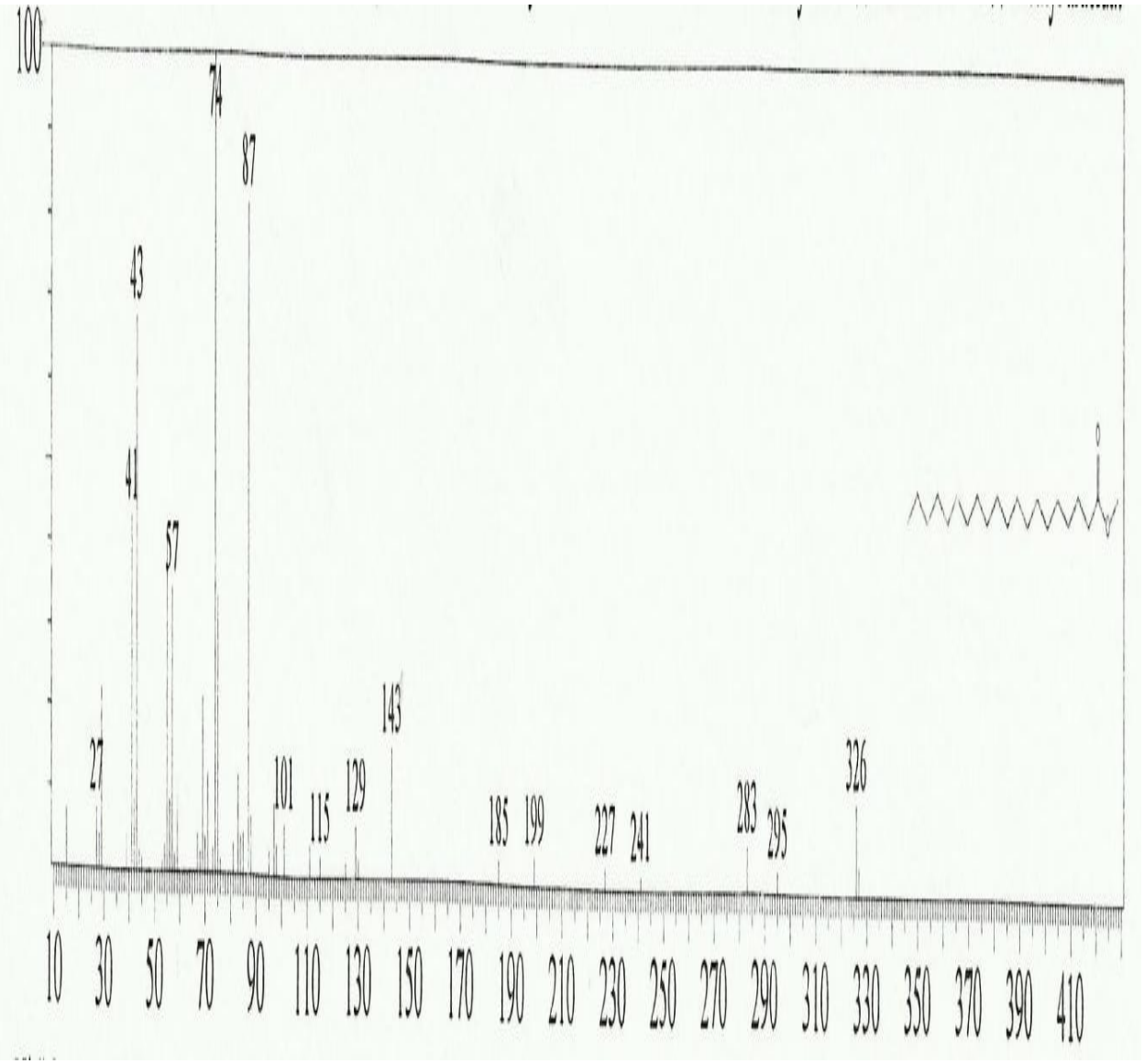
solvent	λ_{max} nm	$\Delta\lambda$	Rf	Mp	FTIR peaks(cm^{-1})
Water	460	-	0.96	304-306	C-H (2816.16)
HCl $_{(aq)}$	510	+50			SO3 (1323-1372)
NaOH $_{(aq)}$	410	-50			C-N (1372-1423)
					Ar (1405-1672)
					N=N (1522-1603)
					C=C (1603-1622)

Where $\Delta\lambda = \lambda_{max}$(solvent – water)

(John *et al.,* 1999; Laurence *et al.,*1989; Silvestein and Wevster, 1997).

4.1.1 GCMS spectroscopy: The compound was analyzed and the peaks representing each of its fragments were identified (Silvestein and Wevster, 1997).

GCMS SPECTRA



4.2 The kinetics data at various pH

The yields were obtained after coupling reaction between diazotized sulphanilic acid and N,N-dimethyl aniline, at various pH values (3-8), coupling time (0-45 min) and concentration of couling component (1.0-1.8 ml). Their masses were taken in grams and then converted to molar concentration (mol/dm^3) see appendices.

4.3 Cumulative product

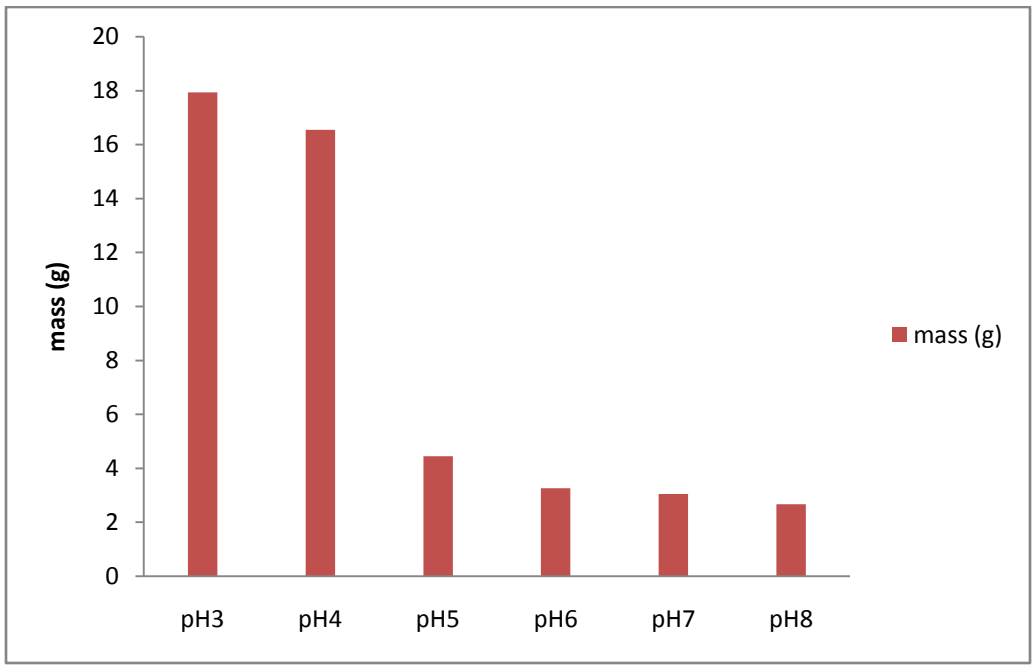


Fig 1: The cumulative yield (g) of Methyl orange at pH 3-8

This is the cumulative mass of the product (methyl orange) at different pH values (3-8), it is observed that the yield (g) was decreasing as the pH values increase.

4.4 Kinetics data for testing of model

Theoretical values were calculated using the model at various pH values (3-5) under which maximum yield was obtained, while actual (experimental) were generated in the laboratory by weighing the mass of the product of coupling reaction between diazotized sulphanilic acid and N,N-dimethyl aniline as shown in Table 1-3 of the appendices.

4.5 Analysis of kinetics data

The kinetic data of the reaction were obtained by using the mass of the product and converted to molar concentration.

Integrated rate equation was used from first to second order kinetics to find the reaction order in [A] as shown below.

4.5.1 Graph of ln[A] against time (s)

A graphs of ln[A] against time (s) were plotted in order to investigate the order of the reaction with respect to [A] (diazonium ion) and the following curves were obtained;

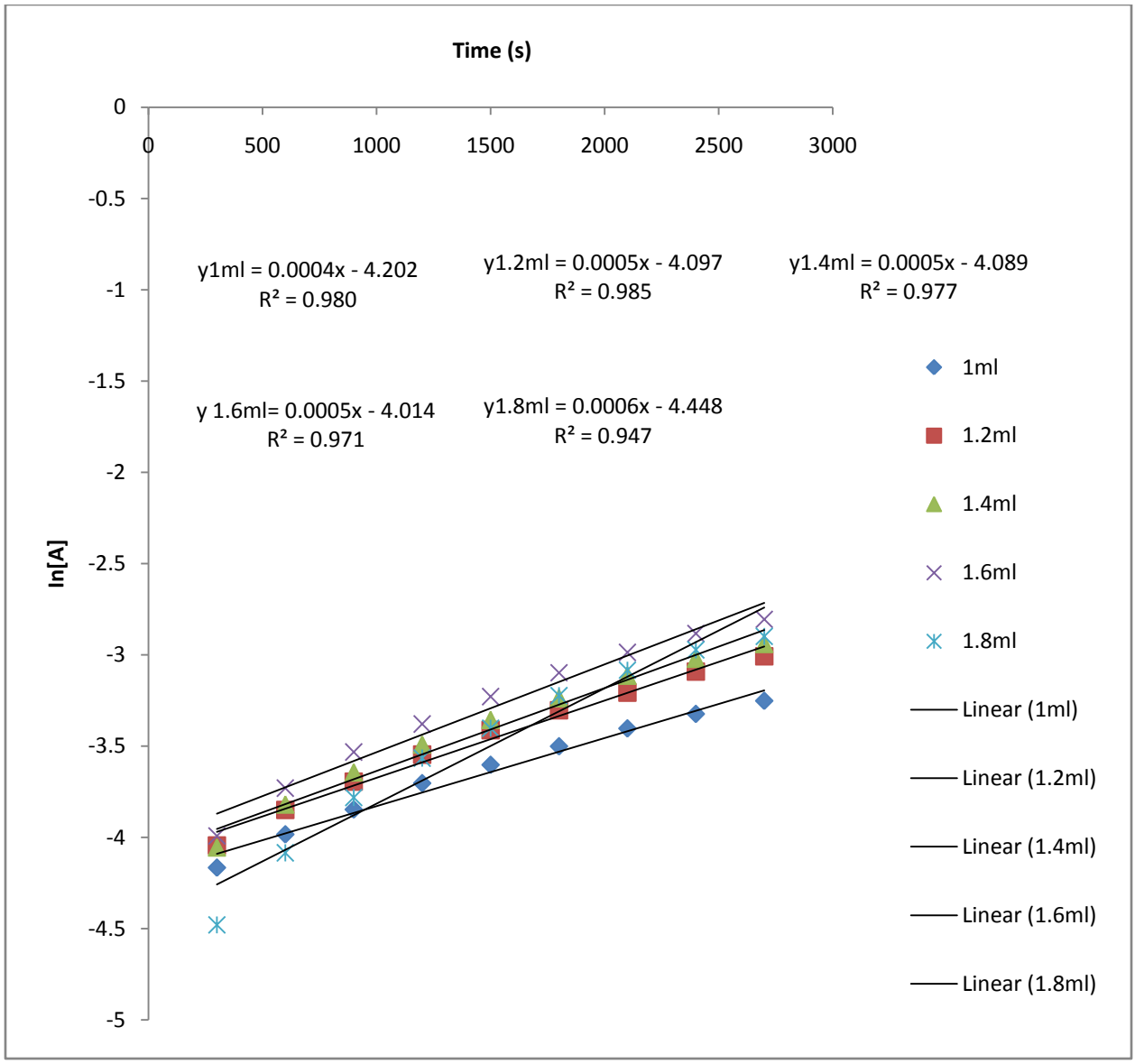


Fig 4.1: The rate curves for first order at pH 3

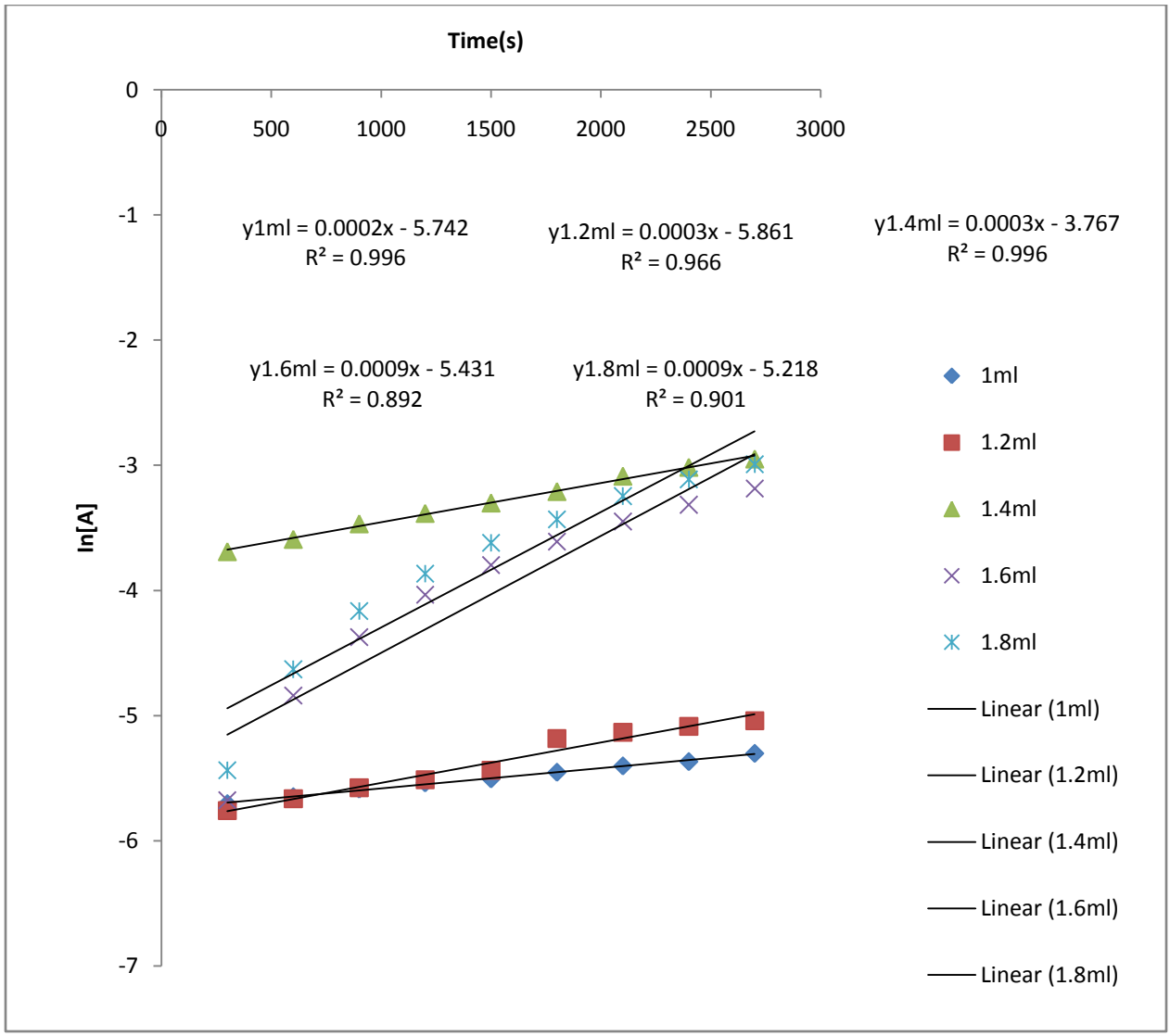


Fig 4.2: The rate curves for first order at pH 4

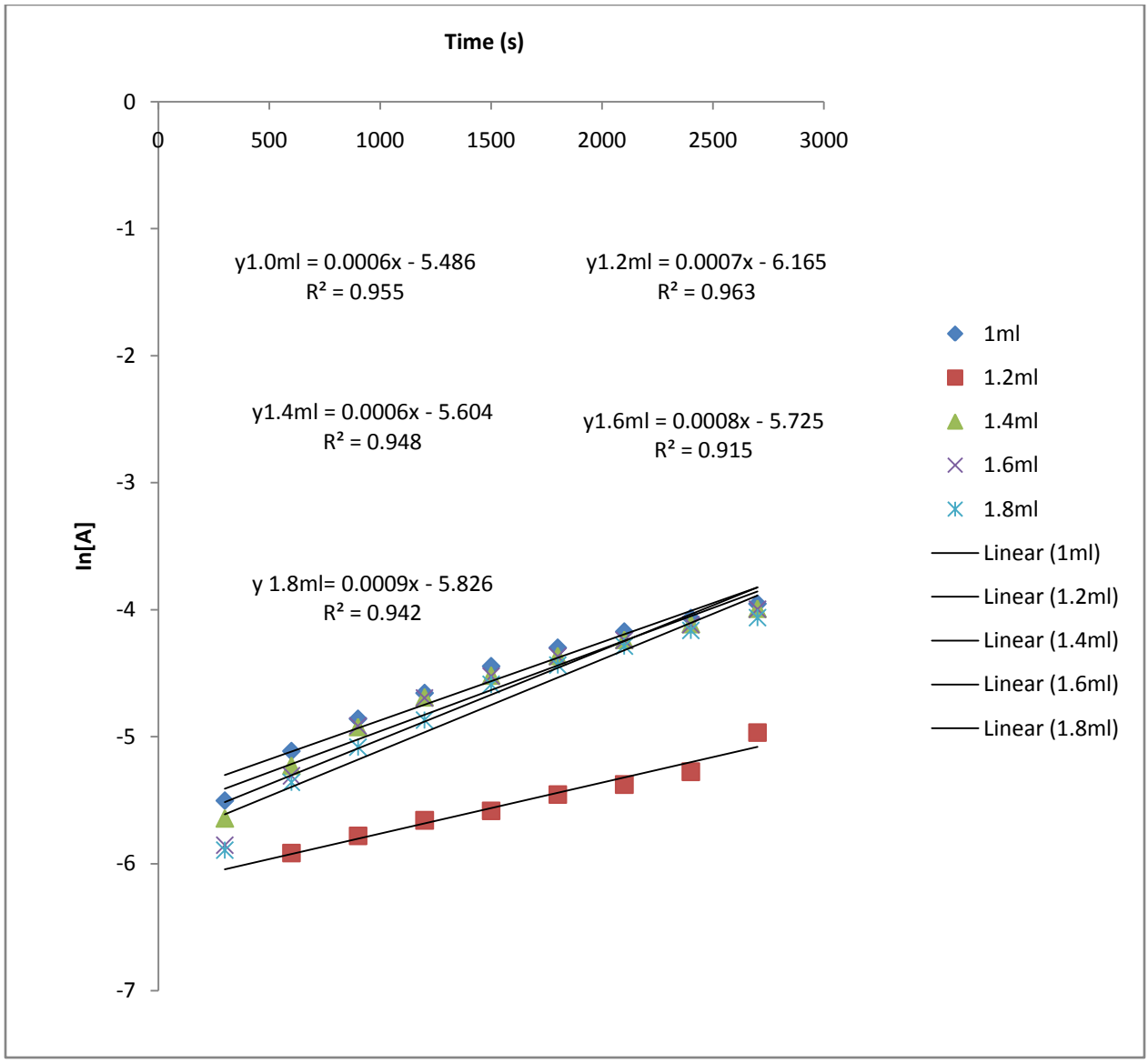


Fig 4.3: The rate curves for first order at pH 5

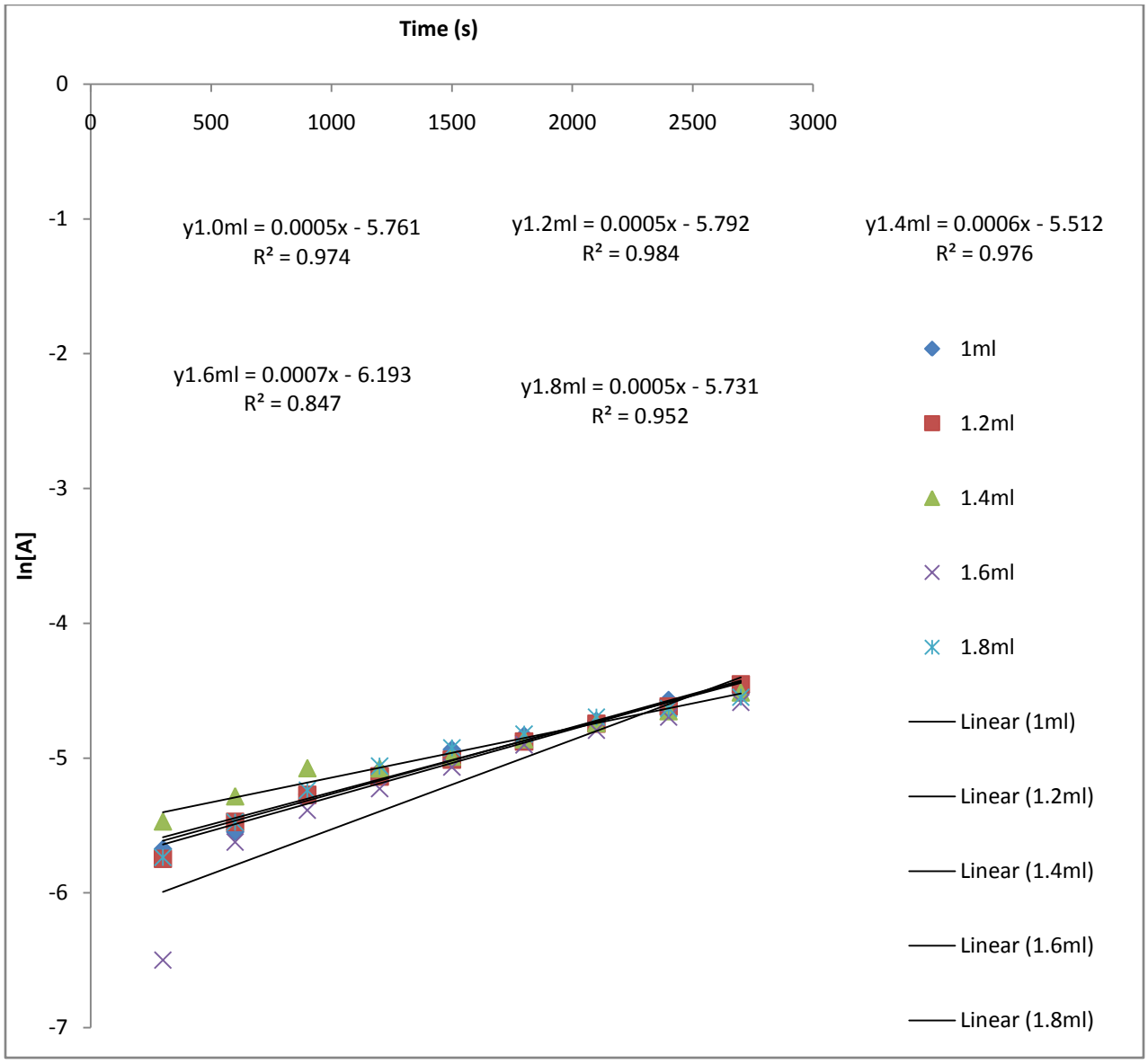


Fig 4.4: The rate curves for first order at pH 6

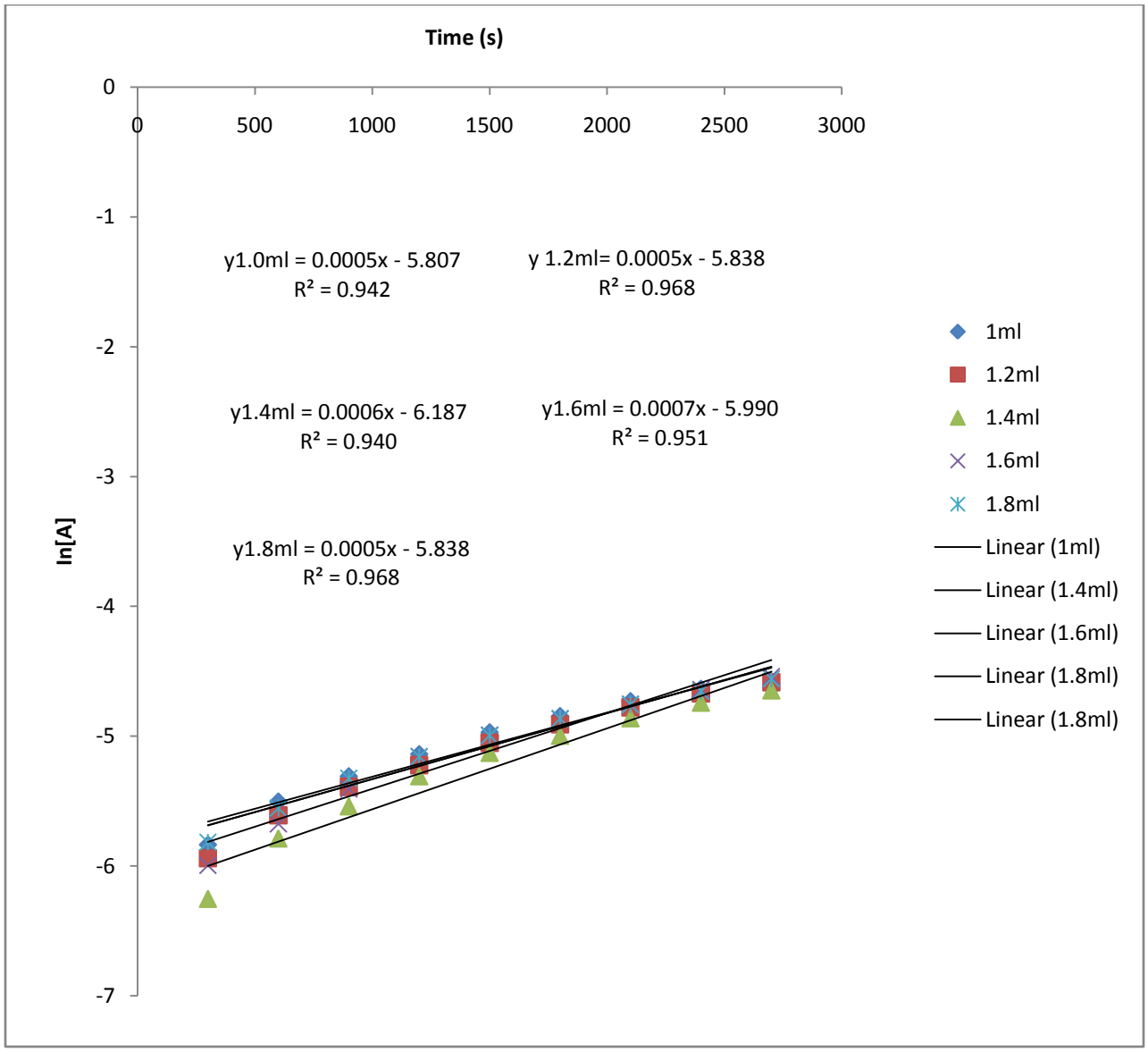


Fig 4.5: The rate curves for first order at pH 7

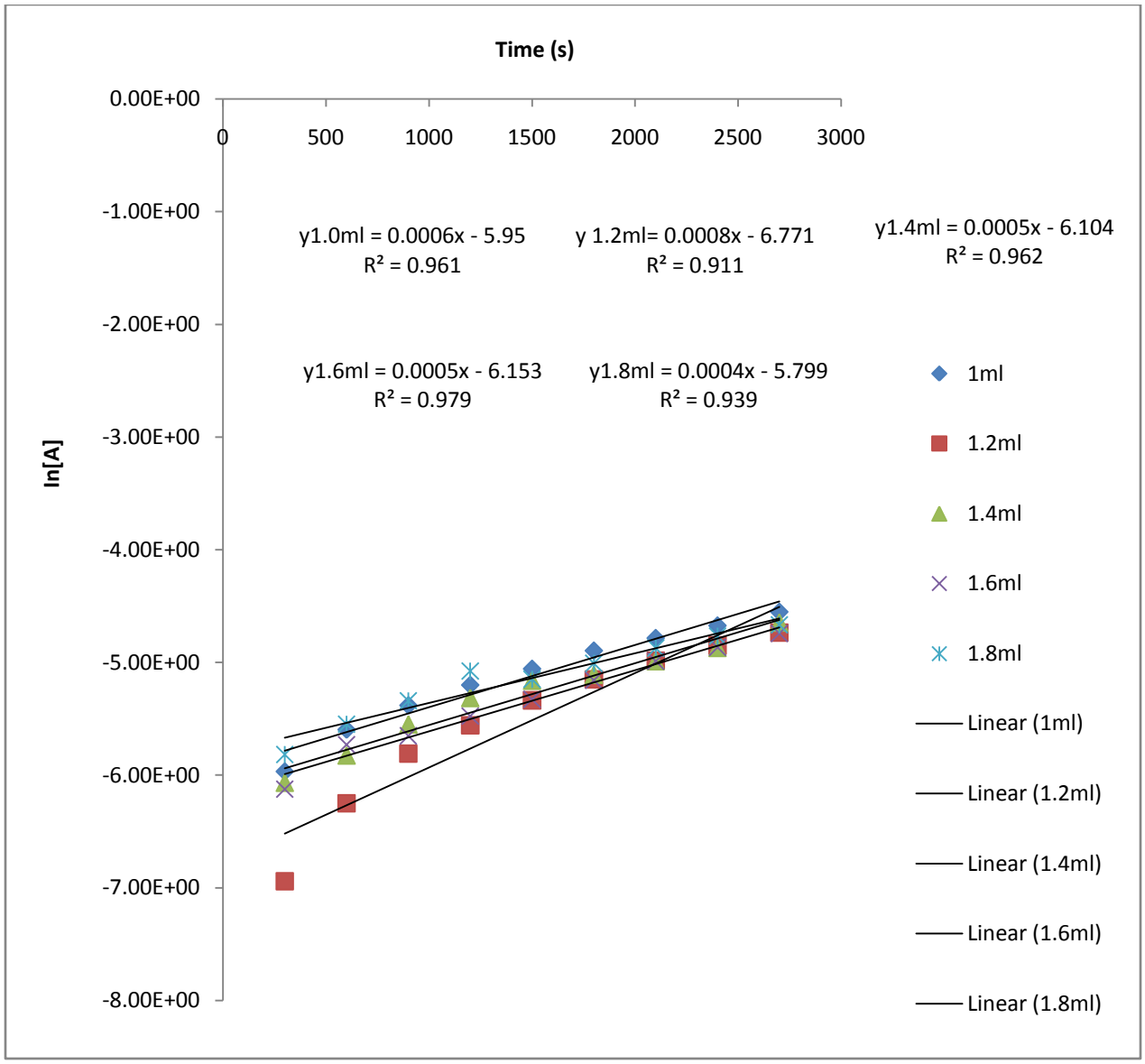


Fig 4.6: The rate curves for first order at pH 8

4.5.2 Graph of 1/[A] against time (s)

A graphs of 1/[A] against time (s) were plotted in order to investigate the order of the reaction with respect to [A] (diazonium ion) and the following curves were obtained:

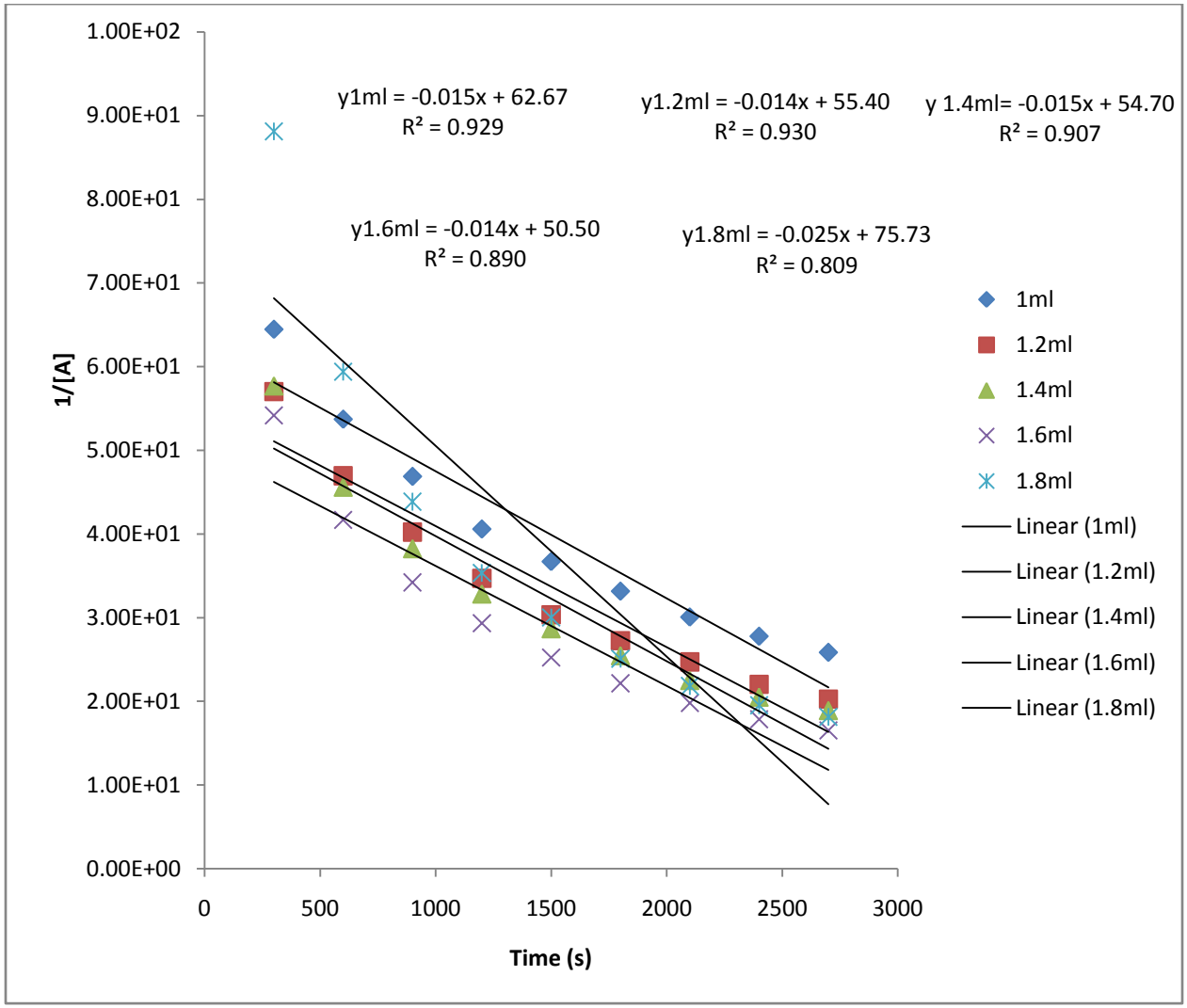


Fig 4.7: The rate curves for second order at pH 3

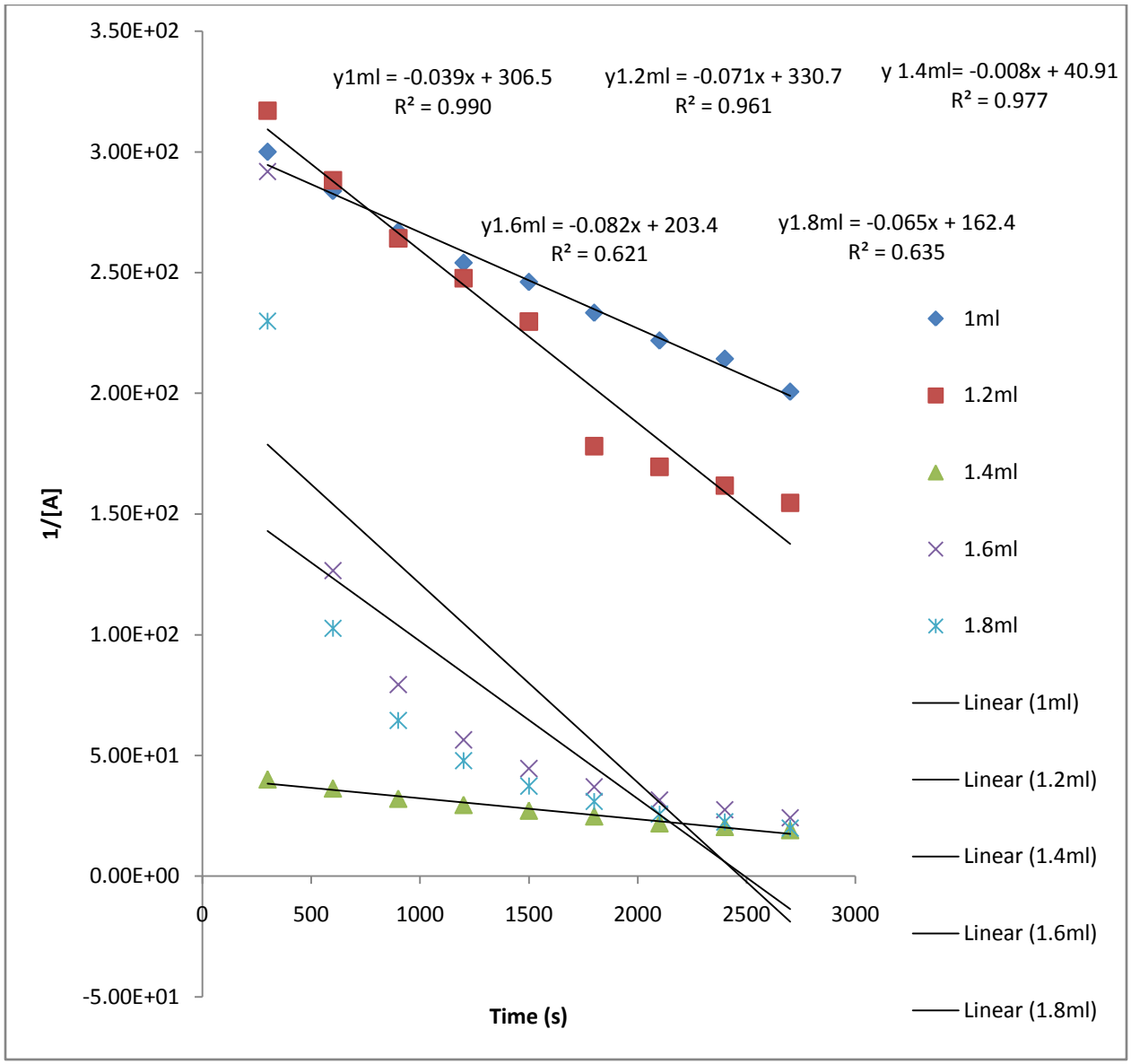


Fig 4.8: The rate curves for second order at pH 4

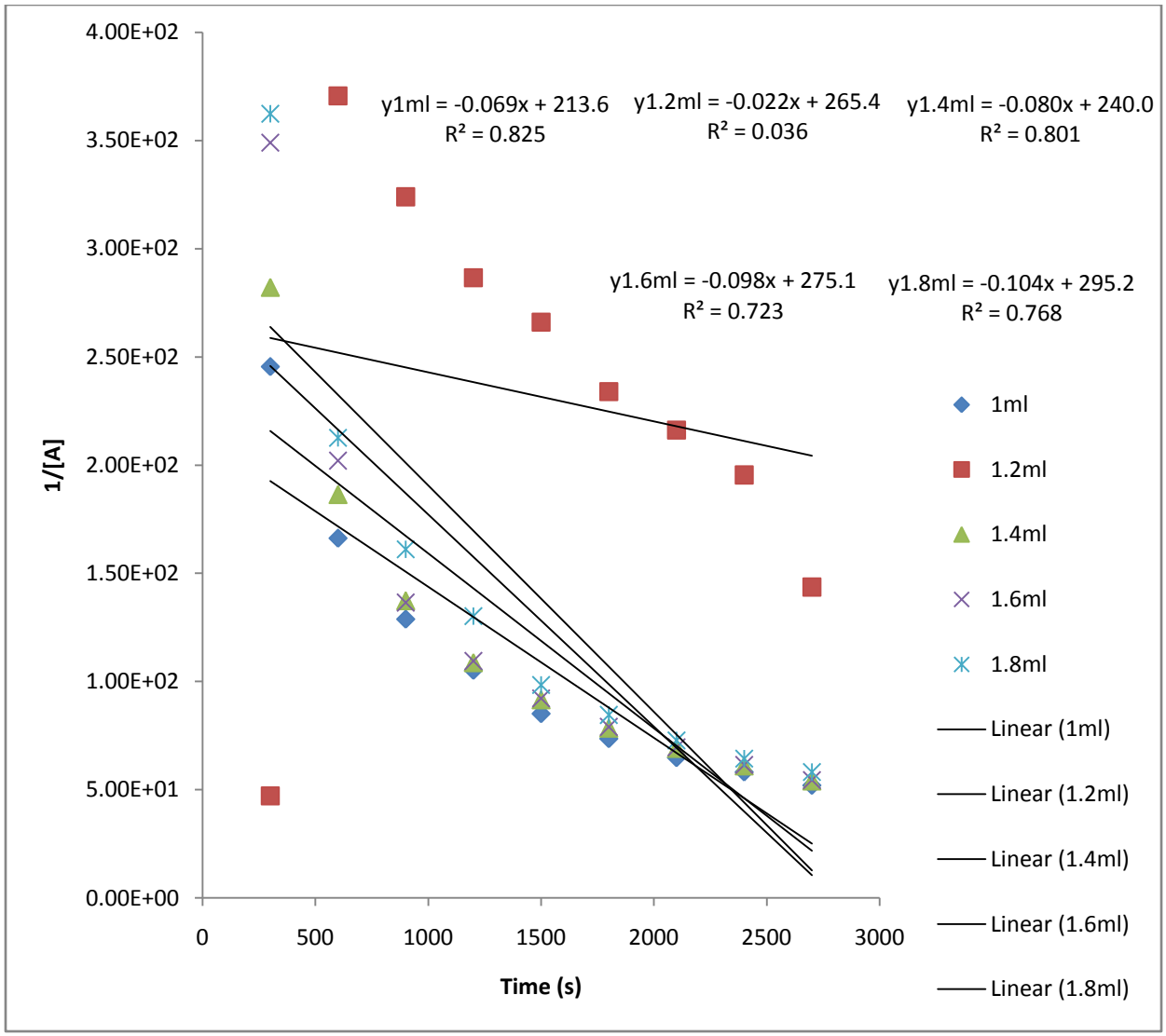


Fig 4.9: The rate curves for second order at

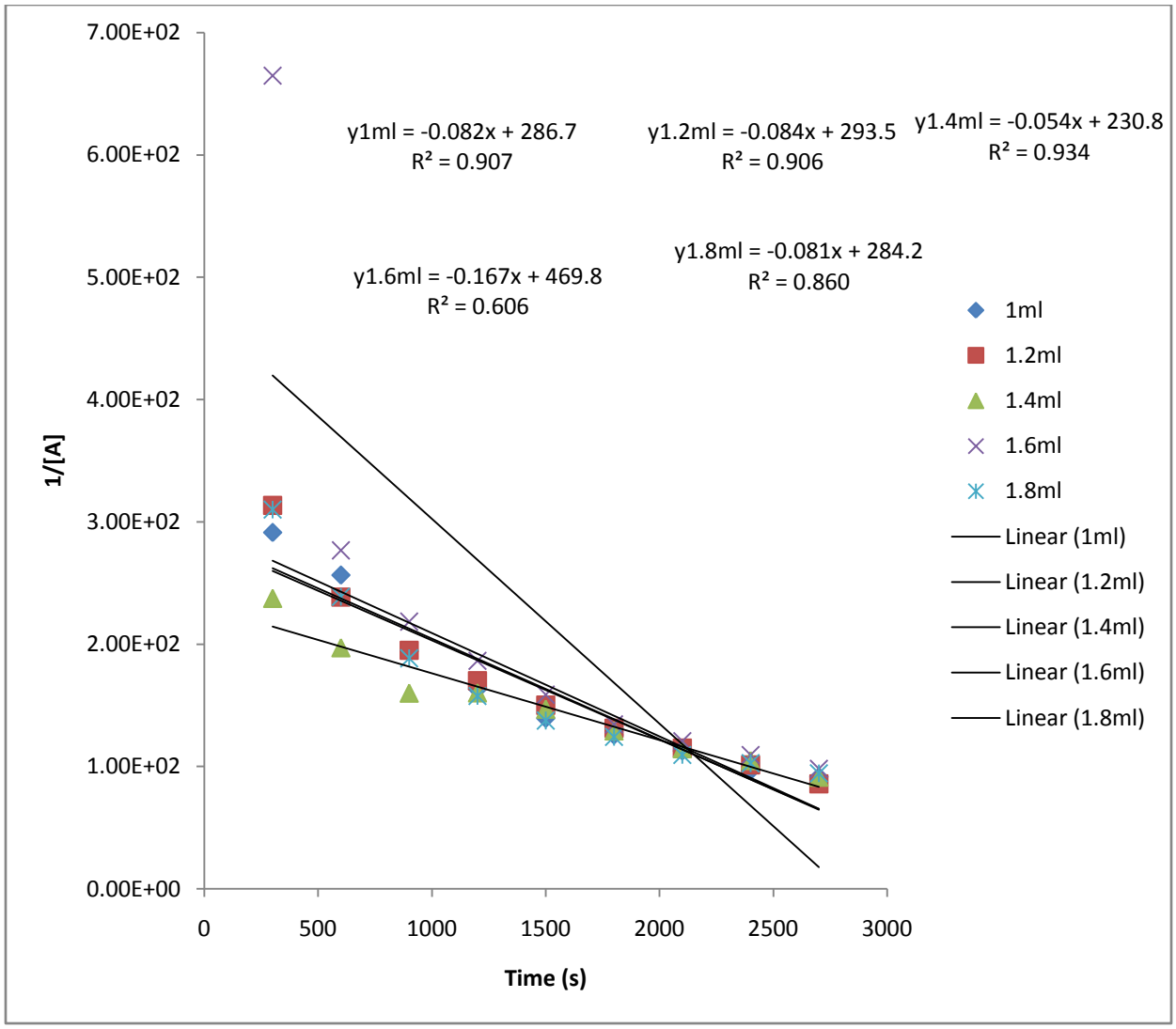


Fig 4.10: The rate curves for second order at pH 6

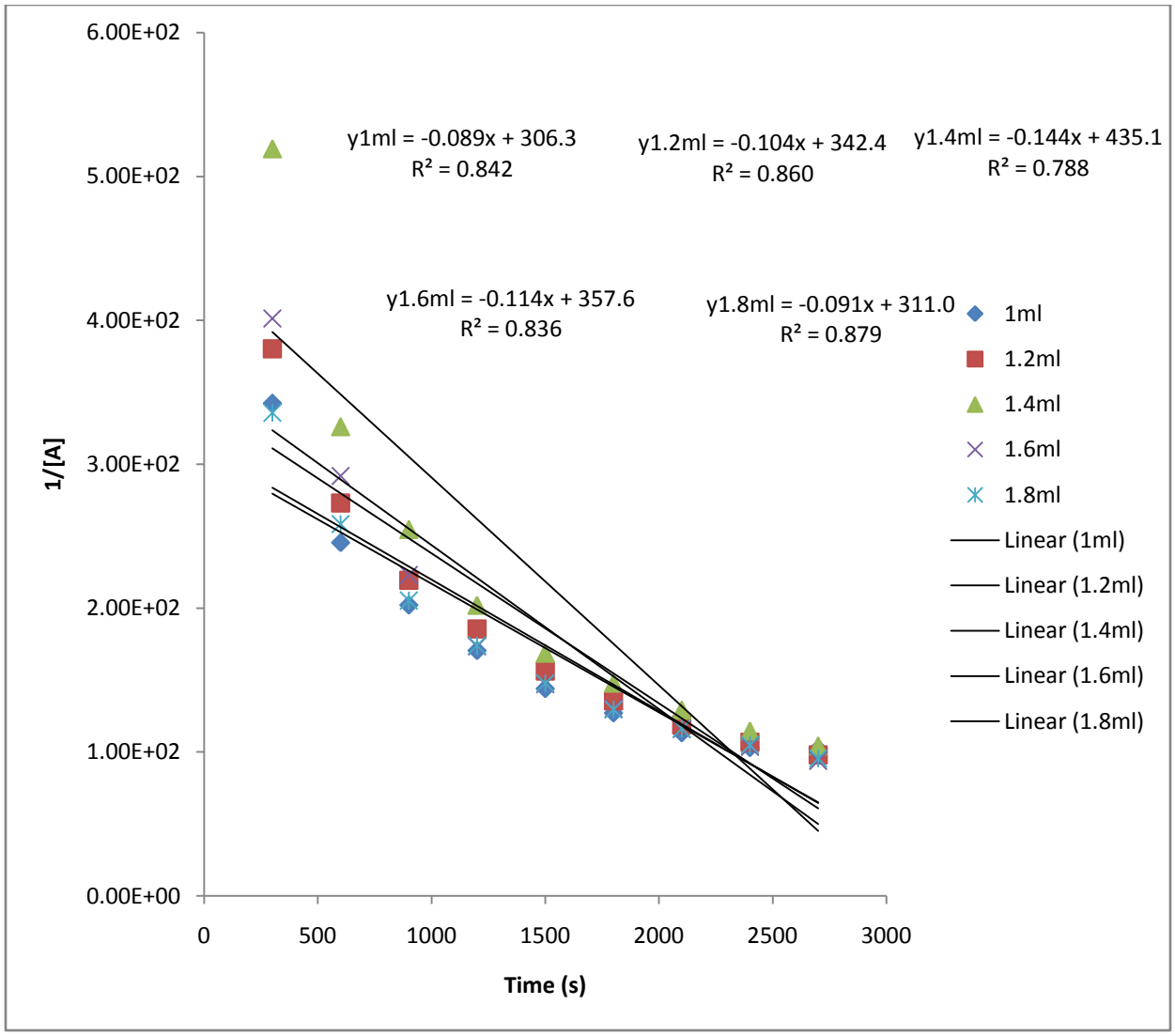


Fig 4.11: The rate curves for second order at pH 7

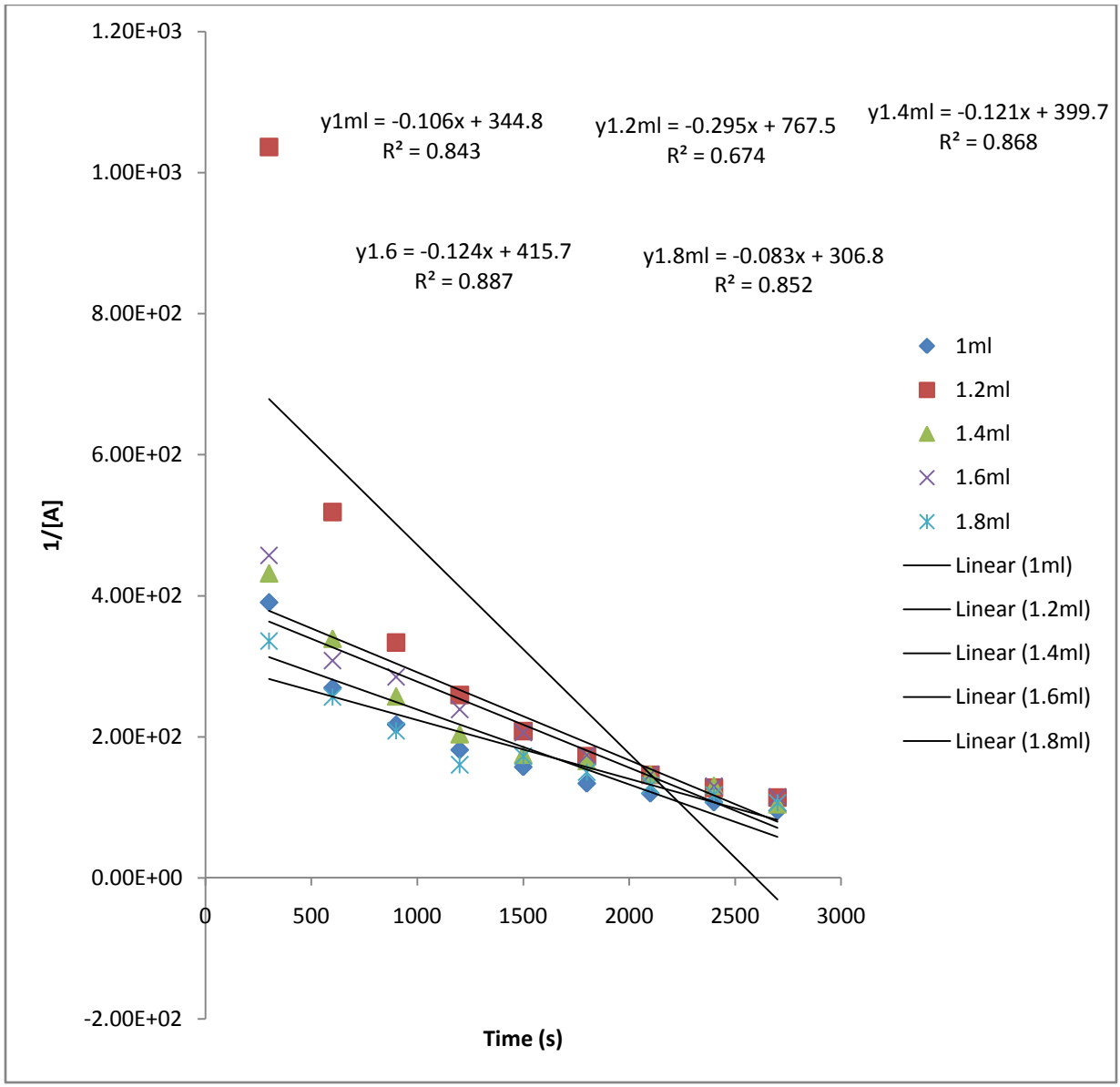


Fig 4.12: The rate curves for second order at pH 8

4.5.3 Graph of log K_{obs} versus log [B]

Graphs of log K_{obs} versus log [B] were plotted in order to investigate the order of the reaction with respect to [B] (coupling component) and the following curves were obtained:

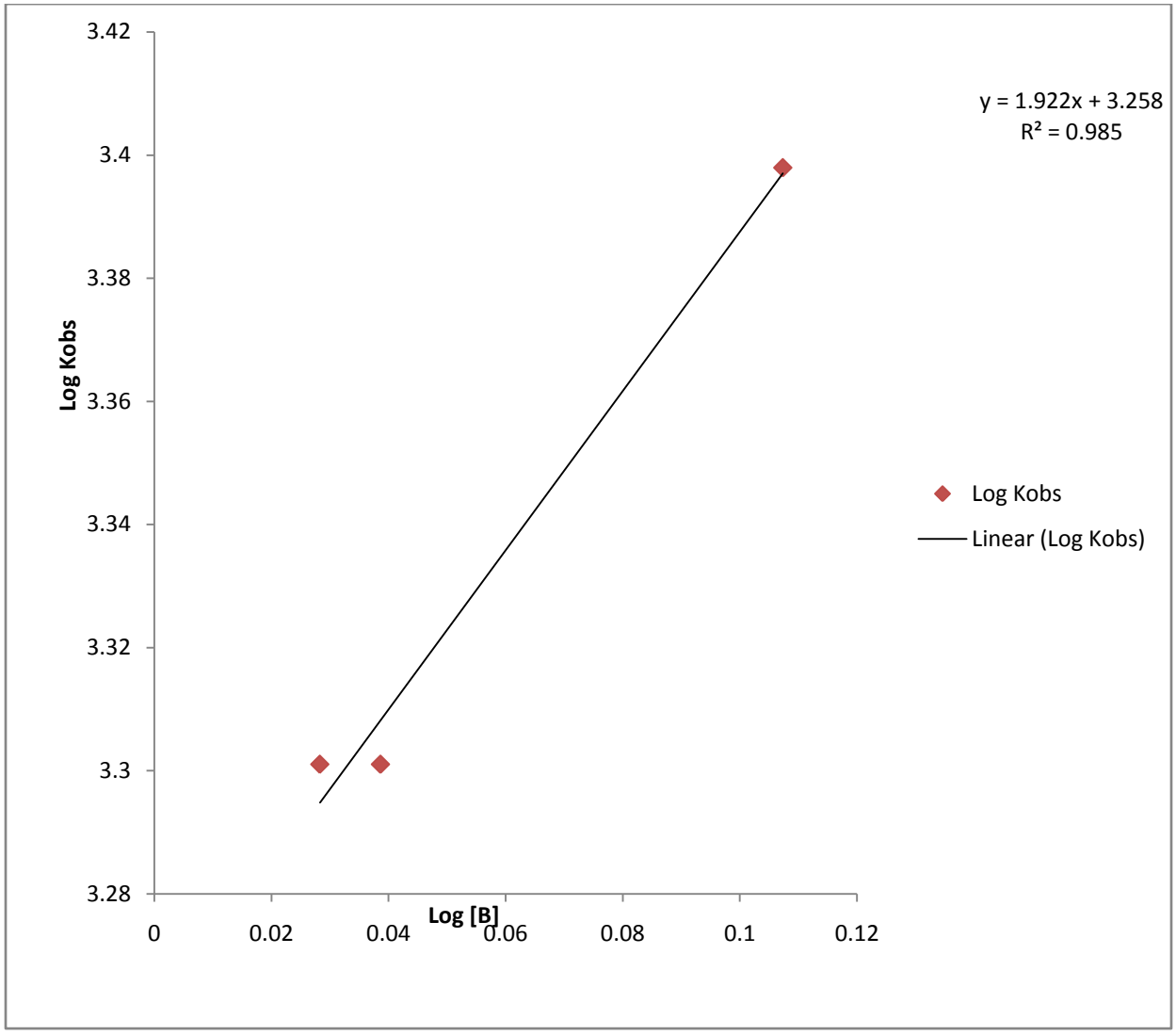


Fig 4.13: The rate curves for reaction order in [B]

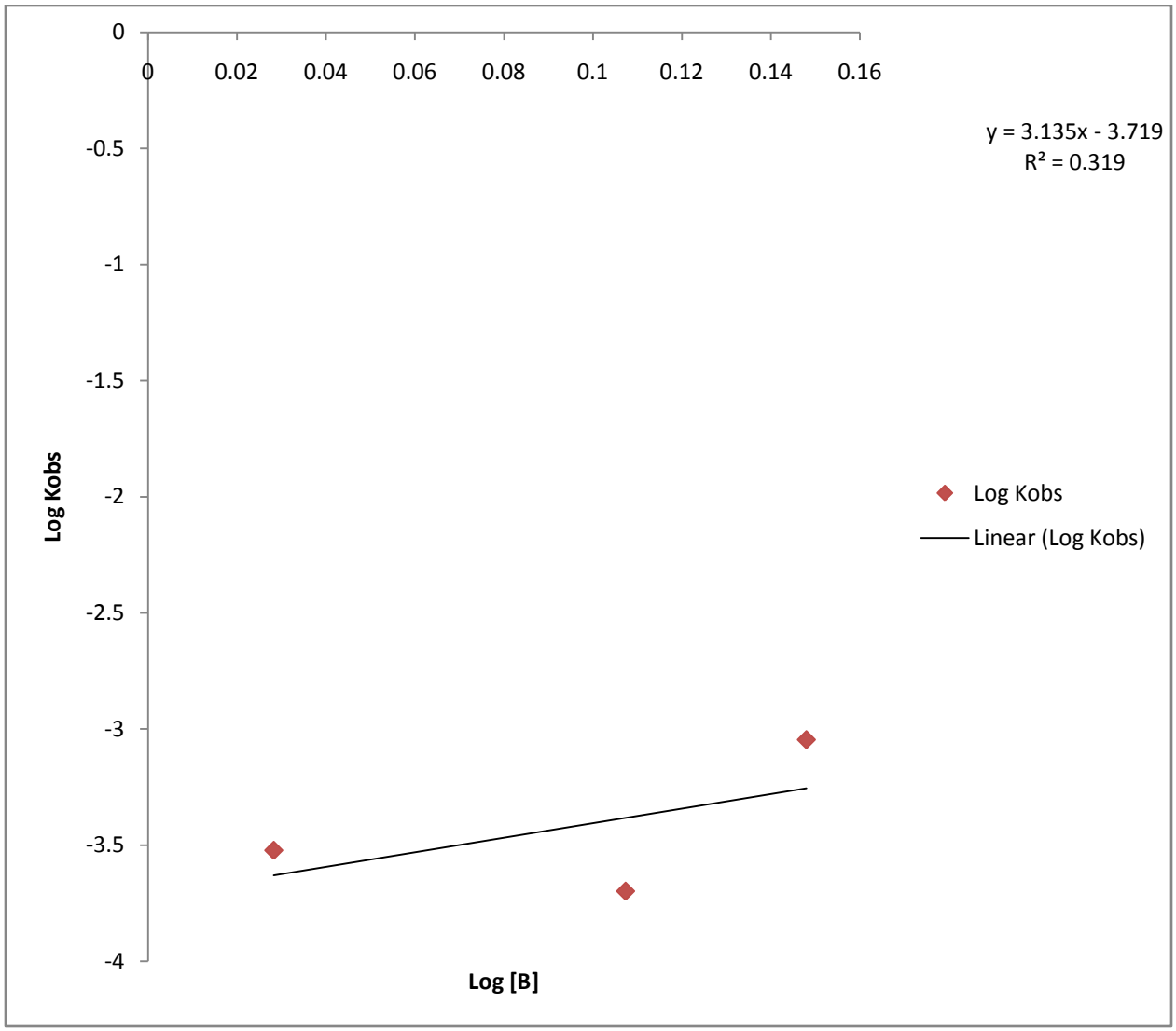


Fig 4.14: The rate curves for reaction order in [B]

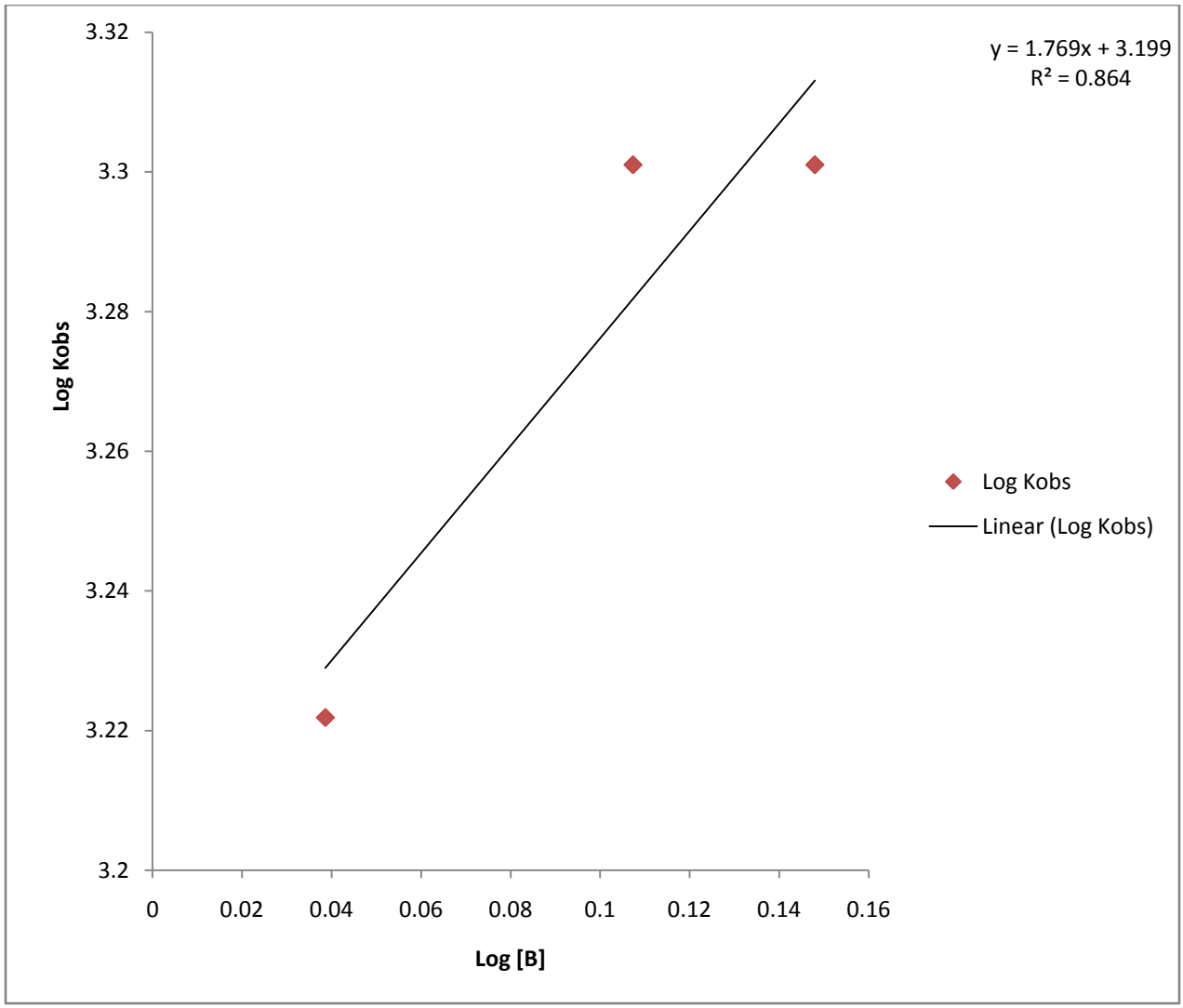


Fig 4.15: The rate curves for reaction order in [B]

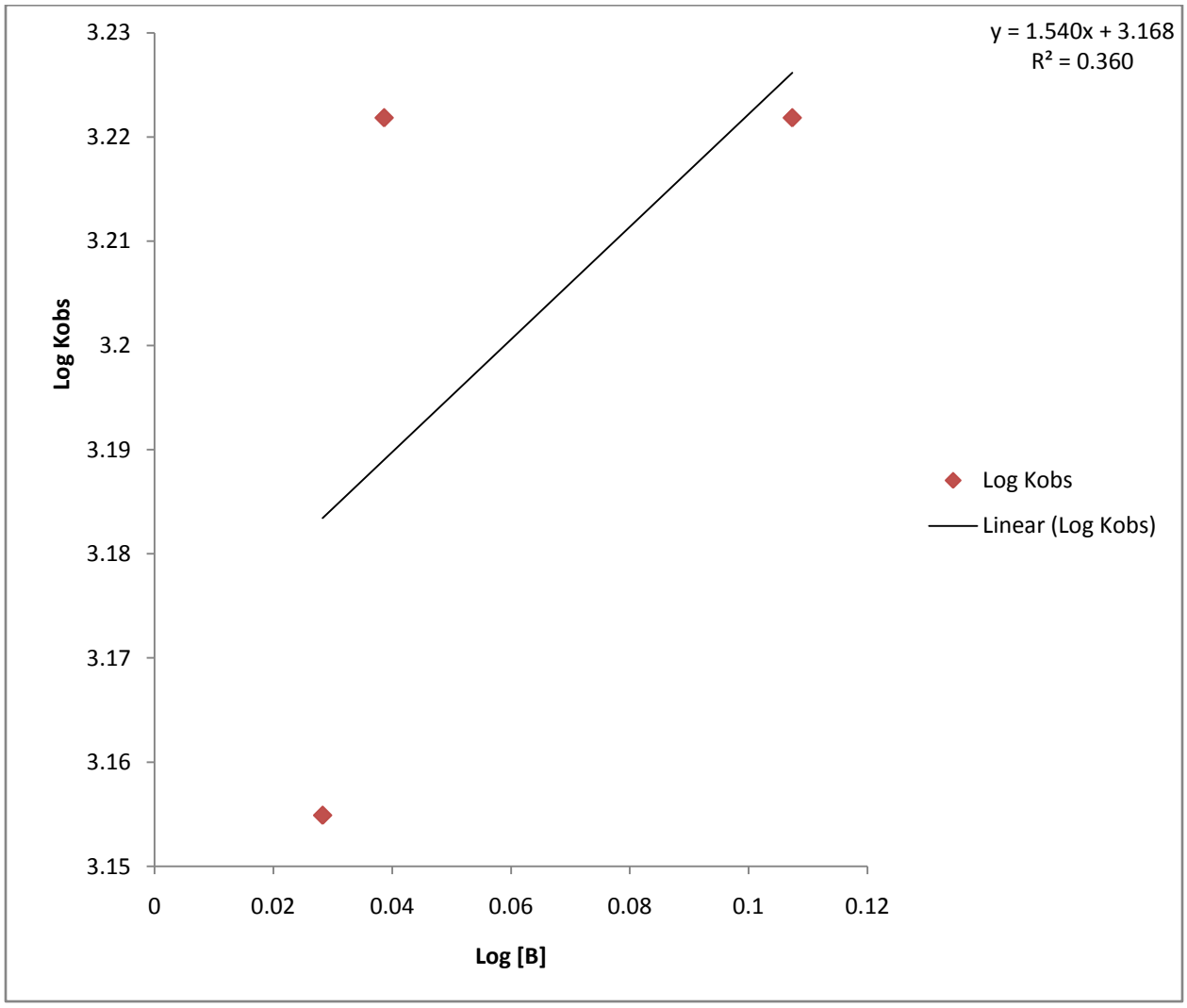


Fig 4.16: The rate curves for reaction order in [B]

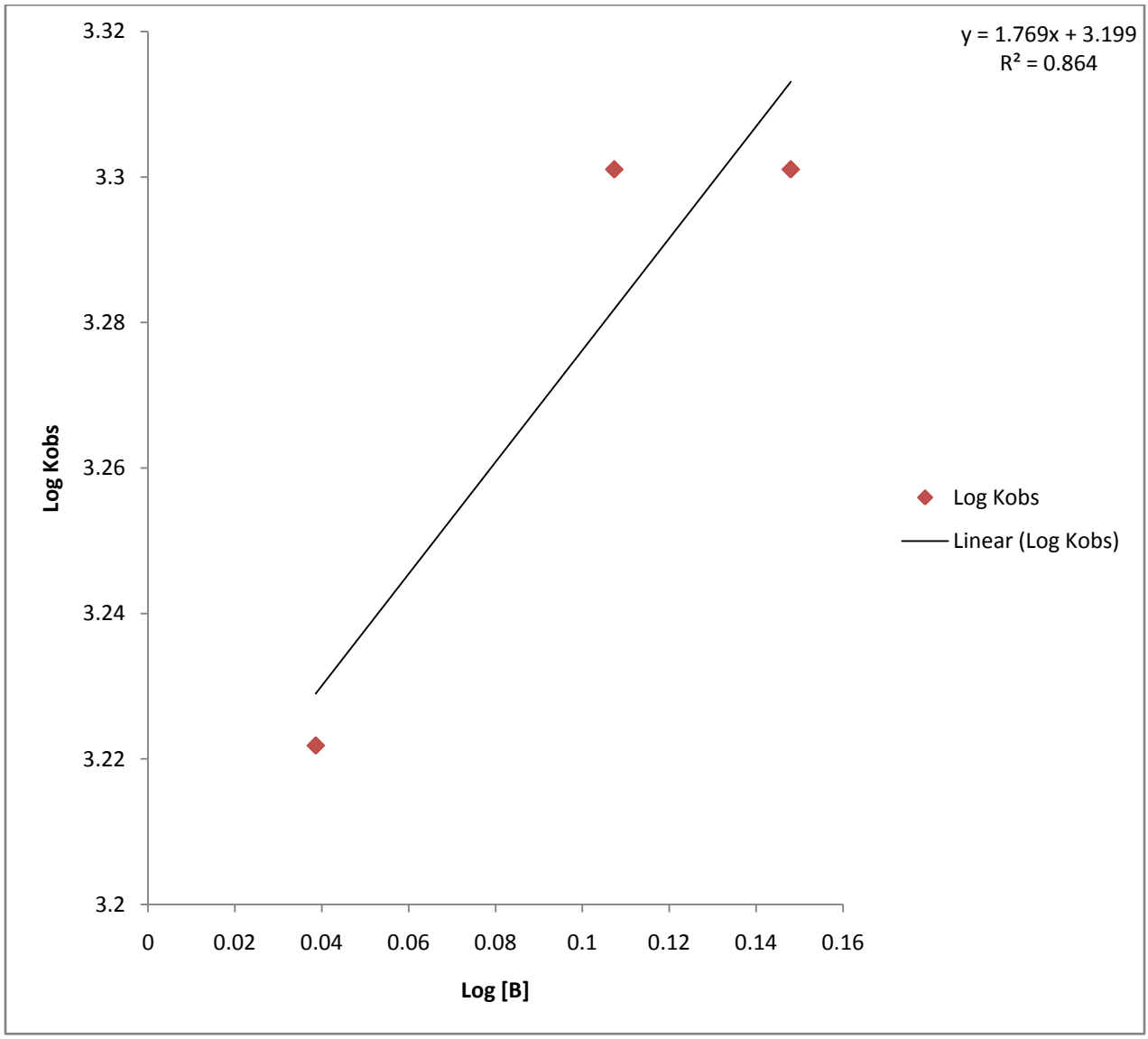


Fig 4.17: The rate curves for reaction order in [B]

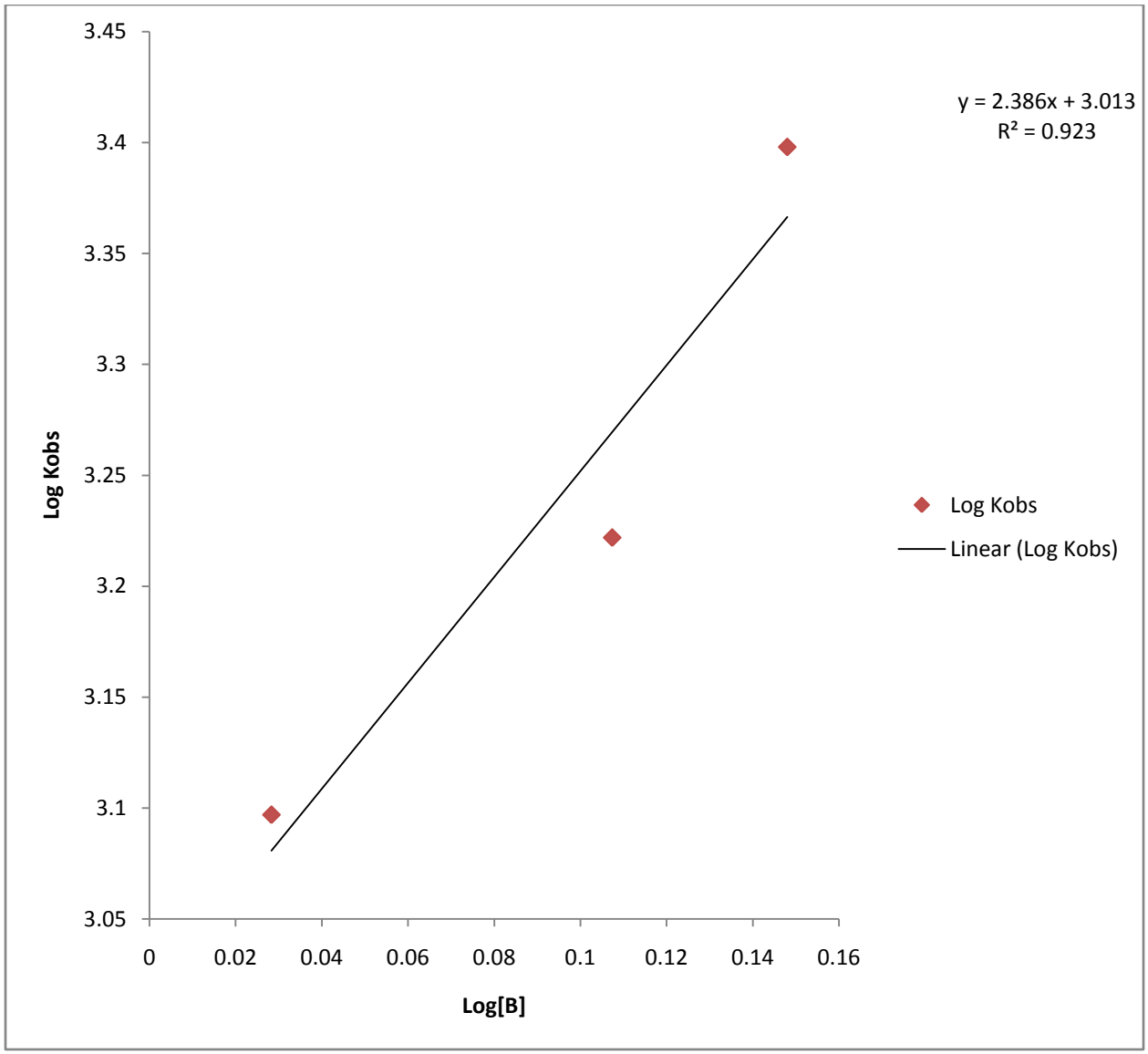


Fig 4.18: The rate curves for reaction order in [B]

4.6 Statistical analysis (SPSS)

The null and alternative hypothesis states that:

H_0: μ theoretical = μ actual

H_1: μ theoretical ≠ μ actual

Decision: If $p \leq \alpha$, then reject H_0, it was observed that p = .769, .159, .909 for pH 3, 4 and 5 respectively is not less than or equal to .05, therefore H_0 not rejected. This implies that there is insufficiant evidence to conclude that the yield of theoretical and actual values are different.

A paired samples t-test failed to reveal a statistically reliable difference between the mean number of theoretical (M = 0.23, s = 0.17) and actual (M = 0.26, s = 0.02), theoretical (M = 0.29, s = 0.13) and actual (M = 0.32, s = 0.11), theoretical (M = 0.32, s = 0.12) and actual (M = 0.32, s = 0.11), that the values have, t (29) = 0.296, 1.446 and 0.115 p = 0.769, 0.159, 0.909 and α = .05 for pH 3, 4 and 5 respectively.

Table 4.2: paired t-test for pH 3

MO	N	Mean	Std.Dev	Std.Dev	df	Cal.(t)	Crit.(t)	P.Sig
Theoretical value	30	0.2260	0.1732	0.0189				
					29	0.296	1.96	0.769
Actual value	30	0.0491	0.0247	0.0027				

Table 4.3: paired t-test for pH 4

MO	N	Mean	Std.Dev	Std.Err	df	Cal.(t)	Crit.(t)	P.Sig
Theoretical value	30	0.2959	0.1262	0.0346				
					29	1.446	1.96	0.159
Actual value	30	0.3224	0.1090	0.1991				

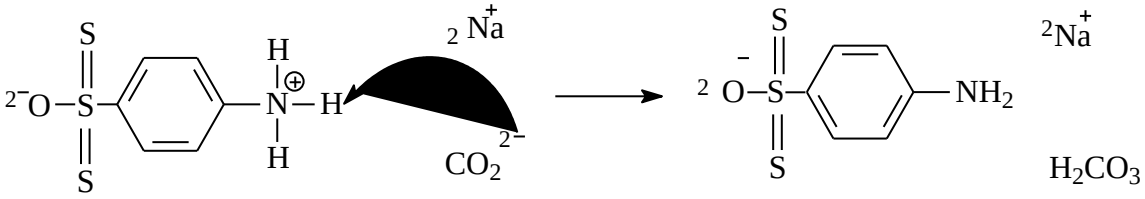
Table 4.4: paired t-test for pH 5

MO	N	Mean	Std.Dev	Std.Err	df	Cal.(t)	Crit.(t)	P.Sig
Theoretical value	30	0.3217	0.1107	0.0202				
					29	0.115	1.96	0.909
Actual value	30	0.3224	0.1090	0.0199				

CHAPTER FIVE

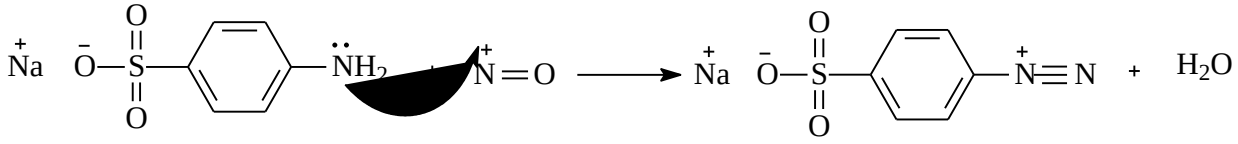
5.0 Discussion

This experiment was designed to investigate the optimization of the production of methyl orange through the study of kinetics of the coupling reaction between sulphanilic acid (diazo component) and N,N-dimethyl aniline (coupling component) at different pH (3-8) as shown in the schemes below:



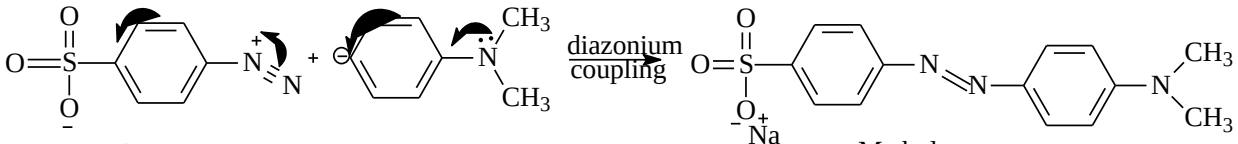
Sulphanilic acid Dissolved sulphanilic acid

Scheme 5.1: Dissolution of sulphanilic acid



Dissolved sulphanilic acid Nitrosonium ion Diazotized sulphanilic acid

Scheme 5.2: Diazotization of sulphanilic acid



Diazotized amine (Sulphanilic acid)

Coupling component (N,N−dimethylaniline)

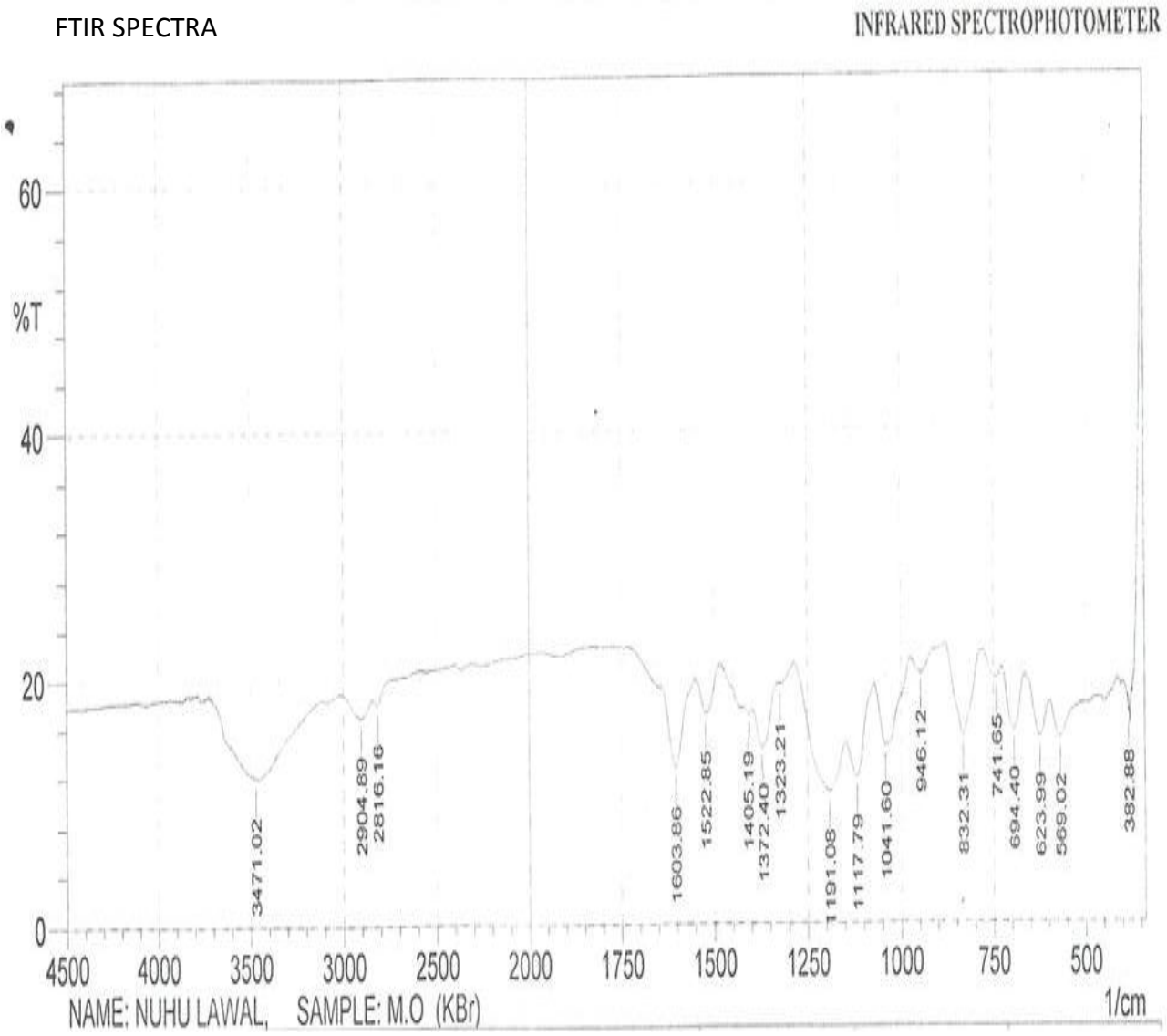
Methyl orange

Scheme5.3 : Coupling of diazotized sulphanilic acid

The influence of specific base catalysis on the pre-equilibria. (i.e the effect of pH on the production of the dye (methyl orange) was also investigated, this also point out the best pH condition under which it should be synthesized.

The dye obtained was purified by recrystallization and thin layer chromatography (TLC), melting point was also determined to confirm its purity. Characterization analysis was also carried out using Fourier Transform Infra red Spectroscopy (FTIR) and Gas Chromatography Mass Spectroscopy (GCMS) as shown below:

FTIR SPECTRA



During this research work, integrated rate law (first and second order) were used to determine the reaction order in [A] (diazonium ion) at different pH values (3-8) where a graph of ln[A] against T time(s) and 1/[A] against T time(s) were plotted.

In case of [B] (coupling component) calibration curves were plotted to obtain K_{obs} and also Graphs of log K_{obs} against log [B] were plotted according to the following equation:

$$k_{obs} = k [B]^n \quad 5.1$$

$$n\log [B] + \log k = \log K_{obs} \quad 5.2$$

To determine the actual rate constant as well as the order of the reaction in [B] (coupling component). From the graphs it can be observed that the coupling reaction (Electrophilic substitution reaction) between sulphanilic acid (diazonium ion) and N,N-dimethyl aniline (coupling component) was first order with respect to [A] when curves of In [A] against t time (s) were plotted at the selected pH (3-8).

Straight line (positive) graph was also obtained. This is a clear indication to prove that the rate of formation of methyl orange has steadily increased with increase in time (s) at all pH values.

It can also be deduced that the reaction between diazotized sulfanilic acid (diazo component) and N,N-dimethyl aniline (coupling component) was not via second order reaction in the case of 1/[A] against time(s).This is because straight line (negative) curve was obtained at all selected pH values (3-8). Actual rate constant (k), reaction order with respect to [A] (n), order of the reaction in [B] and the overall order are also shown in the Table below:

$$P = k [A]^n [B]^m. \quad 5.3$$

Table 5.1: Values of order and rate constant at different pH values

pH	k	n	m	Overall order
3	9.12×10^{-4}	1	2	3
4	3.50×10^{-4}	1	3	4
5	7.31×10^{-4}	1	2	3
6	3.12×10^{-4}	1	2	3
7	2.75×10^{-4}	1	2	3
8	2.12×10^{-4}	1	2	3

A model was established for each pH according to the reaction order in [A] and [B] and used to calculate theoretical values which were compared with actual values generated from the laboratory.

$P\ (mol/dm^3) = 9.12 \times 10^{-4}\ [A]\ [B]^2$ pH 3

$P\ (mol/dm^3) = 3.5 \times 10^{-4}\ [A]\ [B]^3$ pH 4

$P\ (mol/dm^3) = 7.311 \times 10^{-4}\ [A]\ [B]^2$ pH 5

$P\ (mol/dm^3) = 3.124X10\text{-}4\ [A]\ [B]^2$ pH 6

$P\ (mol/dm^3) = 2.754 \times 10^{-4}\ [A]\ [B]^2$ pH 7

$P\ (mol/dm^3) = 2.102X10^{-4}\ [A]\ [B]^2$ pH 8

SPSS statistical package was used to determine their degrees of compliance and the null hypothesis which states that there is no significant difference between theoretical and actual values i.e (H_0: μ theoretical = actual) was accepted.

5.1. The effect of pH on dye yield

Coupling reactions between diazotized sulphanilic acid (diazo component) and N,N-dimethyl aniline (coupling component) was carried out under conditions between strongly acidic and mild alkaline condition. During these reactions the diazo component (sulphanilic acid) and coupling component (N,N-dimethyl aniline) coupled at six different pH values (3,4,5,6,7, and 8) at temperatures of 0-5^{0}C, at each pH concentrations of diazo component (diazotized sulphanilic acid) were kept constant while the concentrations of coupling component (N,N-dimethyl aniline were varied from 1ml, 1.2ml, 1.4ml, 1.6ml and 1.8ml Coupling time was also varied from 0-45 min at intervals of 5min.

The products obtained (methyl orange) were filtered, washed with ethanol and ethyl ether, air dried and weighed. The mass of the product was converted from mass concentration (g) to molar concentration (Mol/dm^3), cumulative products were calculated at each pH and it is observed that the yield decreases as the pH is increasing from 3,4,5,6,7, and 8.

Generally it was observed that at pH 3 the highest yield (g) was obtained at all time in comparison with other conditions (pH 4-8). This simply means that the optimization of the production of this dye (methyl orange) is best at pH 3 and this indicates highest rate constant.

CHAPTER SIX

6.0 Conclusion and recommendation

6.1 Conclusion

At the end of this research, it could be concluded that the synthesis of methyl orange is best at pH 3 (acidic medium). This is because it is at pH 3 that the highest rate was obtained leading to the higher yield of methyl orange production.

It is also concluded that the order of the reaction with respect to [A] is one (1) at all the selected pH values (3-8), and it is two (2) with respect to [B] except pH4 where unusual order (3) was obtained. Therefore the overall order of the reaction was found to be 3 for all the selected pH (3-8) except pH4 with order of (4).

It is finally concluded that there is no significant different between the theoretical and actual values i.e H_O=H_1 since paired samples t-test failed to reveal a statistically reliable difference between the mean number of theoretical (M = 0.23, s = 0.17) and actual (M = 0.26, s = 0.02), theoretical (M = 0.29, s = 0.13) and actual (M = 0.32, s = 0.11), theoretical (M = 0.32, s = 0.12) and actual (M = 0.32, s = 0.11), that the values have, t (29) = 0.296, 1.446 and 0.115 p = 0.769, 0.159, 0.909 and α = .05 for pH 3, 4 and 5 respectively.Therefore the null hypothesis is here by accepted.

6.2 Recommendations

a) it is recommended that further research should be carried out at even lower pH values such as pH (1 and 2).

b) it is also recommended that Thermodynamics studies should also be carried out for the synthesis of methyl orange..

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APPENDICES

Table of results

Table 1: The kinetics data for pH 3

S/N	COUPLING TIME/Min	VOLUMEOF COUPLING COMPONENT/ml	pH	WEIGHT/g (MASS CONCENTRATION)	MOLAR CONCENTRATION (10^{-4}) mol/dm^3
1	0	1.0	3	0.0000	0.0000
2	5	1.0	3	0.1601	4.8880
3	10	1.0	3	0.1920	5.8656
4	15	1.0	3	0.2201	6.7210
5	20	1.0	3	0.2542	7.7625
6	25	1.0	3	0.2817	8.5846
7	30	1.0	3	0.3110	9.5011
8	35	1.0	3	0.3433	10.4787
9	40	1.0	3	0.3710	11.344
10	45	1.0	3	0.3990	12.1895
11	0	1.2	3	0.0040	0.0000
12	5	1.2	3	0.1820	5.5601
13	10	1.2	3	0.2211	6.7516
14	15	1.2	3	0.2580	7.8819
15	20	1.2	3	0.2993	9.1345
16	25	1.2	3	0.3421	10.4481
17	30	1.2	3	0.3810	11.6396
18	35	1.2	3	0.4201	12.8310
19	40	1.2	3	0.4710	14.3891
20	45	1.2	3	0.5122	15.6417
21	0	1.4	3	0.0311	0.0000
22	5	1.4	3	0.1810	5.5295
23	10	1.4	3	0.2290	6.9959
24	15	1.4	3	0.2731	8.3402
25	20	1.4	3	0.3180	9.7149
26	25	1.4	3	0.3642	11.1202
27	30	1.4	3	0.4101	12.5255
28	35	1.4	3	0.4640	14.1752
29	40	1.4	3	0.5091	15.5500
30	45	1.4	3	0.5520	16.8637
31	0	1.6	3	0.0001	0.0000
32	5	1.6	3	0.1940	5.9267
33	10	1.6	3	0.2521	7.6986
34	15	1.6	3	0.3073	9.3789
35	20	1.6	3	0.3582	10.9369
36	25	1.6	3	0.4160	12.7093
37	30	1.6	3	0.4741	14.4807

38	35	1.6	3	0.5301	16.1916
39	40	1.6	3	0.5881	17.9635
40	45	1.6	3	0.6352	19.3993
41	0	1.8	3	0.0002	0.0000
42	5	1.8	3	0.1201	3.6660
43	10	1.8	3	0.1780	5.4379
44	15	1.8	3	0.2411	7.3626
45	20	1.8	3	0.2990	9.1345
46	25	1.8	3	0.3520	10.7536
47	30	1.8	3	0.4211	12.8616
48	35	1.8	3	0.4843	14.7816
49	40	1.8	3	0.5412	16.5276
50	45	1.8	3	0.5826	17.7802

Table 2: The kinetics data for pH 4

S/N	COUPLING TIME/Min	VOLUMEOF COUPLING COMPONENT/ml	pH	WEIGHT/g (MASS CONCENTRATION)	MOLAR CONCENTRATION (10^{-4}) mol/dm^3
1	0	1.0	4	0.0012	0.0000
2	5	1.0	4	0.2641	8.0680
3	10	1.0	4	0.2841	8.6799
4	15	1.0	4	0.3063	9.3450
5	20	1.0	4	0.3240	9.8980
6	25	1.0	4	0.3441	1.0509
7	30	1.0	4	0.3660	1.1181
8	35	1.0	4	0.3870	1.1823
9	40	1.0	4	0.4046	1.2342
10	45	1.0	4	0.4203	1.2823
11	0	1.2	4	0.0000	0.0000
12	5	1.2	4	0.2470	7.5460
13	10	1.2	4	0.2760	8.4326
14	15	1.2	4	0.2991	9.1380
15	20	1.2	4	0.3304	1.0082
16	25	1.2	4	0.3601	1.0998
17	30	1.2	4	0.3882	1.1853
18	35	1.2	4	0.4147	1.2648
19	40	1.2	4	0.4403	1.3442
20	45	1.2	4	0.4701	1.4359
21	0	1.4	4	0.0000	0.0000
22	5	1.4	4	0.2611	7.9741
23	10	1.4	4	0.2982	8.7980
24	15	1.4	4	0.3268	9.9590
25	20	1.4	4	0.3543	10.8243
26	25	1.4	4	0.3851	11.7621

27	30	1.4	4	0.4225	12.8920
28	35	1.4	4	0.4770	14.5726
29	40	1.4	4	0.5127	15.6420
30	45	1.4	4	0.5473	16.716
31	0	1.6	4	0.0000	0.0000
32	5	1.6	4	0.0360	1.1000
33	10	1.6	4	0.0831	2.5369
34	15	1.6	4	0.1324	4.0450
35	20	1.6	4	0.1860	5.6822
36	25	1.6	4	0.2357	7.2011
37	30	1.6	4	0.2840	8.6762
38	35	1.6	4	0.3336	10.1920
39	40	1.6	4	0.3814	11.6523
40	45	1.6	4	0.4338	13.2534
41	0	1.8	4	0.0000	0.0000
42	5	1.8	4	0.0461	1.4053
43	10	1.8	4	0.1036	3.1470
44	15	1.8	4	0.1641	5.0100
45	20	1.8	4	0.2211	6.7524
46	25	1.8	4	0.2830	8..6461
47	30	1.8	4	0.3415	10.4182
48	35	1.8	4	0.4119	12.5560
49	40	1.8	4	0.4708	14.3591
50	45	1.8	4	0.5305	16.1923

Table 3: The kinetics data for pH 5

S/N	COUPLING TIME/Min	VOLUMEOF COUPLING COMPONENT/ml	pH	WEIGHT/g (MASS CONCENTRATION)	MOLAR CONCENTRATION (10^{-4}) mol/dm^3
1	0	1.0	5	0.0000	0.0000
2	5	1.0	5	0.0420	1.2831
3	10	1.0	5	0.0622	1.8949
4	15	1.0	5	0.0809	2.4446
5	20	1.0	5	0.0981	2.9940
6	25	1.0	5	0.1210	3.6972
7	30	1.0	5	0.1404	4.2773
8	35	1.0	5	0.1592	4.8573
9	40	1.0	5	0.1772	5.4072
10	45	1.0	5	0.1980	6.0496
11	0	1.2	5	0.0000	0.0000
12	5	1.2	5	0.0048	0.1226
13	10	1.2	5	0.0280	0.8554
14	15	1.2	5	0.0323	0.9785
15	20	1.2	5	0.0362	1.1060

16	25	1.2	5	0.0390	1.1913
17	30	1.2	5	0.0440	1.3552
18	35	1.2	5	0.0485	1.4661
19	40	1.2	5	0.0531	1.6220
20	45	1.2	5	0.0722	2.2064
21	0	1.4	5	0.0000	0.0000
22	5	1.4	5	0.0370	1.1304
23	10	1.4	5	0.0561	1.7108
24	15	1.4	5	0.0762	2.3218
25	20	1.4	5	0.0961	2.9328
26	25	1.4	5	0.1144	3.4827
27	30	1.4	5	0.1332	4.0632
28	35	1.4	5	0.1516	4.6131
29	40	1.4	5	0.1717	5.2241
30	45	1.4	5	0.1935	5.8962
31	0	1.6	5	0.0000	0.0000
32	5	1.6	5	0.0301	0.9200
33	10	1.6	5	0.0522	1.5890
34	15	1.6	5	0.0770	2.3524
35	20	1.6	5	0.0942	2.9328
36	25	1.6	5	0.1161	3.4827
37	30	1.6	5	0.1340	4.0632
38	35	1.6	5	0.1550	4.6131
39	40	1.6	5	0.1703	5.2241
40	45	1.6	5	0.1961	5.8962
41	0	1.8	5	0.0000	0.0000
42	5	1.8	5	0.0290	0.8860
43	10	1.8	5	0.0494	1.5098
44	15	1.8	5	0.0652	1.9929
45	20	1.8	5	0.0807	2.4659
46	25	1.8	5	0.1068	3.2635
47	30	1.8	5	0.1243	3.7978
48	35	1.8	5	0.1445	4.4153
49	40	1.8	5	0.1631	4.9832
50	45	1.8	5	0.1806	5.5170

Table 4: The kinetics data for pH 6

S/N	COUPLING TIME/Min	VOLUMEOF COUPLING COMPONENT/ml	pH	WEIGHT/g (MASS CONCENTRATION)	MOLAR CONCENTRATION (10^{-4}) mol/dm^3
1	0	1.0	6	0.0000	0.0000
2	5	1.0	6	0.0354	1.0811
3	10	1.0	6	0.0402	1.2280

4	15	1.0	6	0.0531	1.6220
5	20	1.0	6	0.0632	1.9310
6	25	1.0	6	0.0740	2.2613
7	30	1.0	6	0.0820	2.5055
8	35	1.0	6	0.0915	2.7954
9	40	1.0	6	0.1068	3.2631
10	45	1.0	6	0.1128	3.4460
11	0	1.2	6	0.0000	0.0000
12	5	1.2	6	0.0331	1.0112
13	10	1.2	6	0.0435	1.3290
14	15	1.2	6	0.0532	1.6252
15	20	1.2	6	0.0602	1.8618
16	25	1.2	6	0.0691	2.1110
17	30	1.2	6	0.0790	2.4132
18	35	1.2	6	0.0902	2.7561
19	40	1.2	6	0.1024	3.1284
20	45	1.2	6	0.1207	3.6875
21	0	1.4	6	0.0000	0.0000
22	5	1.4	6	0.0440	1.3440
23	10	1.4	6	0.0530	1.6194
24	15	1.4	6	0.0653	1.9950
25	20	1.4	6	0.0652	1.9923
26	25	1.4	6	0.0711	2.1726
27	30	1.4	6	0.0809	2.4720
28	35	1.4	6	0.0912	2.7864
29	40	1.4	6	0.1029	3.0440
30	45	1.4	6	0.1145	3.4981
31	0	1.6	6	0.0000	0.0000
32	5	1.6	6	0.0158	0.4830
33	10	1.6	6	0.0380	1.1612
34	15	1.6	6	0.0481	1.4692
35	20	1.6	6	0.0563	1.7230
36	25	1.6	6	0.0662	2.0220
37	30	1.6	6	0.0781	2.3861
38	35	1.6	6	0.0870	2.6584
39	40	1.6	6	0.0960	2.9336
40	45	1.6	6	0.1070	3.2690
41	0	1.8	6	0.0000	0.0000
42	5	1.8	6	0.0341	1.0423
43	10	1.8	6	0.0443	1.3534
44	15	1.8	6	0.0561	1.7142
45	20	1.8	6	0.0671	2.0500
46	25	1.8	6	0.0768	2.3465
47	30	1.8	6	0.0851	2.6001
48	35	1.8	6	0.0965	2.9480
49	40	1.8	6	0.1029	3.1445

50	45	1.8	6	0.1118	3.4161

Table 5: The kinetics data for pH 7

S/N	COUPLING TIME/Min	VOLUMEOF COUPLING COMPONENT/ml	pH	WEIGHT/g (MASS CONCENTRATION)	MOLAR CONCENTRATION (10^{-4}) mol/dm^3
1	0	1.0	7	0.0000	0.0000
2	5	1.0	7	0.0301	0.9201
3	10	1.0	7	0.0420	1.2830
4	15	1.0	7	0.0510	1.5586
5	20	1.0	7	0.0605	1.8480
6	25	1.0	7	0.0716	2.1874
7	30	1.0	7	0.0811	2.4784
8	35	1.0	7	0.0910	2.7801
9	40	1.0	7	0.1001	3.0586
10	45	1.0	7	0.1009	3.0839
11	0	1.2	7	0.0000	0.0000
12	5	1.2	7	0.0273	0.8340
13	10	1.2	7	0.0380	1.1610
14	15	1.2	7	0.0473	1.4453
15	20	1.2	7	0.0559	1.7087
16	25	1.2	7	0.0664	2.0290
17	30	1.2	7	0.0765	2.3372
18	35	1.2	7	0.0873	2.6670
19	40	1.2	7	0.0971	2.9663
20	45	1.2	7	0.1058	3.2321
21	0	1.4	7	0.0000	0.0000
22	5	1.4	7	0.0201	0.6143
23	10	1.4	7	0.0320	0.9780
24	15	1.4	7	0.0410	1.2526
25	20	1.4	7	0.0517	1.5791
26	25	1.4	7	0.0619	1.8910
27	30	1.4	7	0.0706	2.1570
28	35	1.4	7	0.0808	2.4683
29	40	1.4	7	0.0911	2.7831
30	45	1.4	7	0.1001	3.0587
31	0	1.6	7	0.0000	0.0000
32	5	1.6	7	0.0262	0.8000
33	10	1.6	7	0.0360	1.1000
34	15	1.6	7	0.0471	1.4394
35	20	1.6	7	0.0606	1.8510
36	25	1.6	7	0.0714	2.1812
37	30	1.6	7	0.0808	2.4680

38	35	1.6	7	0.0906	2.7684
39	40	1.6	7	0.1014	3.0981
40	45	1.6	7	0.1126	3.4220
41	0	1.8	7	0.0000	0.0000
42	5	1.8	7	0.0315	0.9625
43	10	1.8	7	0.0409	1.2501
44	15	1.8	7	0.0515	1.5734
45	20	1.8	7	0.0608	1.8572
46	25	1.8	7	0.0716	2.1870
47	30	1.8	7	0.0816	2.4933
48	35	1.8	7	0.0909	2.7770
49	40	1.8	7	0.1007	3.0761
50	45	1.8	7	0.1106	3.3790

Table 6: The kinetics data for pH 8

S/N	COUPLING TIME/Min	VOLUMEOF COUPLING COMPONENT/ml	pH	WEIGHT/g (MASS CONCENTRATION)	MOLAR CONCENTRATION (10^{-4}) mol/dm^3
1	0	1.0	8	0.0000	0.0000
2	5	1.0	8	0.0264	0.8070
3	10	1.0	8	0.0383	1.1702
4	15	1.0	8	0.0475	1.4510
5	20	1.0	8	0.0569	1.7384
6	25	1.0	8	0.0657	2.0070
7	30	1.0	8	0.0772	2.3581
8	35	1.0	8	0.0863	2.6365
9	40	1.0	8	0.0964	2.9457
10	45	1.0	8	0.1089	3.3274
11	0	1.2	8	0.0000	0.0000
12	5	1.2	8	0.0100	0.3060
13	10	1.2	8	0.0200	0.6112
14	15	1.2	8	0.0311	0.9500
15	20	1.2	8	0.0400	1.2220
16	25	1.2	8	0.0499	1.5241
17	30	1.2	8	0.0601	1.8360
18	35	1.2	8	0.0710	2.1690
19	40	1.2	8	0.0812	2.4814
20	45	1.2	8	0.0910	2.7802
21	0	1.4	8	0.0000	0.0000
22	5	1.4	8	0.0242	0.7390
23	10	1.4	8	0.0308	0.9413
24	15	1.4	8	0.0406	1.2405
25	20	1.4	8	0.0513	1.5674
26	25	1.4	8	0.0598	1.8270

27	30	1.4	8	0.0630	1.9257
28	35	1.4	8	0.0711	2.1726
29	40	1.4	8	0.0800	2.4441
30	45	1.4	8	0.1002	3.0600
31	0	1.6	8	0.0000	0.0000
32	5	1.6	8	0.0230	0.7027
33	10	1.6	8	0.0341	1.0423
34	15	1.6	8	0.0369	1.1274
35	20	1.6	8	0.0440	1.3445
36	25	1.6	8	0.0510	1.5586
37	30	1.6	8	0.0604	1.8457
38	35	1.6	8	0.0716	2.1870
39	40	1.6	8	0.0809	2.4720
40	45	1.6	8	0.0915	2.7953
41	0	1.8	8	0.0000	0.0000
42	5	1.8	8	0.0315	0.9625
43	10	1.8	8	0.0412	1.2598
44	15	1.8	8	0.0507	1.5496
45	20	1.8	8	0.0660	2.0160
46	25	1.8	8	0.0612	1.8744
47	30	1.8	8	0.0706	2.1576
48	35	1.8	8	0.0809	2.4723
49	40	1.8	8	0.0900	2.7500
50	45	1.8	8	0.0994	3.0370

Table 1: Kinetics data for pH 3

S/N	pH	VOLUME [B]	TIME (S)	THEORITICAL	ACTUAL
1	3	1.2	300	5.14E-02	4.60E-02
2	3	1.2	600	1.03E-01	9.60E-02
3	3	1.2	900	1.54E-01	1.40E-01
4	3	1.2	1200	2.06E-01	1.86E-01
5	3	1.2	1500	2.57E-01	2.49E-01
6	3	1.2	1800	3.08E-01	3.03E-01
7	3	1.4	300	3.23E-01	0.310
8	3	1.4	600	3.27E-01	0.312
9	3	1.4	900	3.45E-01	0.359

10	3	1.4	1200	3.73E-01	0.371
11	3	1.4	1500	3.41E-01	0.367
12	3	1.4	1800	4.10E-01	0.399
13	3	1.6	300	8.79E-02	0.083
14	3	1.6	600	1.76E-01	0.098
15	3	1.6	900	2.64E-01	0.262
16	3	1.6	1200	3.52E-01	0.336
17	3	1.6	1500	4.39E-01	0.433
18	3	1.6	1800	5.27E-01	0.497
19	3	1.8	300	1.08E-01	0.103
20	3	1.8	600	2.16E-01	0.213
21	3	1.8	900	3.24E-01	0.321
22	3	1.8	1200	4.32E-01	0.364
23	3	1.8	1500	5.40E-01	0.502
24	3	1.8	1800	6.48E-01	0.628
25	3	2.0	300	1.30E-01	0.128
26	3	2.0	600	2.63E-01	0.260
27	3	2.0	900	3.89E-01	0.379
28	3	2.0	1200	5.19E-01	0.513
29	3	2.0	1500	6.49E-01	0.641
30	3	2.0	1800	7.79E-01	0.773

Table 2: Kinetics data for pH 4

S/N	pH	VOLUME [B]	TIME (S)	THEORITICAL	ACTUAL
1	4	1.2	300	1.80E-02	0.028
2	4	1.2	600	4.59E-02	0.05
3	4	1.2	900	4.89E-02	0.053
4	4	1.2	1200	5.19E-02	0.054
5	4	1.2	1500	6.08E-02	0.057
6	4	1.2	1800	7.08E-02	0.059
7	4	1.4	300	1.98E-02	0.019
8	4	1.4	600	3.97E-02	0.036
9	4	1.4	900	5.95E-02	0.057
10	4	1.4	1200	7.93E-02	0.073
11	4	1.4	1500	9.91E-02	0.094
12	4	1.4	1800	1.19E-01	0.14
13	4	1.6	300	2.90E-02	0.028
14	4	1.6	600	5.79E-02	0.054
15	4	1.6	900	8.69E-02	0.083
16	4	1.6	1200	1.16E-01	0.109
17	4	1.6	1500	1.45E-01	0.122
18	4	1.6	1800	1.74E-01	0.165
19	4	1.8	300	3.94E-02	0.036
20	4	1.8	600	7.89E-02	0.0741
21	4	1.8	900	1.18E-01	0.106

22	4	1.8	1200	1.58E-01	0.149
23	4	1.8	1500	1.97E-01	0.158
24	4	1.8	1800	2.57E-01	0.256
25	4	2.0	300	5.20E-02	0.049
26	4	2.0	600	1.04E-01	0.106
27	4	2.0	900	1.50E-01	0.141
28	4	2.0	1200	2.08E-01	0.206
29	4	2.0	1500	2.60E-01	0.248
30	4	2.0	1800	3.12E-01	0.257

Table 3: Kinetics data for pH 5

S/N	pH	VOLUME [B]	TIME (S)	THEORITICAL	ACTUAL
1	5	1.2	300	4.12E-02	0.042
2	5	1.2	600	8.24E-02	0.0821
3	5	1.2	900	1.24E-01	0.121
4	5	1.2	1200	1.65E-01	0.132
5	5	1.2	1500	2.06E-01	0.201
6	5	1.2	1800	2.47E-01	0.239
7	5	1.4	300	5.47E-02	0.052
8	5	1.4	600	1.29E-01	0.125
9	5	1.4	900	1.64E-01	0.129

10	5	1.4	1200	2.19E-01	0.163
11	5	1.4	1500	2.74E-01	0.236
12	5	1.4	1800	3.28E-01	0.310
13	5	1.6	300	7.05E-02	0.067
14	5	1.6	600	1.41E-01	0.134
15	5	1.6	900	2.11E-01	0.204
16	5	1.6	1200	2.82E-01	0.233
17	5	1.6	1500	3.52E-01	0.341
18	5	1.6	1800	4.23E-01	0.406
19	5	1.8	300	8.65E-02	0.0824
20	5	1.8	600	1.73E-01	0.127
21	5	1.8	900	2.60E-01	0.231
22	5	1.8	1200	3.46E-01	0.332
23	5	1.8	1500	4.33E-01	0.431
24	5	1.8	1800	5.19E-01	0.418
25	5	2.0	300	1.04E-01	0.095
26	5	2.0	600	2.08E-01	0.184
27	5	2.0	900	3.12E-01	0.314
28	5	2.0	1200	4.16E-01	0.404
29	5	2.0	1500	5.20E-01	0.506
30	5	2.0	1800	6.24E-01	0.542

Data tables

Table 1: In [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	-4.16579	-4.04329	-4.05509	-3.99197	-4.47855
600	-3.98347	-3.84912	-3.81987	-3.7304	-4.08426
900	-3.84734	-3.69433	-3.6441	-3.53298	-3.78124
1200	-3.70327	-3.54684	-3.49153	-3.3793	-3.56559
1500	-3.6026	-3.41248	-3.35643	-3.22911	-3.40241
1800	-3.50117	-3.30449	-3.23742	-3.09862	-3.22341
2100	-3.40323	-3.20704	-3.1137	-2.98695	-3.08427
2400	-3.32388	-3.09243	-3.02113	-2.8831	-2.97262
2700	-3.252	-3.00896	-2.94003	-2.8062	-2.89957

Table 2: In [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	-5.70378	-5.7589	-3.68899	-5.67613	-5.4374
600	-5.64821	-5.66359	-3.59067	-4.8405	-4.6312
900	-5.58706	-5.57658	-3.46671	-4.37396	-4.16622
1200	-5.53746	-5.51204	-3.3834	-4.0341	-3.86775
1500	-5.50571	-5.43682	-3.30031	-3.79721	-3.62054
1800	-5.45247	-5.18229	-3.20858	-3.61086	-3.4341
2100	-5.40192	-5.13296	-3.08605	-3.44984	-3.24745
2400	-5.36731	-5.08596	-3.01523	-3.31594	-3.11327
2700	-5.3015	-5.04106	-2.94882	-3.18719	-2.99312

Table 3: In [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	-5.50329		-5.64262	-5.85482	-5.89248
600	-5.11341	-5.91509	-5.22823	-5.30834	-5.35946
900	-4.85869	-5.78064	-4.92285	-4.91601	-5.08185
1200	-4.65596	-5.65815	-4.68923	-4.69548	-4.86888
1500	-4.445	-5.58386	-4.51738	-4.52363	-4.58864
1800	-4.29925	-5.45495	-4.36322	-4.36947	-4.43702
2100	-4.17209	-5.3763	-4.23629	-4.24254	-4.28757
2400	-4.06484	-5.27524	-4.11191	-4.11816	-4.16401
2700	-3.95258	-4.96754	-3.99088	-3.99713	-4.06361

Table 4: In [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	-5.67459	-5.74776	-5.46954	-6.49918	-5.73622
600	-5.54719	-5.47447	-5.28314	-5.62302	-5.47503
900	-5.26891	-5.27327	-5.07455	-5.38672	-5.23871
w1200	-5.09453	-5.13736	-5.0759	-5.22737	-5.05981
1500	-4.93663	-5.01174	-4.98927	-5.06735	-4.92473
1800	-4.83408	-4.87795	-4.86016	-4.90178	-4.8221
2100	-4.7246	-4.74509	-4.74044	-4.79372	-4.69653
2400	-4.56989	-4.61838	-4.65202	-4.69521	-4.632
2700	-4.51536	-4.45395	-4.51297	-4.58696	-4.54915

Table 5: In [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	-5.83585	-5.94042	-6.25246	-5.99458	-5.82E+00
600	-5.50337	-5.60962	-5.78744	-5.67613	-5.55E+00
900	-5.30878	-5.39058	-5.53997	-5.40721	-5.32E+00
1200	-5.13847	-5.22317	-5.30834	-5.15572	-5.16E+00
1500	-4.96986	-5.05136	-5.12809	-4.99157	-5.00E+00
1800	-4.84496	-4.90995	-4.99647	-4.86803	-4.86E+00
2100	-4.73009	-4.77795	-4.86166	-4.75317	-4.76E+00
2400	-4.63481	-4.67159	-4.74163	-4.64065	-4.65E+00
2700	-4.62667	-4.58577	-4.6472	-4.54122	-4.56E+00

Table 6: In [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	-5.97E+00	-6.94E+00	-6.07E+00	-6.12E+00	-5.82E+00
600	-5.60E+00	-6.25E+00	-5.83E+00	-5.73E+00	-5.55E+00
900	-5.38E+00	-5.81E+00	-5.55E+00	-5.65E+00	-5.34E+00
1200	-5.20E+00	-5.56E+00	-5.32E+00	-5.48E+00	-5.08E+00
1500	-5.06E+00	-5.34E+00	-5.16E+00	-5.33E+00	-5.15E+00
1800	-4.89E+00	-5.15E+00	-5.11E+00	-5.16E+00	-5.01E+00
2100	-4.78E+00	-4.98E+00	-4.99E+00	-4.99E+00	-4.87E+00
2400	-4.67E+00	-4.85E+00	-4.87E+00	-4.87E+00	-4.77E+00
2700	-4.55E+00	-4.74E+00	-4.65E+00	-4.74E+00	-4.67E+00

Table 1: 1 / [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	6.44E+01	5.70E+01	5.77E+01	5.42E+01	8.81E+01
600	5.37E+01	4.70E+01	4.56E+01	4.17E+01	5.94E+01
900	4.69E+01	4.02E+01	3.82E+01	3.42E+01	4.39E+01
1200	4.06E+01	3.47E+01	3.28E+01	2.94E+01	3.54E+01
1500	3.67E+01	3.03E+01	2.87E+01	2.53E+01	3.00E+01
1800	3.32E+01	2.72E+01	2.55E+01	2.22E+01	2.51E+01
2100	3.01E+01	2.47E+01	2.25E+01	1.98E+01	2.19E+01
2400	2.78E+01	2.20E+01	2.05E+01	1.79E+01	1.95E+01
2700	2.58E+01	2.03E+01	1.89E+01	1.65E+01	1.82E+01

Table 2: 1 / [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	3.00E+02	3.17E+02	4.00E+01	2.92E+02	2.30E+02
600	2.84E+02	2.88E+02	3.63E+01	1.27E+02	1.03E+02
900	2.67E+02	2.64E+02	3.20E+01	7.94E+01	6.45E+01
1200	2.54E+02	2.48E+02	2.95E+01	5.65E+01	4.78E+01
1500	2.46E+02	2.30E+02	2.71E+01	4.46E+01	3.74E+01
1800	2.33E+02	1.78E+02	2.47E+01	3.70E+01	3.10E+01
2100	2.22E+02	1.70E+02	2.19E+01	3.15E+01	2.57E+01
2400	2.14E+02	1.62E+02	2.04E+01	2.75E+01	2.25E+01
2700	2.01E+02	1.55E+02	1.91E+01	2.42E+01	1.99E+01

Table 3: 1 / [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	2.45E+02	4.72E+01	2.82E+02	3.49E+02	3.62E+02
600	1.66E+02	3.71E+02	1.86E+02	2.02E+02	2.13E+02
900	1.29E+02	3.24E+02	1.37E+02	1.36E+02	1.61E+02
1200	1.05E+02	2.87E+02	1.09E+02	1.09E+02	1.30E+02
1500	8.52E+01	2.66E+02	9.16E+01	9.22E+01	9.84E+01
1800	7.36E+01	2.34E+02	7.85E+01	7.90E+01	8.45E+01
2100	6.49E+01	2.16E+02	6.92E+01	6.96E+01	7.28E+01
2400	5.83E+01	1.95E+02	6.11E+01	6.14E+01	6.43E+01
2700	5.21E+01	1.44E+02	5.41E+01	5.44E+01	5.82E+01

Table 4: 1 / [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	2.91E+02	3.13E+02	2.37E+02	6.65E+02	3.10E+02
600	2.57E+02	2.39E+02	1.97E+02	2.77E+02	2.39E+02
900	1.94E+02	1.95E+02	1.60E+02	2.18E+02	1.88E+02
1200	1.63E+02	1.70E+02	1.60E+02	1.86E+02	1.58E+02
1500	1.39E+02	1.50E+02	1.47E+02	1.59E+02	1.38E+02
1800	1.26E+02	1.31E+02	1.29E+02	1.35E+02	1.24E+02
2100	1.13E+02	1.15E+02	1.14E+02	1.21E+02	1.10E+02
2400	9.65E+01	1.01E+02	1.05E+02	1.09E+02	1.03E+02
2700	9.14E+01	8.60E+01	9.12E+01	9.82E+01	9.46E+01

Table 5: 1 / [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	3.42E+02	3.80E+02	5.19E+02	4.01E+02	3.36E+02
600	2.46E+02	2.73E+02	3.26E+02	2.92E+02	2.58E+02
900	2.02E+02	2.19E+02	2.55E+02	2.23E+02	2.05E+02
1200	1.70E+02	1.86E+02	2.02E+02	1.73E+02	1.74E+02
1500	1.44E+02	1.56E+02	1.69E+02	1.47E+02	1.48E+02
1800	1.27E+02	1.36E+02	1.48E+02	1.30E+02	1.30E+02
2100	1.13E+02	1.19E+02	1.29E+02	1.16E+02	1.16E+02
2400	1.03E+02	1.07E+02	1.15E+02	1.04E+02	1.05E+02
2700	1.02E+02	9.81E+01	1.04E+02	9.38E+01	9.56E+01

Table 6: 1 / [A] versus time(s)

Time	1ml	1.2ml	1.4ml	1.6ml	1.8ml
300	3.90E+02	1.04E+03	4.32E+02	4.57E+02	3.36E+02
600	2.69E+02	5.19E+02	3.39E+02	3.08E+02	2.56E+02
900	2.17E+02	3.34E+02	2.57E+02	2.85E+02	2.08E+02
1200	1.81E+02	2.59E+02	2.04E+02	2.39E+02	1.60E+02
1500	1.57E+02	2.08E+02	1.75E+02	2.06E+02	1.72E+02
1800	1.34E+02	1.73E+02	1.66E+02	1.74E+02	1.50E+02
2100	1.19E+02	1.46E+02	1.47E+02	1.47E+02	1.31E+02
2400	1.07E+02	1.28E+02	1.31E+02	1.30E+02	1.17E+02
2700	9.47E+01	1.14E+02	1.04E+02	1.15E+02	1.06E+02

Table 1: log Kobs versus log [B]

[B]	kobs	log [B]	log Kobs
7.81E-01	0.0004	0.10735	3.39794
9.37E-01	0.0005	0.02826	3.30103
1.09E+00	0.0007	0.03862	3.30103

Table 2: log Kobs versus log [B]

[B]	kobs	log [B]	log Kobs
7.81E-01	0.0002	0.10735	-3.69897
9.37E-01	0.0003	0.02826	-3.52288
1.41E+00	0.0009	0.147985	-3.04576

Table 3: log Kobs versus log [B]

[B]	kobs	log [B]	log Kobs
7.81E-01	0.0006	0.10735	3.22185
9.37E-01	0.0007	0.02826	3.1549
1.09E+00	0.0006	0.03862	3.22185

Table 4: log Kobs versus log [B]

[B]	kobs	log [B]	log Kobs
7.81E-01	0.0005	0.10735	3.30103
1.09E+00	0.0006	0.03862	3.22185
1.41E+00	5.00E-04	0.147985	3.30103

Table 5: log Kobs versus log [B]

[B]	kobs	log [B]	log Kobs
7.81E-01	0.0005	0.10735	3.30103
1.09E+00	6.00E-04	0.03862	3.22185
1.41E+00	5.00E-04	0.147985	3.30103

Table 6: log Kobs versus log [B]

[B]	kobs	log [B]	log Kobs
7.81E-01	6.00E-04	0.10735	3.22185
9.37E-01	8.00E-04	0.02826	3.09691
1.41E+00	4.00E-04	0.147985	3.39794

Table 7: of cumulative product at various pH

pH	Mass (g)
3	17.931
4	16.544
5	4.453
6	3.266
7	3.046
8	2.664