SYNTHESIS AND APPLICATION OF DIRECT DYES DERIVED FROM TEREPHTHALIC AND ISOPHTHALIC ACIDS ON COTTON FABRICS

BY

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M.Sc/SCIE/04006/2010-2011

A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL IN PARTIAL FULFILMENT FOR THE REQUIREMENTS FOR THE AWARD OF MASTERS OF SCIENCE (M.Sc.) DEGREE IN COLOUR CHEMISTRY AND TECHNOLOGY

DEPARTMENT OF TEXTILE SCIENCE AND TECHNOLOGY,
FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY ZARIA

JANUARY, 2013

DECLARATION

I hereby declare that this thesis was conducted and written by me and it is a record of my own research work and it has not been presented before in any previous application for a higher degree. References made to published literature have been duly acknowledged.

_____	_____	_____
Ishegbe, Joyce Eko	Signature	Date

CERTIFICATION

This thesis entitled "Synthesis and application of direct dyes derived from terephthalic acid and isophthalic acid on cotton fabric" by Ishegbe Joyce Eko meets the regulations governing the award of M.Sc degree of Ahmadu Bello University Zaria and it is approved for its contribution to knowledge and literary presentation.

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Prof. A. A. Joshua Dean, School of postgraduate studies	Signature	Date

DEDICATION

This research work is dedicated to a family I cherish so much; my husband, Sunday Ishegbe and my children Fidelia, Seth and Cephas.

ACKNOWLEDGEMENTS

Sincere gratitude to the Lord Almighty for his mercies and grace, He alone is worthy of praise for giving me the strength to carry out this research work.

My profound gratitude goes to my supervisors, Prof. K. A. Bello and Dr. A. A. Kogo for their immense support, guidance, motivation, encouragement and supervision throughout the duration of this work.

Many thanks also go to the following; my Head of Department; Prof M. K. Yakubu, Prof E. G. Kolawale, Prof P. O. Nkeonye, Dr A. Giwa, Dr. Abdullahi Danladi, Mr Ameru and all the teaching staff and non-teaching staff for their support, especially Mr Abdullahi, Mr Omata, Mr Okeje and Mallam Nuhu for their assistance during my practical in the laboratory. My immense gratitude also goes to all M.Sc postgraduate colleagues for cordial interactions, useful discussions and numerous supports. Special thanks to Solomon Hassan-Kuta for his assistance and many others.

Sincere and special thanks go to my dearest husband Sunday Ishegbe and precious children for their support, love, understanding, tolerance and perseverance throughout the period of my programme.

Once again, many thanks to Prof. K. A. Bello for all his support.

I sincerely pray that God Almighty will reward you all abundantly.

ABSTRACT

The synthesis of direct dyes derived from terephthalic and isophthalic acid using J and H-acids was undertaken with the view of replacing benzidine moiety in the production of direct dyes. The amide derivatives of isophthalic and terephthalic acids were used as the coupling components while aniline and its derivatives were used as the source of diazo components. The amide derivatives were characterized by GC/MS and Infra-red analysis. The spectroscopic properties of the dyes in various solvents were also examined and most of the dyes showed bathochromic shifts when the solvent was changed to more polar solvents. The dyes also showed positive and negative halochromism with the addition of few drops of hydrochloric acid (HCl). The synthesized dyes were applied to cotton fabrics and their performance properties evaluated. They have good exhaustion in the presence of electrolyte and have good wash fastness properties upon application of after-treating agents of values of 3-4, 4 and 4-5. They also had good fastness properties to light of values between 4-7. Their resistance to rubbing and perspiration had values between 3 and 4-5. The toxicity of the dyes was also studied and they were found to be non-toxic.

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CHAPTER ONE

1.1 INTRODUCTION

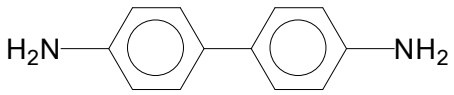
Benzidine is an organic chemical belonging to the class of amines and used in making numerous dyestuffs. The azo dyes derived from benzidine are important because, unlike simpler classes of azo dyes, they become strongly fixed to cotton without a mordant (Schwenecke and Mayer, 2005).

Benzidine is prepared from nitrobenzene by reduction in alkaline medium to hydrazobenzene ($C_6H_5NHNHC_6H_5$), which is converted to benzidine by treatment with strong acid. This process is the simplest case of a general reaction, the benzidine rearrangement. The benzidine rearrangement which proceeds intramolecularly, is a classic mechanistic puzzle in organic chemistry (March, 1992).

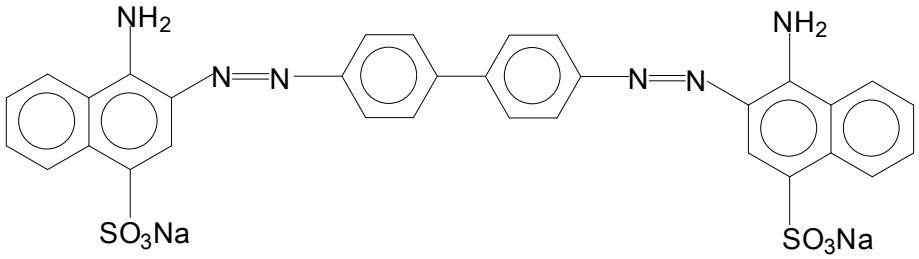
The chemical reactions of benzidine are typical of aromatic primary amines; with nitrous acid it yields the bisdiazonium salt, which may be coupled with aromatic amino or hydroxyl compounds to produce azo dyes.

Benzidine, a colourless, crystalline solid, practically insoluble in water, is toxic, causing dermatitis and bladder tumours. It is used in forensics for the identification of bloodstains (Joseph, 1985).

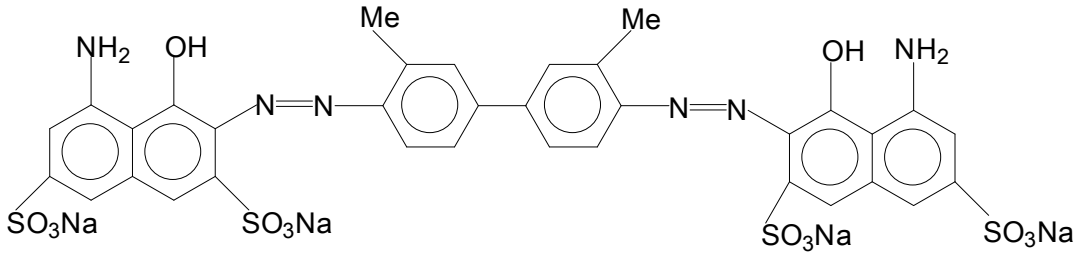
It is well known that benzidine is both a mutagenic amine and a human carcinogen (Wojciechowski, 2003). Prior to the realization of these facts, many dyestuffs were produced that employed benzidine or a benzidine congener such as ortho-tolidine or ortho-dianisidine as a precursor.By the 1980s, however, dyes derived from benzidine as shown below and certain of its derivatives were designated as cancer-suspect agents, and alternatives were sought (Wojciechowski, 2003).



Benzidine



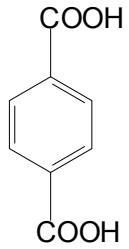
Congo Red



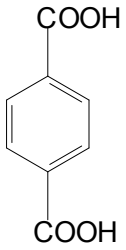
C.I. Direct Blue 14 (Trypen Blue)

However, because benzidine is carcinogenic, its use for the production of dyes was forbidden. Another important group of direct dyes includes urea types manufactured by the acylation of aminoazo derivatives with phosgene. This process allows the rapid preparation of valuable dyes, but requires the use of toxic phosgene and hermetic and thus, expensive apparatus (Wojciechowski, 2003). The problems associated with the synthesis of direct benzidine and urea dyes has resulted in the search for new dyes whose production and use would meet high environmental and safety requirements.

This work is focused on the possibilities of using terephthalic acid and isophthalic acid as "bridging groups" for the synthesis of symmetrical direct dyes.



Terephthalic acid



Isophthalic acid

From time immemorial cotton has been and still remains the single most important textile fibre on account of its overall excellent properties and it is dyed cheaply with direct dyestuffs. This necessitates the use of varied colorants that are non-mutagenic and carcinogenic to meet up the ever increasing demand in the use of these substrates. It is hoped that the new dyes to be derived from this work will give better performance properties to replace the existing carcinogenic dyes from benzidine.

1.2 OBJECTIVES OF THE STUDY

The aim of this study is to substitute benzidine with other compounds/intermediates that are not carcinogenic and to produce a range of direct dyes that are environmentally friendly, non-toxic and non-carcinogenic.

This study will also examine and determine the effects of bridging systems on the spectrophotometric and application properties of symmetrical direct disazo dyes derived from J-acid and H-acid.Other objectivesinclude:

(i) Analysis of the structures of amide derivatives of isophthalic and terephthalic acid by using infra-red spectroscopy (IR), gas chromatography (GC), mass spectroscopy (MS), and UV/Visible spectroscopy.

(ii) Application of the dyes to woven cotton fabric.

(iii) Evaluation of the performance properties such as wash, light and perspiration fastness.

1.3 STATEMENT OF THE PROBLEM

Direct dyes derived from benzidine have been known to be toxic and carcinogenic. The focus is to replace benzidine with another compound that is non-toxic and non-carcinogenic and can be used as a bridging link in the synthesis of symmetrical direct dyes.

1.4 JUSTIFICATION OF THE STUDY

Prior to the realisation that benzidine is carcinogenic,many direct dyes have been produced with this intermediate. As a result of this development,dye chemists have been kept busy to find alternative intermediate for the replacement of benzidine in the production of direct dyes. The present work is justified by the production of amide derivatives of isophthalic and terephthalic acids as bridging unit for the replacement of benzidine in the synthesis of symmetrical direct dyes.

1.5 SCOPE OF THE STUDY

These include synthesis of the coupling components and direct dyes derived from Isophthalic and terephthalic acids using J-acid and H-acid as intermediates for the coupling components, while aniline, p-anisidine , p-chloro aniline and p-nitroaniline to be used as source of diazo components.

The synthesized dyes and intermediates were purified and characterized using the UV visible, IR, GC- MASS spectrophotometers.

The toxicity of the synthesized coupling components and dyes was determined using Dietrich Lorke / LD_{50} method on Albino mice

The dyes were applied to cotton fabric.The effect of varying the concentration of electrolyte,time and temperature,percentage shade as well as % exhaustion of the dyes were carried out.Evaluation performance properties e.g wash, light,rubbing and perspiration fastness of the dyed fabric were carried out as well.

CHAPTER TWO

2.0 LITERATURE REVIEW

The art and science of dyes began more than 10,000 years ago. The very first dyes may have been crude compounds made of plants mixed with water by early - uncivilized man for the purpose of tribal rituals, to identify, differentiate class of status group or simply amuse children with colours (Shore, 1990).

A dye is an organic substance used to impart colour to other materials by dyeing or pigmentation. Dyes are used to colour natural fibres, such as cotton, silk, wool and linen and synthetic fibres, such as nylon, cellulose acetate and polyester. They are also used on other type of substrates such as leather, wood, food, paper and in photography. Dyes for home use are the same as those used in industry and they are applied by same methods (Iyun, 2008).

2.1 DYES AND THEIR REQUIRED PROPERTIES

A dye is a deeply coloured organic compound usually soluble in water, but not all coloured compounds are textile dyes. Some are only useful as indicators in chemical titration (e.g. methyl orange), while some are used as stains or solvent dyes for colouring solvent such as petrol, etc.(Nkeonye, 1993).

For a dye to be useful as a textile dye,it must have the following properties:

(a) Intense colour-arising mainly from charge transfer.

(b) Attraction or affinity for the fibre.

(c) Substantivity; capable of being absorbed and retained by the fibre after application and/or fixation, and reactivity, -ability to be chemically combined with the fibre.

(d) Sufficient degree of resistance (fastness) to common agencies encountered during use of the coloured materials e.g. light, water, rubbing, etc.

(e) Solubility in aqueous solution either permanently or during the dyeing operation. This is because the dyes are usually in form of salts.

In addition to colouring textiles, some textile dyes can be used to colour substances such as paper, leather, fur, etc.

2.2 .0 CLASSIFICATION OF DYES

Dyes may be classified according to chemical structure or according to their method of application. Classification according to their chemical constitution/structure is mostly useful to the dye chemist who may be interested in dye synthesis and relationship between chemical structure and properties of dye. Classification according to method of application is most useful to the technologist concerned with coloration of textile products (Perkin, 1996).

2.2.1 Dye classes according to application method

Eight major dye classes according to method of application are commonly used. The five classes used mainly on cellulose fibres are direct dyes, sulphur dyes, azoic dyes, reactive dyes and vat dyes. The three classes mainly used for protein and synthetic fibres are acid dyes,basic dyes and disperse dyes. All of these are synthetic organic compounds that have been discovered since the synthesis of the first synthetic dye by W.H.Perkin in 1856 (Perkin, 1996).

Direct dyes are so named because of their natural affinity for cellulose and can be applied without using any auxillary chemicals. In practice,the dyeing rate can be improved by adding inorganic salts such as sodium chloride or sodium sulphate to the dye bath. The direct dyes are widely used on cotton and rayon. The greatest advantage of direct dyes is their simplicity

of application. The greatest limitation is that their fastness to washing is not good enough for some purposes. Wash fastness is improved by resin treatment of dyed fabrics or by various after treatments (Abrahart, 1997).

Sulphur dyes are complex organic compounds synthesized by heating simple amines or phenolic compounds in the presence of sulphur. Sulphur dyes exist as a pigment form which does not have affinity for cellulose. They are converted to water soluble form having affinity for cellulose by treatment with a reducing agent under alkaline conditions, after application to the fibre, sulphur dyes must be oxidized back to their pigment form. The greatest advantage is relatively low cost while their biggest limitation is that they are not bright enough in colour for many uses (Iyun, 2008).

Azoic dyes are coloured compounds that are synthesized inside the fibre by coupling of two components neither of which is a dye itself. The two components are an aromatic diazonium salt and an aromatic hydroxyl compound, often a naphthol. Because of the use of naphthol as a coupling component in the reaction,they are often called naphthol dyes. Although the coloured material produced in azoic dyeing is a pigment, the azoics are classified as dyes because the naphthol component have affinity for cellulose and is applied like a dye before the diazo component is added. The greatest advantage is that they provide an economical way to obtain certain shades,especially red. The greatest limitation is that they sometimes posses poor fastness to crocking (Trotman, 1984).

Reactive dyes are relatively new, having been developed in the 1950s. They are sometimes called ‘fibre reactive dyes’.Reactive dyes chemically react with the fibre forming covalent bonds and since the covalent bond between the dye and the fibre are strong, reactive dyes have excellent wash fastness. Outstanding wash fastness isthe greatest but by no means the only advantage of reactive dyes.Its limitation includes higher cost than some other classes

Vat dyes are like sulphur dyes in that they are pigments which must be reduced and oxidised during application. Vat dyes have excellent wash fastness and light fastness as a class. Their biggest disadvantage is relatively high cost (Rys and Zollinger, 1972).

Acid dyes are so called because they contain acidic groups in their structure which react with basic groups in protein and polyamide fibres forming organic salts. Individual acid dyes vary greatly in properties and are sub grouped according to properties and compatibility (Lillie, 1997).

Basic dyes are sometimes called cationic dyes because the chromophore in basic dye molecule contains a positive charge. These basic or cationic groups react with acidic groups in acrylic, cationic dyeable polyester and nylon, or occasionally protein fibres. The salt linkages are similar to those formed between acid dyes and fibre containing basic groups. The limitation is that their fastness to light is sometimes not satisfactory,especially on protein fibres.

Disperse dyes are used mostly for polyester,nylon and cellulose acetate although they will dye some other fibres. These dyes are almost insoluble in water and have to be dispersed in water to make the dye bath. They are the only acceptable dye class for cellulose acetate and unmodified polyester fibres (Venkataraman, 1972).

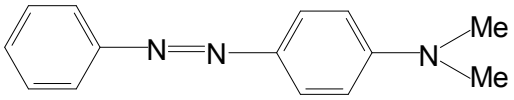
2.2.2 Dye classes according to chemical structure.

Dyes are classified by the type of chromophore present in them as follows.

2.2.2.1 Azo dyes.

They contain at least one azo group [-N = N -] but can contain, two, three or more, rarely four azo groups. The characteristic azo groups in the dye molecule form bridges between organic molecules, of which is usually an aromatic nucleus (March, 1992).

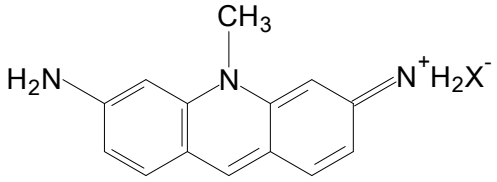
Diazotization of aromatic primary amines in the presence of sulphuric or hydrochloric acid and sodium nitrite at freezing temperature, produces a diazonium salt which in turn coupled with aromatic compounds, phenol, naphthol, etc. producing azo dyes.



Azo Colorant

2.2.2.2 Acridine dyes

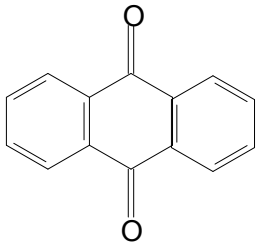
Acridine dyes are derived from acridine. The general formular shows the chromophore to be a quinoid ring, positively charged which is shown on the nitrogen atom attached to the quinoid ring and the dyes are consequently basic (Lillie, 1997).



Acridine dyes

2.2.2.3 Anthraquinone dyes

They are derived from anthracene. They have the general formular,



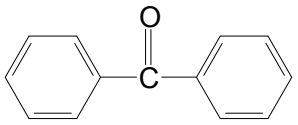
Anthranquinone

The general formular shows the chromophore to be a quinoid ring. Anthraquinone is a fairly coloured compound and does not possess dyeing properties until when electron donors such

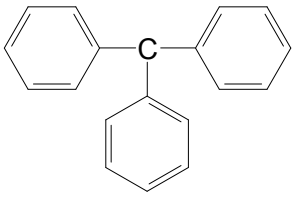
as OH, NH_2 NHAr etc are attached to the general structure. These electron donors also provide the compound with the ability to absorb in any desired region of the visible spectrum. They are synthesized by cyclisation and reduction reaction between components containing several reactive positions.

2.2.2.4 Aryl methane dyes

They are dyes derived from methane but in which some of the hydrogen atoms are replaced with aryl rings. Since a synonym for aryl is phenyl, they may also legitimately be called phenylmethane dyes. It could be diaryl or triarylmethane depending on the number of the aryl ring replacing the hydrogen atom. The hue and the dyeing properties depend on the nature and number of auxochromic groups that are attached to the chromophore. The pararosanin homologues are good examples of triarylmethane each of the three aryl rings has an amino group. The quinoid ring is the chromophore.



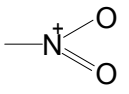
Diarylmethane



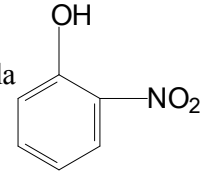
Triarylmethane

2.2.2.5 Nitro dyes

Nitro dyes contain the nitro chromophore.



With a general formula



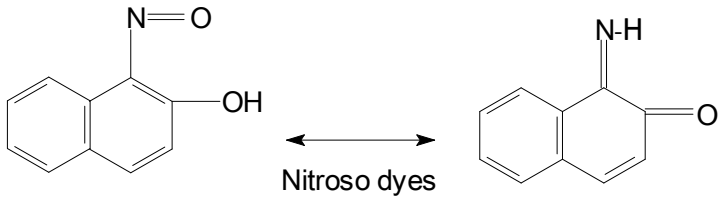
Nitro dyes

The empirical way of designating the nitro group does not indicate that its electrons are delocalized. The bonds to the two oxygen atoms are of equal strength and are shown as a single and double bond only for convenience. The electrons from both are shared, and these delocalized electrons are integrated with the delocalized electrons of the aryl rings of dyes causing absorption in the visible range. The dyes so formed are invariably acid dyes e.g. picric acid and martius yellow. These dyes are now of only minor commercial importance but of interest for their small molecular structure (Hsieh, 1990).

2.2.2.6 Nitroso dyes

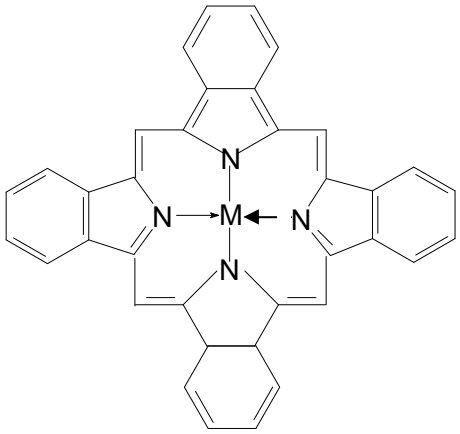
Nitroso dyes are meta complex derivatives of o- nitrosophenols or naphthols. Tautomerism is possible in the meta-free precursor between the nitrosohydroxy tautomer and the quinoneoxime tautomer.

The only nitroso dyes of Important commercially are the iron complexes of sulfonated 1-nitroso- 2-naphtol, these inexpensive colorants are used mainly for colouring paper.



2.2.2.7 Phthalocyanine dyes

Phthalocyanines are analogs of the natural pigments chlorophyll and haemin. However, unlike these natural pigments, which have extremely poor stability, phthalocyanines have good stability and are probably the most stable of all the colourants in use today (Rys and Zollinger, 1972). Substituents have only a minor effect on the colour thus their hues are restricted to blue and green. Consequently, phthalocyanines are used extensively in printing inks and paints.



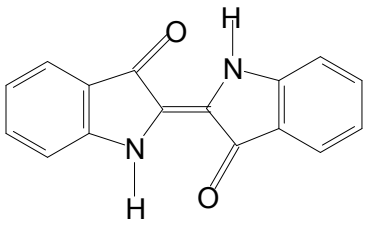
Phthalocyanine

2.2.2.8 Sulphur dyes

They are synthesized by heating aromatic amines, phenols or nitro compound with sulphur or alkali polysulfides. The chromogen for sulphur dyes can easily be defined because it is likely that they consist of macromolecular structures of the phenothiazonethianthrone type in which the sulphur is present as sulphide bridging links and as thiazine groups. Sulphur dyes are used for dyeing cellulosic fibres (Kirk, 1965)

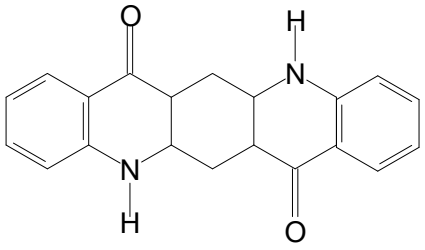
2.2.2.9 Indigoid colorants.

This substantial class of vat dyes and pigments has declined gradually in importance to the anthraquinone derivatives. The pre-eminent representatives are indigo. In indigo and thioindigo the chromophoric system is symmetrical. These dyes can exist in both cis and transform; the latter is the more stable form and predominates in the solid state.



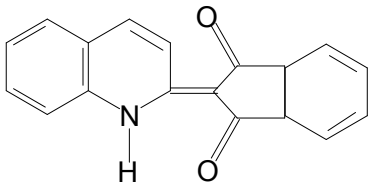
Indigo

2.2.2.10 Quinacridone pigments: This chromophore is somewhat reminiscent of the indigoid and anthraquinonoid types but it has not yielded useful vat dyes.



Quinacridone

2.2.2.11 Quinophthalone dyes: This class is precisely associated with quinophthalone e. g



Quinophthalone

Other classes of dyes are;
Stilbene dyes
Quinine imine dyes
Thiazole dyes
Formazan dyes
Xanthene dyes.

2.3.0 DYEING PRINCIPLES

The dyeing of textile fibres is carried out in an aqueous solution known as dye liquor. Uniformity and colour fastness requirements are major determining factors in selection of dyes and dyeing methods for textile materials. The depth of colour achieved depends mainly on how much dye is added to the fibre. The location of dye on the fibre has some influence on the apparent depth of colour. Dye close to the surface of the fibre or near the surface of the yarn or fabric contributes more to the apparent depth than does deeply penetrated dye. Often auxiliary chemicals are added to the dyebath to improve exhaustion. Most dyeing processes

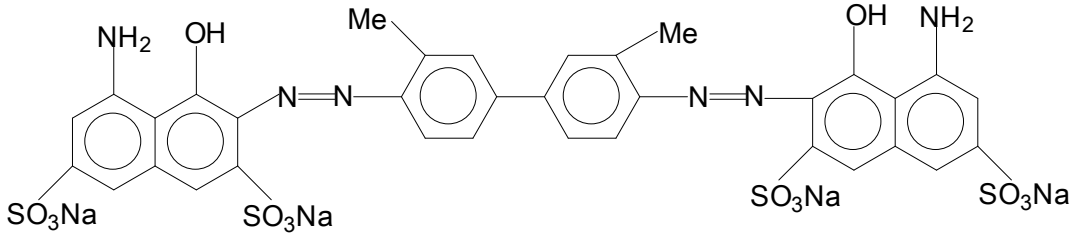
are reversible. The time required to reach equilibrium depends on many factors such as temperature, type of dye, type of fibre, and presence of dye auxiliaries. Equilibrium dyeing time may range from a few minutes to many hours (Perkins, 1996).

2.3.1 General features of direct dyes

Direct dyes are water soluble dyestuffs which are absorbed directly by cellulosic fibres such as cotton, linen and rayon from an aqueous solution containing electrolyte. Nearly all direct dyes are azo compounds containing sulphonic acid groups to impact aqueous solubility, the dyes themselves being the sodium salt of these aromatic sulphonic acids. Direct dyes depend on secondary forces such as hydrogen bonds and vander Waals forces to bond with cellulosic fibres. Since secondary forces are relatively weak, the interaction of the dye and fibre is greater if the dye molecule is large (Abrahart, 1997).

Therefore, direct dyes are high molecular weight compounds,(typically about 400 to 1200) containing 2, 3, or more azo groups. The great majority of direct dyes are azo structures. Although a few monoazo products are known but disazo and trisazo structures are more common because the higher molecular weight structures have better wash fastness (March, 1992).

C.I.Direct blue 14 is a good example to show the important structural characteristics of directdyes.



C.I. Direct Blue 14 (Trypen blue)

The trans configuration of the azo groups gives the molecule a generally linear shape. Linearity in the structure is important so that the dye molecule can align and interact well with the cellulose chains in the fibre. The aromatic rings in the structure must also have the capacity to rotate into a coplanar arrangement with one another, coplanarity of the aromatic ring is important for two reasons. First,it makes the molecular shape generally flat allowing good interaction between the dye and the fibre. Also,it is required for overlap of the pi-orbitals and delocalization of electrons(resonance). Resonance is an important factor in light absorption and colour of organic molecules. The presence of too many ionized solubilizing group/sodium sulphonate groups makes the dye molecule polar enough to dissolve in water. Degree of exhaustion of the dye from the dye bath to the fibre depends on the relative attraction of the dye molecules for these two phases (Abrahart, 1997). The solubility of direct dyes in water increases dramatically with an increase in temperature, and hot water is usually required to dissolve the dye in the dyebath. The sulphonate groups on direct dye molecules are salts formed by the reaction between a sulphonic acid group and a strong base.

$DYE{-}SO_3H + NaOH \rightarrow DYE{-}SO_3^-Na^+ + H_2O$

Free acid form *sodium salt form of a dye*

Direct dyes also generally contain groups such as amino or hydroxyl which is capable of forming hydrogen bonds with hydroxyl groups in the cellulosic fibre.

2.3.2 Dyeing methods

Direct dye may be applied either by batch or continous method. Exhaust dyeing procedures consist of the following steps:

1. Dye is dissolved in water and the fabric which has been appropriately prepared for dyeing is immersed in the dyebath solution.

2. The temperature of the dye-bath is gradually increased to near boiling point of water and held at this temperature for some period of time. It may be decreased in the latter stage of dyeing to enhance exhaustion.

3.Common salt or Glauber's salt is added to enhance exhaustion of the dye. The timing of salt addition depends on the particular dyes selected.

4. The dye liquor is removed and the fabric is rinsed to remove residual salt and dye that did not exhaust.

5. An after-treatment to improve color fastness of the dyed material may be done at the end of dye cycle or during a subsequent finishing process.

Continuous and semi-continuous dyeing methods include a padding step. The concentrationof dye in a pad formulation must be much higher than(as much as 50 times) than the concentration of dye in batch process. Padding methods that can be used for direct dyes include pad-jig,pad-batch on hot roll and pad steam (Perkin, 1996).

2.4.0 AFTERTREATMENT OF DIRECT DYES

The main set back of direct dyes is their rather low fastness to wet treatment and sometimes also to light. Their washing fastness may be described as poor to moderate while their fastness to light is improved in suitable cases by subjecting the dyed material to an after-treatment. Dyeing is sometimes aftertreated to improve its properties and this depends upon two factors; the fastness required of the dyed material and the chemical structure of the dye (Abrahart, 1997).

Aftertreatments generally work on the principle of increasing the size of the dye molecules or decreasing its solubility in water.

Treatment of the fabric with a resin finish usually improves fastness to washing. This probably results mostly from the crosslinking effects of the resin on cellulose. Crosslinking

decreases the tendency of cellulose to swell in water which restricts diffusion of the dye out of the fabric. It is also possible that chemicals in the resin finish react with the dye molecules increasing their size and restricting their ability to diffuse out of the fibre.

Direct dyes which contain a primary amino group attached to an aromatic ring can be diazotized and coupled to a naphtol component. The naphtol component is called a developer, and dyes which have this capability are called direct-developed dyes. This process adds an azo group to the dye structure so the colour is usually affected. The final colour depends on the colour of the developer used. Primuline is a classic example of a direct-developed dye.

Aftertreatment with a cationic fixation agent can improve their wash fastness. Such cationic agents are usually surface active agents. They are believed to combine with the sulphonic acid groups in the dye to produce large organic salts which are insoluble in water and therefore more difficult to wash from the fabric.

Direct dyes which have atoms containing unshared electrons pairs at certain positions in the dye molecules will form complexes with metal ions such as copper and chromium. Thetreatment with metal salts improves both wash and light fastness. Improvement in light fastness is associated with copper while improvement in wash fastness is associated with chromium(Perkin, 1996).

2.4.1 Effect of electrolyte on dye absorption of direct dyes

Addition of salts such as sodium chloride is believed to increase the degree of aggregation of ionic dyes in water. This is sometimes called the ‘common ion effect’. Since larger aggregates will be attracted to water, the dye may transfer to the fibre more easily. This ‘salting out’ effect may be one of the reasons why addition of salts causes increased exhaustion of dye in some dyeing systems.

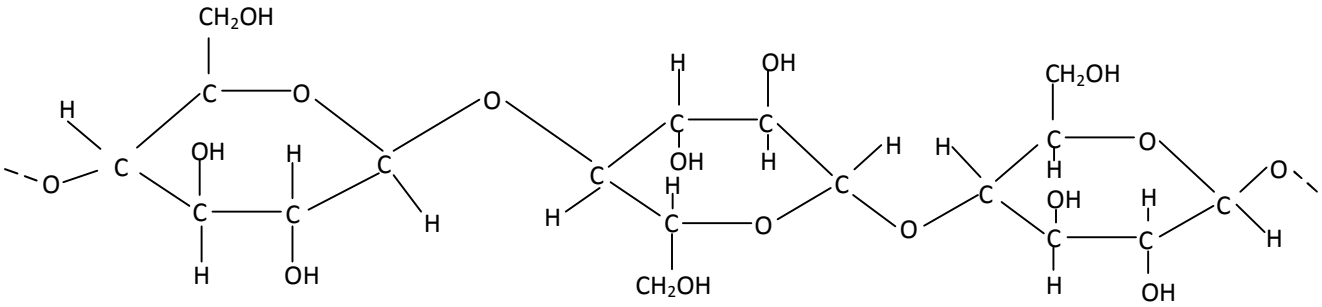
Tetra sulphonated dyes are affected more by the presence of salts than are dibasic dyes. Cellulose assumes a negative charge when in contact with water. Since the direct dye

chromogen is also negatively charged, the dye and the fibre repel one another. In order for dyeing to occur, this electrical repulsion must be overcome by other forces of attraction between the dye and the fibre. The donnan model for dye adsorption on cellulose is based on the concept that the water layer very close to the fibre surface, called the internal solution, is influenced by the charge on the fibre. According to the donnan model, dyeing occurs by transfer of dye from theexternal to the internal solution. When salt is added to the dyebath, the ions distribute between the external and internal solution so that the surface charge of the fibre is neutralized. This neutralization allows the dye molecules to approach the fibre closely enough for the forces of attraction between the fibre and dye to take effect (Bird and Boston, 1975).

2.5.0 Fibre structure in relation to dyeing

2.5.1 Natural fibre

Cotton consists of almost pure cellulose, the most abundant of all organic polymers, natural orotherwise. Cellulose is a linear polymer of glucose molecules.



Structure of cellulose

The cellulose chain bristles with cellulose polar –OH Groups. These groups form many hydrogen bonds with OH groups on adjacent chains, bundling the chains together (Doree, 1947).

The presence of –OH group, the size and configuration of the glucose units, are of great importance in the physics and chemistry of cotton dyeing. It will be seen that each hexose

unit has three –OH groups and these can be acetylated, cellulose triacetate (CT) being the fully acetylated product. By controlled alkaline hydrolysis, some of the acetyl groups can be removed from the triacetates and the productcontaining an average of about 2.3 acetyl groups per hexoseunit is known as secondary acetate (CA). These products, which are widely used as fibres, differ from cellulose in being solublein certain solvents, (CT in chloroform; CA in acetone) whereas cellulose is not. Moreover, the direct dyes used in cottondyeing have little or no substantivity for either the triacetatesor secondary acetates (Abrahart, 1997).

2.5.2 Mechanism of dyeing with ionized dyes on substrates without sites.

Under normal dyeing conditions with direct dyes, cellulosic fibres remain largely un-ionized, with no formally charged sites at which dye interaction can occur, although there may possibly be a small number of ionized carboxylic acid groups. The substrates is water swollen and contain a system of pores and channels,the dye being able to enter via the dye solution contained in this system. The dyes generally contain two or more ionized sulphonic acid groups and, when absorbed on the pore surfaces, they are still accompanied by attendant (usually Na^+) gegeions to preserve electrical neutrality. When sodium chloride is added to the dye solution,the diffusion of sodium cation is facilitated by mass action and the amount of dye anions adsorbed by the fibre is increased. The diffusion coefficient of the dye is therefore a function of both dye and electrolyte concentration (Bird and Boston, 1975).

CHAPTER THREE

3.0 EXPERIMENTALS

These were carried out using the materials and methods as listed in section 3.1.1 and 3.1.2

3.1 MATERIAL AND METHODS

The materials and methods used are listed in section 3.1.1 and 3.1.2

3.1.1 Chemicals and reagents

Analytical grade reagents and chemical from Sigma Aldrich were used for this research work. These include; thionyl chloride, terephthalic acid, isophthalic acid, J-acid (1-napthol-6 amino-3-sulphonic acid and H-acid (1-napthol-8-amino-3,6-disulphonicacid), chlorobenzene, dimethylformamide (DMF), sodium nitrite, sulphuric acid, concentrated hydrochloric acid, aniline, p-chloroaniline, p-toluidine, p-nitroaniline, urea, ethanol, sodium hydroxide, sulphuric acid, sodium carbonate and ethanol. These chemicals and reagents were used without further purification.

3.1.2 MATERIALS

Woven cotton fabric, filter paper, magnetic stirrer, round bottom three neck flasks and a condenser, hot plate, grey scale, steam bath, starch iodide paper.

3.2.0 METHODS

The methods used are as shown in section 3.2.1

3.2.1 Synthesis of coupling components

The coupling components were synthesized using the methods shown in section 3.2.1.1 to

3.2.1.6

3.2.1.1 Preparation of chlorides of terephthalic acid.

Terephthalic acid (8.3g, 0.05mol) was heated with thionyl chloride (11ml) in chlorobenzene (250ml) in the presence of DMF (1ml) as catalyst (Wojciechowski, 2003). The process was carried out at a temperature of 60-70^{0}C for 6-9hrs. The obtained acidic chloride, without separation was used for the acylation of J and H-acids (Scheme 1a)

3.2.1.2 Synthesis of coupling component using terephthalic acid and J-acid as intermediate-N,N'-bis-(8 – hydroxyl -6-sulphony-naphthalene-2-(3)-yl)-phthalamides of terephthalic acid.(TJA)

Acid chloride dissolved in chlorobenzene (250 ml) was added to an aqueous solution of J-acid (0.01mol, 2.4g) at a temperature of 10^{0}C and at such a rate as to obtain a pH of 6.8-7.2 (Wojciechowski, 2003).The mixture was heated to 50^{0}C and stirred at this temperature for 30 minutes. The solution was then cooled, its pH was adjusted to 7.5-7.75 with 10% aqueous NaOH and the product was salted out,filtered, wash with brine (pH= 7.7) and dried (Scheme 1a).

3.2.1.3 Synthesis of coupling component usingterephthalic acid and H-acid as intermediate- N,N'-bis-(8-hydroxy-3,6–disulphonynaphthalene-2-(3)-yl)-phthalamides of terephthalic acid (THA)

Acid chloride dissolved in chlorobenzene (250 ml) was added to an aqueous solution of H-acid (0.01mol, 3.2g) at a temperature of 10^{0}C and at such a rate as to obtain a pH of 6.8-7.2 (Wojciechowski, 2003). The mixture was heated to 50^{0}C and stirred at this temperature for 30 minutes. The solution was then cooled, its pH was adjusted to 7.5-7.75 with 10% aqueous NaOH and the product was salted out,filtered, wash with brine (pH= 7.7) and dried (Scheme 1b)

3.2.1.4 Preparation of chlorides of isophthalic acid.

Isophthalic acid (8.3g, 0.05mol) was heated with thionyl chloride (11ml) in chlorobenzene (250ml) in the presence of DMF (1ml) as catalyst. The process was carried out at a temperature of 60-70^{0}C for 6-9hrs. The obtained acidic chloride, without separation was used for the acylation of J and H-acid (Scheme 2a).

3.2.1.5 Synthesis of coupling component using isophthalic acid and H-acid as intermediate-N,N'-bis-(8-hydroxy-3,6-disulphony-naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (ISH)

Acid chloride dissolved in chlorobenzene (250ml) was added to an aqueous solution of H-acid (0.01mol, 3.2g) at a temperature of 10^{0}C and at such a rate as to obtain a pH of 6.8-7. The mixture was heated to 50^{0}C and stirred at this temperature for 30 minutes. The solution was then cooled, its pH was adjusted to 7.5-7.75 with 10% aqueous NaOH and the product was salted out,filtered, wash with brine (pH= 7.7) and dried (Scheme 2a)

3.2.1.6 Synthesis of coupling component using isophthalic acid and J-acid as intermediate-N, N' – bis-(8 – hydroxyl -6-sulphony-naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (IJA).

Acid chloride dissolved in chlorobenzene (250ml) was added to an aqueous solution ofJ-acid (0.01mol, 2.4g) at a temperature of 10^{0}C and at such a rate as to obtain a pH of 6.8-7.2. The mixture was heated to 50^{0}C and stirred at this temperature for 30 minutes. The solution was then cooled, its pH was adjusted to 7.5-7.75 with 10% aqueous NaOH and the product was salted out,filtered, wash with brine (pH= 7.7) and dried (Scheme 2b).

3.3.0 GENERAL METHOD OF DIAZOTISATION

Aniline, p-chloro aniline, p-nitroaniline and p-anisidine were diazotized in a conventional manner using direct and suspension methods (Perkins, 1996).

3.3.1Diazotisation of aniline and p- anisidine

The amines (0.00365mol, 0.4g aniline) and (0.00365mol, 0.5g p-anisidine) were respectively dissolved in 1ml of HCl and cooled to 0-5^{o}C in an ice bath equipped with a magnetic stirrer.Sodium nitrite (0.7g, 0.00673 moles) dissolve in 10ml of distilled water was added dropwisely over a period of 30 minutes while stirring for another 45 minutes. Urea (0.5g) was then added to the mixture and stirring was continued for another 10 minutes to achieve complete diazotization.

3.3.2 Diazotization of p-chloro aniline and p- nitro aniline

The amine (0.00365mol, 0.5g) was dissolve in 1ml of hot concentrated HCl and cooled very rapidly to 0-5^{o}C in an ice bath equipped with a magnetic stirrer by addition of ice to obtain a fine suspension of the amine-hydrochloride. Sodium nitrite (0.7g) dissolve in 10ml of distilled water was added drop wisely over a period of 30 minutes while stirring for another 45 minutes. Urea (0.5g) was then added to the mixture and stirring was continued for another 10 minutes to achieve complete diazotization.

3.3.2.1 Preparation of dyes A_1, A_2, A_3 and A_4

The primary amines(aniline, p-anisidine, p-chloroaniline and p-nitroaniline) respectively were diazotized using the procedures in sections 3.3.1 and 3.3.2 respectively and were each coupled with the coupling component obtained using terephthalic acid and J-acid as intermediate-(N, N'-bis-(8-hydroxy-6-sulphony-naphthalene- 2 - (3)-yl)-phthalamides of terephthalic acid) (Scheme 3).

Disazo dyes were prepared by coupling the diazotized amines (aniline, p-anisidine, p-chloroaniline and p-nitroaniline (0.013mol) from above procedures with (0.005mol, 3.12g) of the coupling component(N,N' – bis-(8 – hydroxyl – 6 – sulphony – naphthalene-2-(3)-yl)-phthalamides of terephthalic acid)dissolved in 50ml of water at pH=12-12.5 and 10-15^{0}C. The dye was salted out using NaCl (20%) filtered off and dried in air (Scheme 3).

3.3.3 Preparation of dyes A_5, A_6, A_7 and A_8

The dyes were obtained by coupling the diazonium ions obtained from aniline, p-anisidine, p-chloroaniline and p-nitroaniline respectively, with(0.005mol, 3.63g) of the coupling component obtained using terephthalic acid and H-acid (N, N'-bis-(8-hydroxy-3,6-disulphony-naphthalene-2-(3)-yl)-phthalamides of terephthalic acid) (Scheme 4).

3.3.4 Preparation of dyes B_1, B_2, B_3, and B_4

The procedure is same as in section 3.3.3, except that the coupling component used was obtained using J-acid and isophthalic acid- N,N'-bis-(8-hydroxy-6-sulphony-naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (IJA) (Scheme 5).

3.3.5 Preparation of dyes B_5, B_6,B_7 and B_8

The procedure is same as in section 3.3.3 above, except that the coupling component used was obtained using isophthalic acid and H-acid (N,N'-bis-(8-hydroxy-3,6-disulphony-naphthalene-2-(3)-yl)-phthalamides of isophthalic acid) (Scheme 6).

3.4.0 Melting point determination

The melting points of the dyes synthesized were determined using Gallenkamp melting point apparatus. The values obtained are shown in Table 4.1

3.4.1 UV-Visible analysis of the dyes.

The peak for maximumabsorption wavelength for each dye was determined in distilled water using UV-visible spectrophotometer (Jenway UV/visible spectrophotometer; model: 6405). The effect of the solvent polarity on the absorption maxima of the dyes was also investigated in ethanol, dimethylformamide (DMF). Similarly the effect of acid on the absorption maxima of the dyes was studied.

Using the λ_{max} obtained in distilled water for each of the 16 dyes, the absorbance was recorded for a known concentrationof each of the dyes. The path length (L) was 1cm. The molar extinction coefficient of each dye was calculated using the formula given below. The results are shown in Table 4.4

$\varepsilon = A/CL$

Whereε= molar extinction coefficient ($dm^3mol^{-1}cm^{-1}$)

A=Absorbance at λ_{max}

C=concentration in mol/dm^3

L=path length of cell

3.4.2 Infra-red and GC-MS Analysis of the dyes

The infra-red spectra of some of the dyes were determined using the FTIR spectrophotometer to determine the functional groups present. Also the structures of the intermediates were determined using the GC-MS spectrophotometer. The results are summarised in Table 4.2

3.4.3Application of dyes on cotton fabrics

1% stock solution of each dye was prepared,using a liquor ratio of 50:1 and 2% shade O.W.F and 1g of cotton fabric. The volume of the stock solution required was calculated using the formula below.

$$V=\frac{P \times W}{C}$$

Where P =percentage shade on weight of fabric

W = weight of fabric

C = percentage concentration of stock solution

3.4.4 Dyeing of the cotton fabric

The dye bath was prepared using a liquor ratio of 50:1; the volume of dye required was 2ml to give 2% depth of shade on weight of fabric measured in a beaker.1g of fabric was wetted in water for aminute and excess water squeezed out. The wetted fabric was then introduced into the beaker/dye bath containing electrolyte (0.7g NaCl), on a thermostated steam bath with the dyeing liquor temperature at 40^{o}C and raised to the boil after a period of 30 minutes while constantly agitating the sample. The dyeing was carried out at this temperature for 1 hour. After dyeing was completed, the fabric was removed, thoroughly rinsed in cold tap water and dried in air at room temperature. The optical density of the dyebath liquor was measured before and after dyeing for the calculation of percentage exhaustion.

3.4.5 Effect of varying the concentration of electrolyte

In order to determine the optimum dyeing conditions for the synthesized dyes, a series of dyeing using 2% shade O.W.F in five dye baths were carried out at different salt concentration ranging from 5, 10, 20, 50 and 70%. The effect of varying concentration on dye exhaustionare summarized in Table 4.5

3.4.6 Effect of time on dyeing

A series of dyeing was carried out using 2% shade O.W.F using 70% electrolyte,varying time from 15 - 60 minutes at an interval of 15 minutes each. The influence of dyeing time on dye exhaustion is summarized in Table 4.6

3.4.7 Effect of temperature on dyeing

The dyeing temperature was varied from 40^{o}C to 100^{o}C using a series of dyeing at 70% salt concentration to determine optimum dyeing temperature and its effect on dye exhaustion. The results are summarized in Table 4.7

3.4.8 Effect of percentage shade on dyeing

The percentage shade was varied using 1 to 5% shade on weight of fabric in a series of dyeing to determine the effect of increasing percentage shade on dye exhaustion. The results are shown in Table 4.8

3.5.0 Wash fastness test

Current I.S.O 3 washing tests (Nunn, 1979)

The I.S.O.3 standard procedure for washing was used to determine the wash fastness test. The washing conditions required or used are as follows;

Soda ash 2g/l

Soap 5g/l

Liquor ratio 50:1

Temperature $60 \pm 2^{o}C$

Time 30 minutes

A composite specimen was prepared by stitching the dyed samples between an undyed cotton and undyed nylon. The composite specimen was agitated in 100ml beaker containing the soap solution, plus other additives as mentioned above in the specified conditions of liquor ratio,temperature and time.

The composite specimen was then removed,rinsed and the components separated and dried. The change in colour of the dyed samples and the staining on adjacent undyed cloths were assessed using the appropriate grey scale. The results are shown in Table 4.9

3.5.1 Aftertreatment of the dyed samples and wash fastness test

An aftertreatment was carried out on the dyed samples using 8%formaldehyde,liquor ratio of 50:1, at 60^{o}C for 60 minutes for each sample. The samples were removed,rinsed in water and dried. The wash fastness test as stated above was carried out on the aftertreated samples and the results are shown in Table 4.10

3.5.2 Fastness to rubbing test

The fastness to rubbing was carried out using a crockmeter. The rubbing was done for both wet and dry samples at 10 rubbing cycles. The results are shown in table 4.12

3.5.3 Light fastness test

The dyed samples and blue wool standard were exposed facing due south and inclined at an angle to the horizontal approximately equal to the latitude of the place where the exposure is being made. Adequate ventilation of the samples during exposure was ensured. The partly covered samples were exposed to UV radiation. As exposure proceeded for 19 days,the samples under test and the blue wool standards were examined at intervals and the change in colour of the samples compared visually with the changes that occur in the standards. The light fastness of the sample is the number of the standard that shows a similar visual contrast between the exposed and unexposed part of the samples. The exposure was terminated when the blue wool standard 7 fades or when fully exposed and non-exposed test samples is equivalent to grade 3 on the grey scale. The light fastness was evaluated according to ISO 3 standards (Nunn, 1979). The results are shown in Table 4.11

3.5.4 Fastness to perspiration

The test was carried out using 0.5g of histidine and 2-2.5g of sodium dihydrogen orthophosphate per litre in acid and alkaline solutions brought to a pH of 5.5 with 0.1N HCl

and a pH of 8 with 0.1N NaOH respectively. The composite specimen was wetted out in the solution at a pH of 8 for alkaline in a liquor ratio of 50:1 and allowed to remain for 30 minutes at room temperature. The specimen was placed between two plates of the pespirometer or a similar apparatus at a pressure of 12.5Kpa at 37^{o}C for 4 hours. The procedure was repeated for the other composite specimen at a pH of 5.5 for acid and placed in another perspirometer. The samples were removed,opened up and allowed to dry. Both specimens are then assessed for colour change of the test fabric and staining of the adjacent fabric. The results are shown below in Table 4.13

3.5.5 Acute toxicity test

The acute toxicity test was carried out in two steps;

1.In the initial investigation,the range of doses producing the toxic effects was established.

2.Based on these results,further specific doses were administered to calculate an LD_{50}. (Zbinden and Flury-Rovers, 1981)

This is achieved by giving widely differing doses to the animals. e.g 10,100,1000mg/kg body weight. The result shows whether the substance is very toxic,toxic,less toxic,or only slightly toxic.

Albino mice were used for this test. The mice were weighed and the doses were given based on the mice's weight.

Three (3) animals each were injected for each dose (10,100,1000mg/kg body weight) making a total of nine (9) mice for the initial investigation. Their body reactions were observed immediately and at intervals for 72 hours (Bass et al, 1982).

Further higher doses of 600,1000,1600,2900mg/kg body weight were prepared and injected into another set of four new animals and its effects was examined and observed at interval for another 72hours. The number of death that occurred was recorded and the LD_{50} was calculated from the minimum toxic dose and maximum tolerated dose.The results are shown in Table 4.3

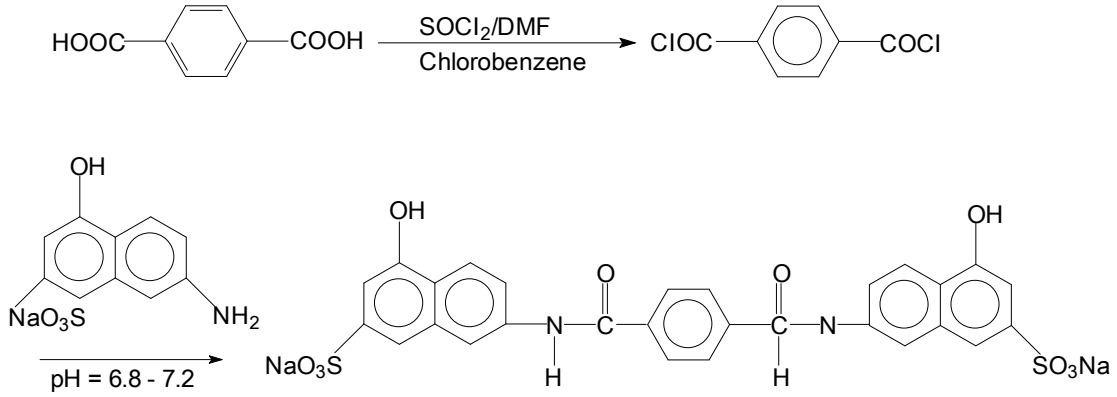
CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

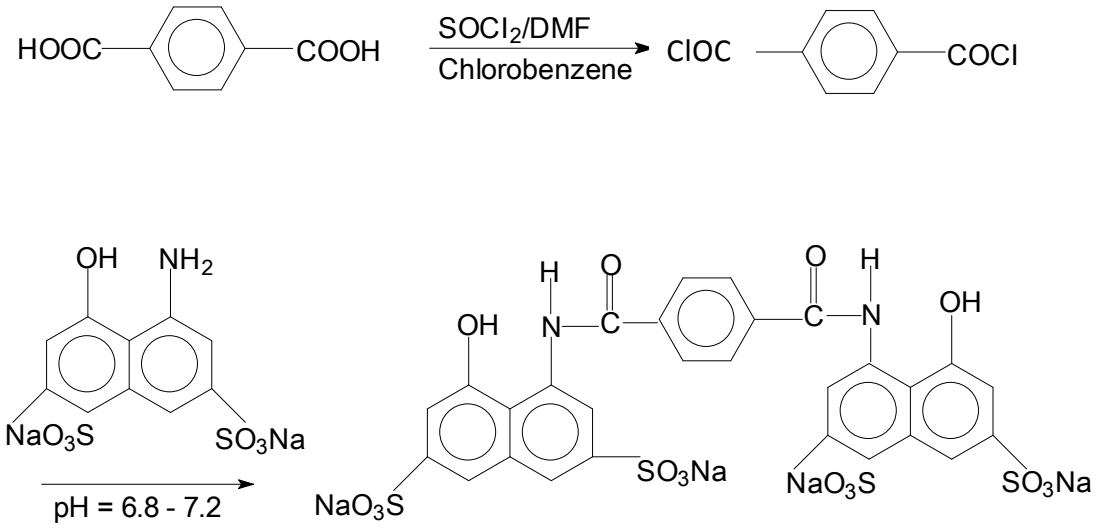
The results obtained are discussed in section 4.1 to 4.16.5

4.1 SYNTHESIS OF COUPLING COMPONENTS

Four coupling components were synthesized in the present study. The first two were obtained by heating terephthalic acid in chlorobenzene for 6–9hours at a pH of 6.8- 7.2 in the presence of dimethylformamide as a catalyst. Further reactions were made by reacting the acidic chlorides of terephthalic acids obtained with J-acid and H-acid respectively as shown in Scheme 1.The molar mass of N,N' – bis-(8 – hydroxyl – 6 – sulphony – naphthalene – 2-(3)-yl)-phthalamides of terephthalic acid (TJA)was 624 and has a melting point of 265^{o}C and the colour obtained was brownish with a yield of 81%,while N,N'-bis-(8-hydroxy - 3,6 – disulphony – naphthalene-2-(3)-yl)-phthalamides of terephthalic acid (THA)has a molar mass of 726 and a melting point of 270^{o}C. The colour obtained was black and has a yield of 79%.



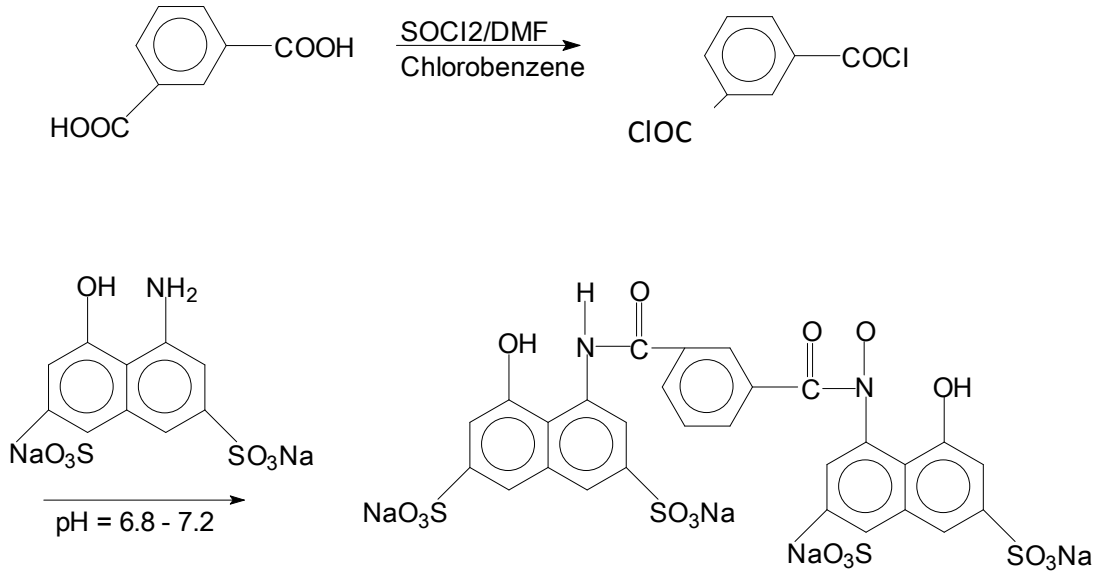
Scheme (1a): Synthesis of coupling component using terephthalic acid and J-acid as intermediate - N, N' – bis - (8 – hydroxyl – 6 – sulphony – naphthalene – 2 - (3) -yl) - phthalamides of terephthalic acid (TJA)



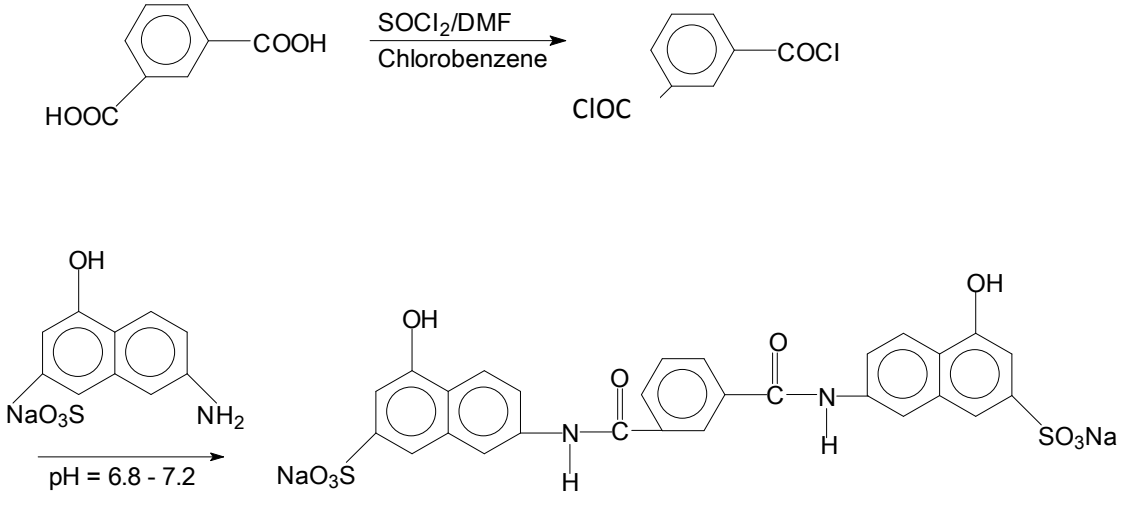
Scheme (1b): Synthesis of coupling component using terephthalic acid and H-acid as intermediate N, N'- bis - (8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid (THA)

The other two coupling components were obtained by heating isophthalic acid in chlorobenzene as above and the acidic chlorides of isophthalic acids were reacted further with J-acid and H-acid respectively as shown in Scheme 2.

N,N' – bis-(8 – hydroxyl –6–sulphony – naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (IHA)has a molar mass of 624 and a melting point of 266^{o}C. The colour was brownish and it has a yield of 78%. While N,N' – bis-(8-hydroxy-3,6-disulphony-naphthalene-2-(3)-yl)-phthalamides of isophthalic acid (ISH) has a molar mass of 726 and a melting point of 260^{o}C. The colour obtained was cream and it has a yield of 80%. These were synthesized based on the literature methods(Wojciechowski,2003). The structures and physical characteristics are shown in Table 4.1. The coupling components were analysed using GC/MS spectrophotometer.



Scheme(2a): Synthesis of coupling component using isophthalic acid and H-acid as intermediate N, N' – bis - (8 – hydroxyl – 3, 6 – disulphony – naphthalene – 2 - (3)-yl) - phthalamides of isophthalic acid (ISH)

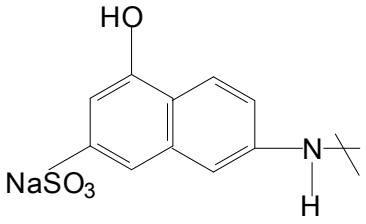


Scheme (2b): Synthesis of coupling component using isophthalic acid and J-acid as intermediate N, N' – bis - (8 – hydroxyl – 6 – sulphony - naphthalene-2 - (3) - yl) - phthalamides of isophthalic acid (IJA)

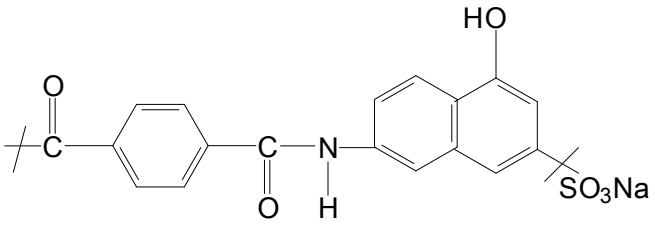
4.2 GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

Chromatograph sample-TJA is the chromatograph of synthesized coupling component-N, N' – bis - (8 – hydroxyl – 6 – sulphony – naphthalene – 2 - (3) -yl) - phthalamides of terephthalic acid (TJA). The chromatograph shows 5 peaks;2 sharps peaks and 3 other less pronounced peaks. The mass spectrograph gave major fragments ions with molecular mass ion as shown in Appendix 1

Peak 1 has a molecular mass of 73 which is due to SO_3H fragment/cleavage 80± 7.Peak 2 has a molecular mass ion of 256 which may be due to $C_{17}H_{11}O_2N$ cleavage. Peak 3 has a molecular mass ion of 280 which corresponds approximately to molecular mass of 284±4.

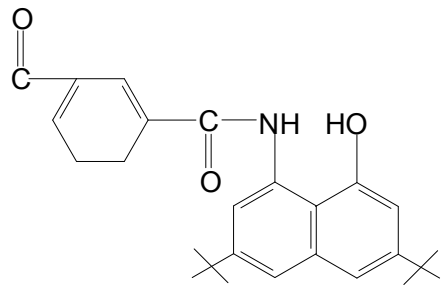


Peak 2

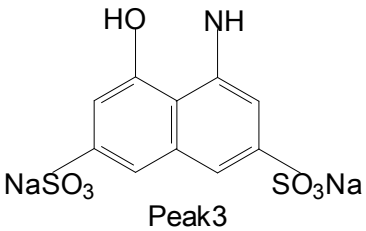


Peak 3

Similarly the chromatograph of N,N' – bis-(8 – hydroxyl -3,6 – disulphony – naphthalene – 2-(3)-yl)-phthalamides of isophthalic acid(IHA) shows two sharp peaks and one less pronounced peak. Peak 2 has amolecular mass of 288 ± 4 corresponding to 284g. Peak 3 has a molecular mass fragment of 308± 10.

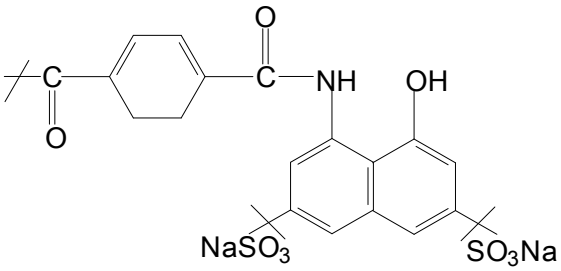


Peak 2

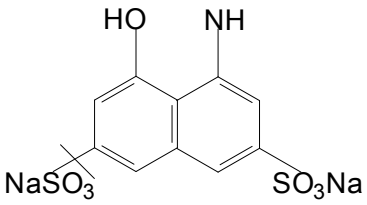


Peak3

Also the chromatograph of N, N'-bis - (8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid (THA) shows two sharp peaks and one less pronounced peak.Peak 1 showed M/Z molecular mass of 103g which may bedue to SO_3Na cleavage corresponding to molecular mass of 103g. Peak 2 has a mass of 288 corresponding to 288 ±4 and peak 3 has a mass of 275g corresponding to 280±5.



Peak 2



Peak3

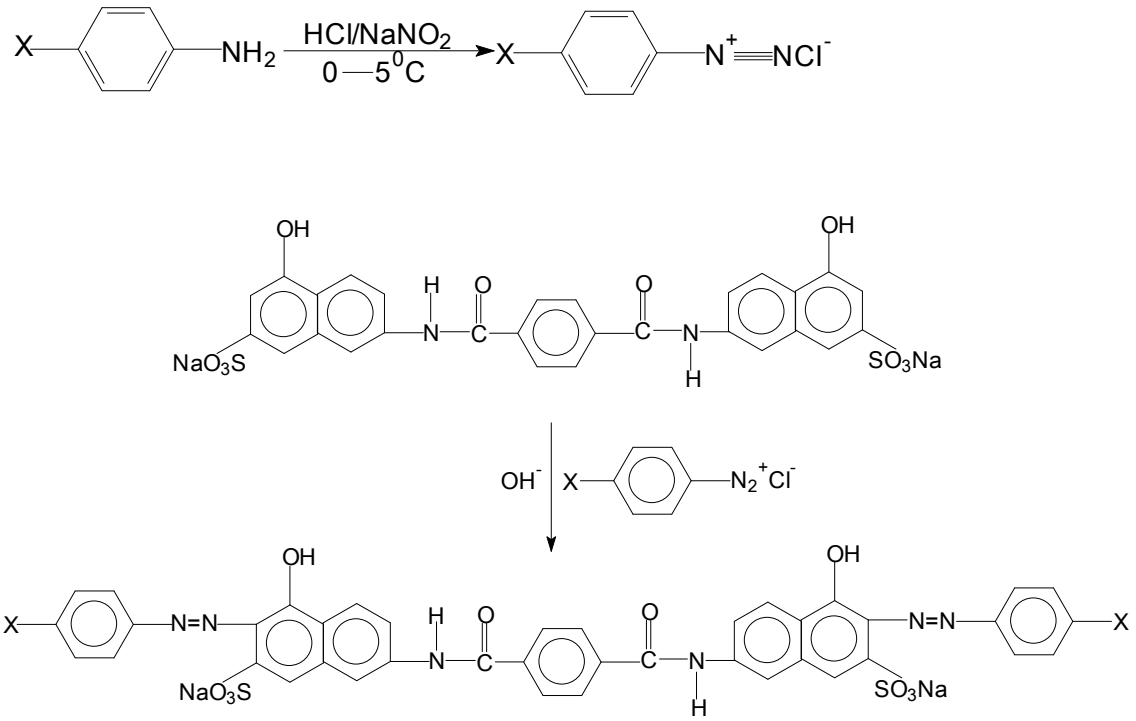
A small peak in the natural abundance of an ion is called 'isotope satellite' peak. High resolution instrument give an idea of mass defects, i.e difference between the true atomic/molecular weight and nominal whole number value. In determination of molecular weight, a volatile compound is essential as the molecular ion peak has to be identified (M+1) peak with chemical ionisation with methane but peaks due to impurities should be ignored.

The molecular weight determination by mass spectroscopy may not be the same as that calculated from atomic weights, if parent compound contains certain elements with high isotopic abundances (Khopkars, 2008).

This may account for the slight difference/change in numerical value of molecular weights of the samples under examination. Also the difference in melting points of the tested samples and the column oven temperature of 80^{o}C and injection temperature of 250^{o}C may also account for the inaccuracy/variation of structures,as the melting points of samples should be considered before injecting the samples.

4.3 SYNTHESIS OF THE DYES

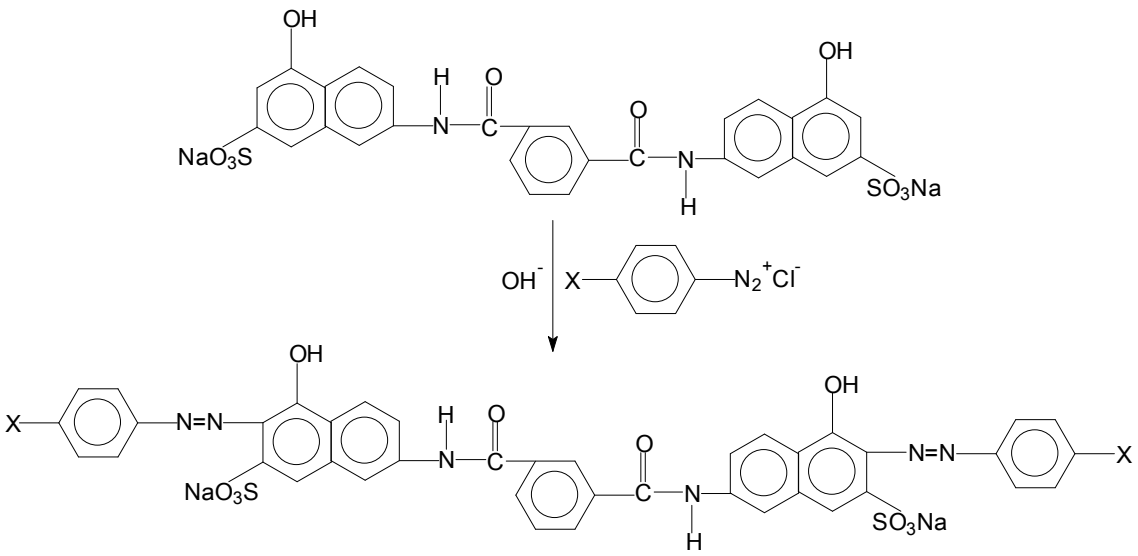
The dyes synthesized were obtained by diazotising four primary aromatic amines namely; aniline, p-anisidine, p-chloroaniline and p-nitroaniline using direct and suspension methods of diazotisation. The diazo component was each coupled to the four coupling components obtained above to get sixteen different dyes as shown in Table 4.1. The yields of the dyes were relatively high and the dyes had sharp melting point which may be due to absence of impurity. The colours of crystals obtained were bright ranging from different shades of orange,purple,brown,green,navy blue and red. The colours of the dyed materials were of bright and brilliant shades as well.



A_1, X = H

A_2, X = OCH_3, A_3, X = Cl and A_4, X = NO_2

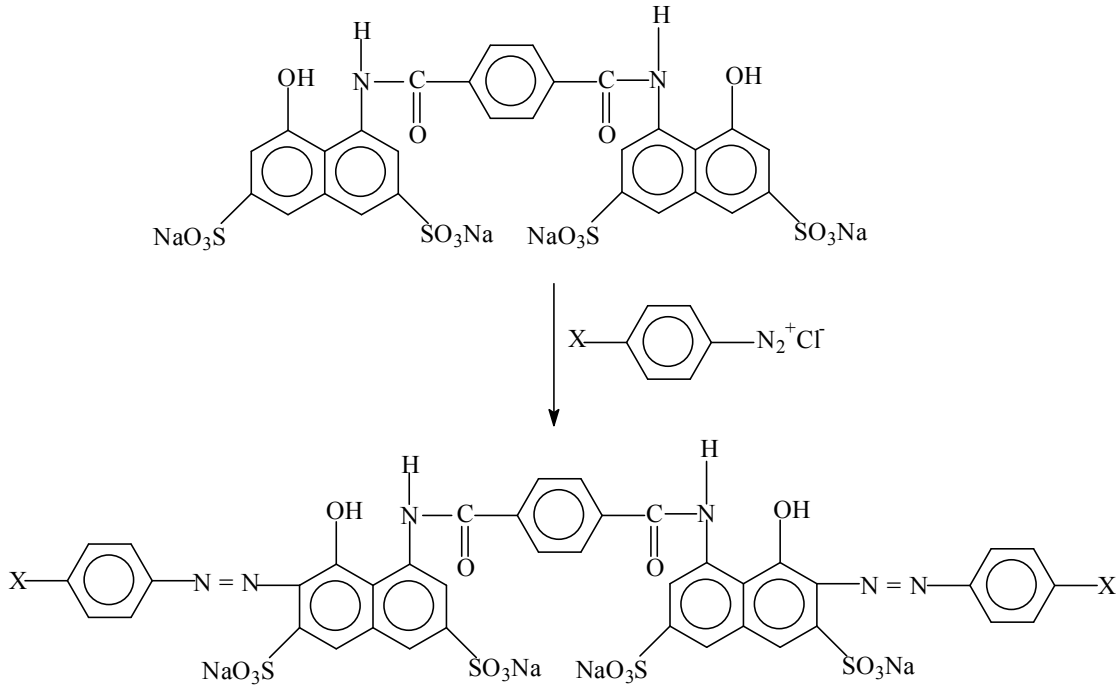
Scheme 3: Reaction scheme for the synthesis of dyes A_1, A_2, A_3, A_4 derived from J-acid and terephthalic acid.



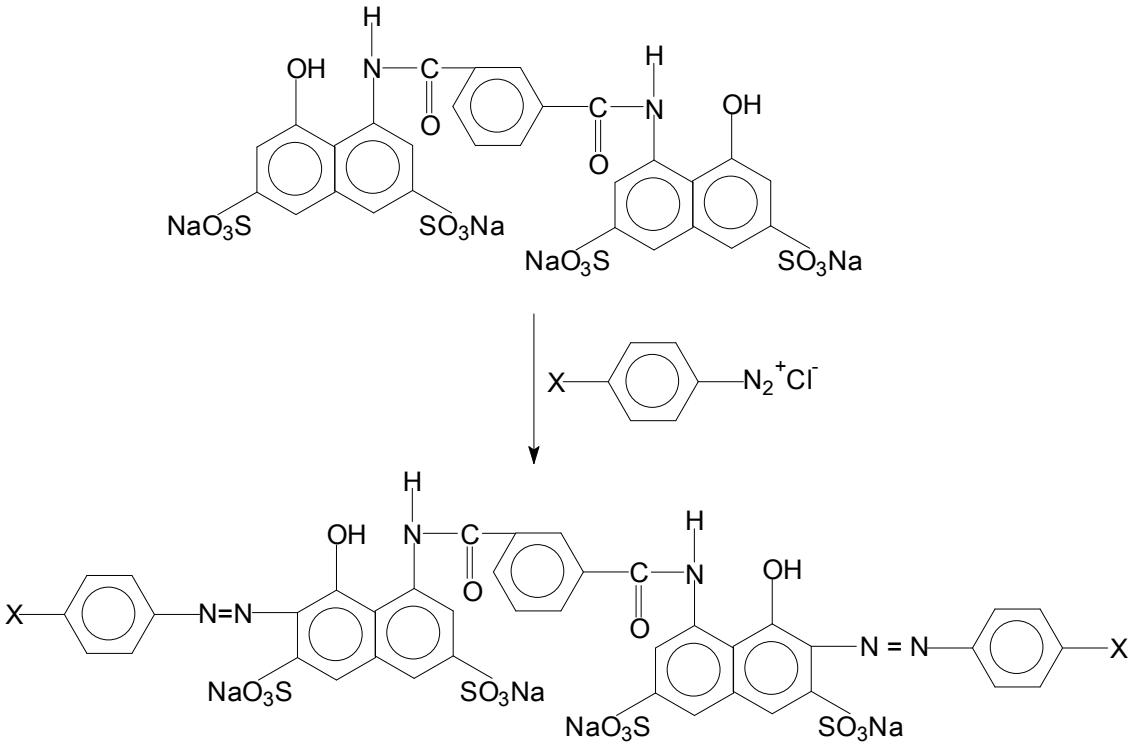
A_5, X = H

A_6, X = OCH_3, A_7, X = ClandA$_8$,X = NO_2

Scheme 4: Reaction scheme for the synthesis of dyes A_5, A_6, A_7 and A_8 derived from J- acid and isophthalic acid



B_1, X = H
B_2,X = OCH_3,
B_3, X = Cl
B_4,X = NO_2
Scheme 5: Reaction scheme for the synthesis of dyes B_1, B2, B_3 and B_4 derived from H – acid and terephthalic acid



B_5, X = H
B_6, X = OCH_3,
B_7, X = Cl
B_8, X = NO_2
Scheme 6: Reaction scheme for the synthesis of dyes B_5, B_6, B_7 and B_8 derived from H-acid and isophthalic acid

4.4 PHYSICAL CHARACTERISTICS AND STRUCTURES OF THE DYES

The molar mass,melting point,yield,colour of crystals and colour of dyed samples as well as structures of the dyes synthesized are shown in Table 4.1

Table 4.1 physical characteristics and structures of the dyes.

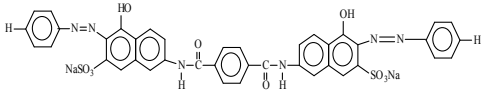
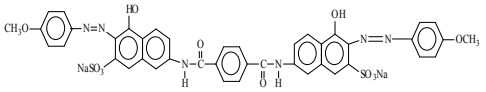
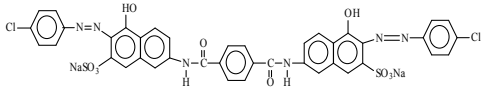
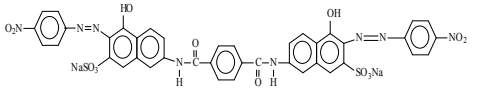
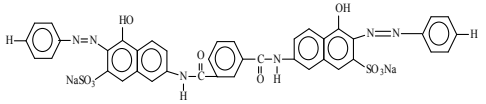
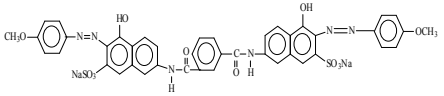
DYE NO.	MOLAR MASS($gmol^{-1}$)	MELTING POINT(^0C)	%YIELD	COLOUR OF CRYSTAL	COLOUR OF DYED SAMPLE	STRUCTURE OF THE DYES
A_1	834	116-117	81	Orange	Yellow	
A_2	847	199	72	Purple	Brown	
A_3	903	226	64	Deep Orange	Brown	
A_4	878	242-245	68	Brown	Dark brown	
A_5	834	208	70	Deep orange	Orange	
A_6	847	205	69	Purple	Brown	

Table 4.1 continued

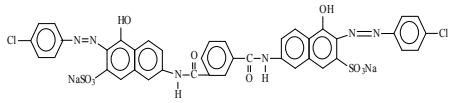
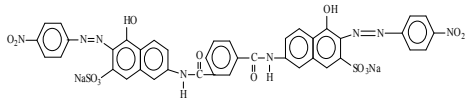
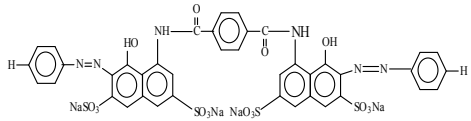
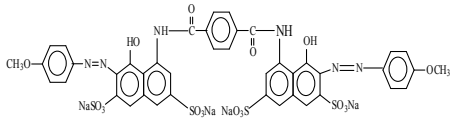
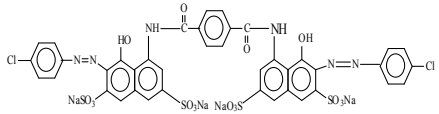
DYE NO.	MOLAR MASS($gmol^{-1}$)	MELTING POINT(^{o}C)	%YIELD	COLOUR OF CRYSTAL	COLOUR OF DYED SAMPLE	STRUCTURE OF THE DYES
A_7	903	206	80	Orange	Brown	
A_8	878	209	74	Brown	Dark brown	
B_1	1040	238	72	Brown	Yellow	
B_2	1053	241-246	83	Light purple	Pink	
B_3	1109	262	78	Dark green	Light green	

Table 4.1 continued

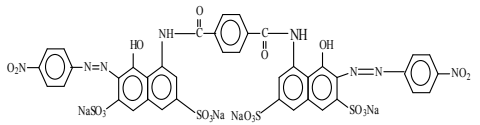
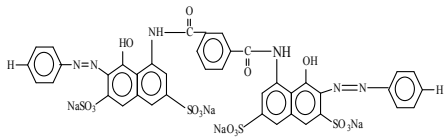
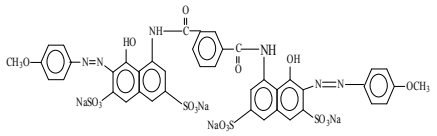
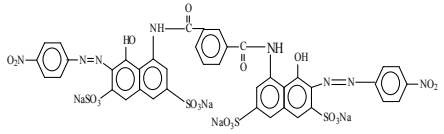
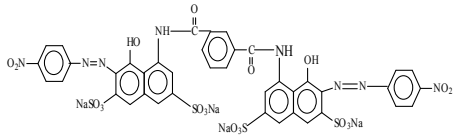
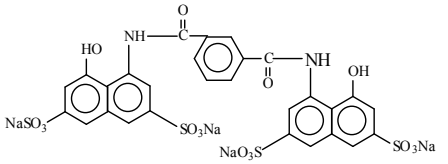
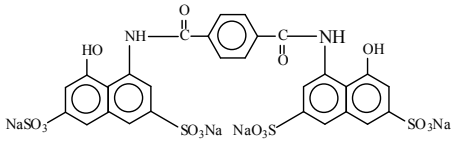
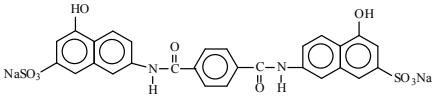
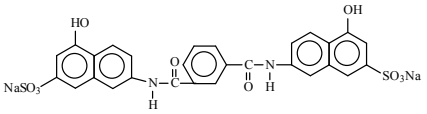
DYE NO.	MOLAR MASS($gmol^{-1}$)	MELTING POINT(^oC)	%YIELD	COLOUR OF CRYSTAL	COLOUR OF DYED SAMPLE	STRUCTURE OF THE DYES
B_4	1084	245	81	Dark purple	Army green	
B_5	1040	183	75	Orange	Yellow	
B_6	1053	190-191	68	Dark green	Light green	
B_7	1109	200	72	Purple	Light purple	
B_8	1084	155	73	Navy blue	Army green	

Table 4.1 continued

DYE NO.	MOLAR MASS($gmol^{-1}$)	MELTING POINT(^{o}C)	%YIELD	COLOUR OF CRYSTAL	COLOUR OF DYED SAMPLE	STRUCTURE OF THE DYES
ISH	726	260	80	Cream	-	
THA	726	270	79	Black	-	
TJA	624	265	81	Brownish	-	
IJA	624	266	78	brownish	-	

ISH = N, N' – bis - (8 – hydroxyl - 3, 6 – disulphony – naphthalene – 2 - (3) -yl) - phthalamides of isophthalic acid

THA = N, N'-bis-(8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid

TJA = N, N'-bis-(8-hydroxy - 6 – sulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid

IJA = N, N' – bis - (8 – hydroxyl – 6 – sulphony - naphthalene-2 - (3) -yl) - phthalamides of isophthalic acid.

4.5 THE INFRA-RED SPECTRA OF SOME OF THE DYES

The infra red spectra of the dyes showed similar or closely related absorption band due to presence of similar groupings or bonds present in the dye structures.

Dye A_1,A_2, and A_3obtained from the same coupling component, N, N'-bis-(8-hydroxy - 6 – sulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid showabsorption peaks due to double bonds –C=C- in aromatic rings between the range1631-1642cm^{-1}. The presence of acarbonyl group C=O gave rise to a stretching vibrations in these dyes between 1642 - 1840cm^{-1}.They also gave N-H bending vibrations at region of 1631-1642cm^{-1}. The peak due to hydrogen bond stretching shows a peak due to vibrations of hydrogen and other atoms (Koji and Philipa, 1997).

At a region of between 3392-3425cm^{-1} hydrogen bonding broadens the peak and shifts them to lower wavelength. They also show absorption peaks due to C=N stretching at a region of 1631-1642cm^{-1} and peaks due to C-SO_3H at 1250-1300cm^{-1}.

Dyes A_5 and A_7 obtained from the same coupling component, N, N'-bis-(8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid shows absorption peaks due to double bonds –C=C- in aromatic rings between the range 1640cm^{-1}. The presence of a carbonyl group C=O gave rise to a stretching vibrations at 1646cm^{-1}. They also gave N-H bending vibrations at region of 1641-1642cm^{-1}.

Table 4.2; THE INFRA-RED SPECTRA OF THE DYES

Functional group	-N=N-	-C =C	C=O	N-H	C=N	C-H	O- H	CSO_3H
Type of vibration	stretching	bending	stretching	bending	stretching	stretching	stretching	
	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	
A_3	1575	1642	1642	1642	1642	3000	3425	1260
B_3	1630	1646	1651	1646	1646	2850	3422	1350
A_7	1580	1642	1646	1642	1642	2940	3442	1300
A_1	1550	1642	1558	1642	1642	3192	3392	1300
A_2	1631	1631	1634	1631	1631	2085	3420	1250
B_7	1575	1651	1651	1651	1651	2087	3394	1275
A_5	1630	1641		1641	1641			1310

The peak due to hydrogen bond stretching shows a peak due to vibrations of hydrogen at a region of between 3442cm^{-1}. Hydrogen bonding broaden the peak and shift them to lower wavelength. They also show absorption peaks due to C=N stretching at a region of 1641-1642cm^{-1} and peaks due to C-SO_3H at 1300-1310cm^{-1}.

Dyes B_3 and B_7shows absorption peaks due to double bonds –C=C- in aromatic rings between the range 1575-1630cm^{-1}. The presence ofacarbonyl group C=O gave rise to a stretching vibrations at 1651cm^{-1}.They also gave N-H bending vibrations at region of 1646-1651cm^{-1}. The peak due to hydrogen bond stretching shows a peak due to vibrations of hydrogen at a region of between 3394- 3422cm^{-1}. They also showed absorption peaks due to C=N stretching at a region of 1646-1651cm^{-1} and peaks due to C-SO_3H at 1275-1350cm^{-1}.

Generally all the dyes have absorption peaks due to –N=N- stretching at between 1575-1631cm^{-1} which is prominent in all dyes spectra.These regions are in conformity with the characteristics of IR absorption peaks (Khopkars, 2008).

4.6 ACUTE TOXICITY OF THE COUPLING COMPONENTS

The toxicity results of the coupling components are shown in Table 4.3

TABLE 4.3: ACUTE TOXICITY OF THE COUPLING COMPONENTS THA AND IJA

THA-stage 1

STOCK	10mg/ml			100mg/ml			1000mg/ml		
	no on mouse	wt of mouse(g)	Vol. of injection(ml)	no on mouse	wt of mouse(g)	Vol. of injection(ml)	no on mouse	wt of mouse(g)	Vol. of injection(ml)
	1	21	0.21	4	20	0.2	7	27	0.27
	2	21	0.21	5	21	0.21	8*	20	0.2
	3	30	0.3	6	24	0.24	9	20	0.2

Stage 2

STOCK	600mg/ml	1000mg/ml	1600mg/ml	2900mg/ml
No on mouse	1	2	3	4*
Weight of mouse(g)	31	36	29	31
Volume of injection(ml)	0.31	0.36	0.29	0.31

IJA -stage 1

Stock	10mg/ml			100mg/ml			1000mg/ml		
No on mouse	Wt on mouse(g)	Vol. of injection(ml)	No on mouse	Wt of mouse(g)	Vol of injection(ml)	No on mice	Wt of mouse(g)	Vol. of injection(ml)	
1	23	0.23	4	27	0.27	7	22	0.22	
2	21	0.21	5	21	0.21	8	18	0.18	
3	27	0.27	6	25	0.25	9	26	0.26	

Stage 2

Stock	1200mg/ml	1600mg/ml	2900mg/ml	5000mg/ml
No on mouse	1	2	3*	4*
Weight of mouse	23	25	26	28
Volume of injection(ml)	0.23	0.25	0.26	0.28

LD_{50} = [Maximum tolerated dose x minimum toxic dose]$^{1/2}$

= [1600 x 2900] ^{½} =2154

The synthesized coupling components were used for the acute toxicity test. The test was carried out in two stages. In the initial investigation, different doses of 10mg/ml, 100mg/ml and 1000mg/ml were prepared and given to the animals (albino mice) based on their respective body weight (which was obtained using a weighing balance) as shown in Table 4.3.After injecting the substance into the 9 albino mice, they were observed for 72 hours for change in body reaction base on the effect of the injected substance. Initially some of the mice were cold and calm but resumed movement after a little while. At the end of 48hours, only mice number 8 of 20g which was injected with 0.2ml of 1000mg/ml in stage 1 died.

In stage 2, Further higher doses (600mg/ml, 1000mg/ml, 1600mg/ml and 2900mg/ml) were given to 4 mice to establish a toxic effect. At the end of 72 hours, mice number 4 having 31g body weight which was injected with 0.31ml of 2900mg/ml concentration died. The maximum tolerated dose is1600mg/ml and the minimum toxic dose is 2900mg/ml.

Similarly, using IJA coupling component,the same procedure was followed in stage 1as above and none of the 9 mice died after 24 and 48 hours.

In stage 2,further higher doses(1200mg/ml,1600mg/ml, 2900mg/ml and 5000mg/ml) were given to the 4 mice. At the end of 72 hours,mice number 3 which was injected with 2900mg/ml and mice number 4 which was injected with 5000mg/ml died. Therefore,the maximum tolerated dose is also 1600mg/ml and the minimum toxic dose is 2900mg/ml. Therefore, an LD_{50} was calculated and obtained as 2154 to establish a range of toxicity using the above formula.Therefore the coupling components (THA and IJA) usedwere non-toxic

based on the LD_{50} obtained from the test. This may be due to the low LD 50 value of 2154, as values above 5000 have toxic effect (Bass, 1982).

4.7 SPECTROSCOPIC PROPERTIES OF THE DYES.

The maximum absorption wavelengths in distilled water, dimethylformamide, ethanol, ethanol + hydrochloric acid are shown in Table 4.4.

TABLE 4.4: SPECTROSCOPIC PROPERTIES OF THE DYES

Dye No	ε_{max} x 10^4 in water $Lmol^{-1}cm^{-1}$	λ_{max} in water(nm)	λ_{max} in DMF(nm)	λ_{max} in ethanol(a)	λ_{max} in ethanol +a drop HCl (b)	Change in λ_{max}(b-a)
A_1	9.30	510	505	510	515	+5
A_2	4.93	505	510	505	510	+5
A_3	6.16	480	505	505	510	+5
A_4	4.41	490	505	505	505	0
A_5	8.33	485	505	510	505	-5
A_6	7.89	495	535	505	510	+5
A_7	8.09	505	510	510	505	-5
A_8	5.79	500	505	505	505	0
B_1	9.79	510	505	510	510	0
B_2	5.25	480	510	510	510	0
B_3	7.69	480	505	510	515	+5
B_4	5.34	505	520	505	505	0
B_5	8.79	505	525	505	510	+5
B_6	7.23	520	510	510	515	+5
B_7	8.58	505	505	505	508	+3
B_8	7.05	510	505	505	505	0

From the results in Table 4.4, dye A_1 which was obtained from aniline using terephthalic acid and J- acid to obtain N, N'-bis-(8-hydroxy - 6 – sulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid (TJA) absorbed at 510nm in distilled water. Dye A_2 which was obtained using p- anisidine and TJA as coupling component absorbed at 505nm. Similarly, dye A_3 and A_4 obtained from p- chloroaniline and p- nitroaniline using TJA as coupling component absorbed at480nm and 490nm respectively. Thus dye A_1 is more bathochromic than dyes A_2, A3and A_4 as it absorbed at a longer wavelength.

Dyes A_5, A_6, A_7 and A_8 were obtained using the same coupling component N, N' –bis-(8-hydroxy - 6 – sulphony – naphthalene – 2 - (3) - yl) - phthalamides of isophthalic acid (IJA). A5 absorbed at 485nm in distilled water while dyes A_6, A_7 and A_8 absorbed at 495nm, 505nm and 500n m respectively in distilled water. Thus, dyes that absorbed at a lower wavelength indicate that they require higher energy for excitation.

Dye B_1 which was obtained from aniline using terephthalic acid and H-acid to obtain N, N'-bis-(8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of terephthalic acid(THA) absorbed at 510nm in distilled water. Dyes B_2 and B_3 obtained from the same coupling component THA both absorbed at a wavelength of 480nm in distilled water while dye B_4 absorbed at 505nm. Thus dye B_1 is more bathochromic than B_2, B_3 and B_4 by a wavelength of 30nm and 5nm respectively.

Similarly, dyes B_5 obtained from aniline using isophthalic acid and H-acid to obtain N, N'-bis - (8-hydroxy - 3, 6 – disulphony – naphthalene – 2 - (3) - yl) - phthalamides of isophthalic acid(IHA) absorbed at 505nm in distilled water. B_6, B_7 and B_8 obtained using same coupling component IHA absorbed at 520nm, 505nm and 510nm respectively. Thus dye B_6 is more bathochromic than B_5, B_7 and B_8, while dyes B_5 and B_7 are more hypsochromic than dyes B_6 and B_8.

Spectrophotometric measurements therefore showed that the spectra of the disazo dyes possesses visible absorption peaks whose intensity changes with the polarity of the solvent. This is probably due to the aggregation of the dyes.

A strongly polar solvent such as water considerably affected the spectra/absorption maxima of the dyes. The dyes derived from J-acid, derivatives of terephthalic acid (A_1-A_4), exhibited bathochromic shift in relation to bands of dyes derived from isophthalic acid (A_5-A_8).While in the case of dyes derived from H-acid,an opposite effect was observed, i.e the absorption bands of dyes derived from terephthalic acid (B_1-B_4) shifted hypsochromically in relation to dyes derived from isophthalic acid (B_5- B8). This confirms the existence of conjugation betweentwo parts of dye.

4.8 SOLVATOCHROMIC EFFECTS

Solvatochromism is the ability of a chemical substance to change colour due to change in solvent polarity. With increasing polarity of the solvent, the absorption maximum is shifted to longer wavelengths (Marini and Munoz, 2010).

Generally, in many dye molecules the ground state is less polar than the excited state so that the polar solvent will tend to stabilize the excited state more than the ground state leading to bathochromic shift in the visible absorption maximum, which is termed positive solvatochromism. The interaction of the solvent with the dye molecule is greater in polar solvent (Reichardt andWelton,1991).

The phenomenon of solvatochromism arises from a change in the electronic structure and distribution of charge of the excited state as compared with the ground state. If the excited state is more polar than the ground state,it will be better stabilized by polar solvation and its

energy lowered, so that the transition will occur at longer wavelengths, i.e there will be a bathochromic shift (red shift) with increasing solvent polarity (Marini and Munoz, 2010).

Solvatochromism is commonly used in many fields of chemical and biological research to study bulk and local polarity in macro systems (membranes, etc.) or even the conformation and binding of proteins. Despite its widely use, solvatochromism still remains a largely unknown phenomenon due to extremely complex coupling of many difference interaction and dynamic processes which characterize it.

Most of the shifts in maximum absorption wavelength observed were bathochromic for majority of the dyes where measurements were done in solvent of higher polarity. The maximum absorption wavelengths values shifted to longer wavelengths when the solvent is changed from ethanol to dimethylformamide (DMF), e.g dye A_2 absorbs at 505nm in distilled water, 505nm in ethanol and 510 in DMF. Likewise, dye A_6 absorbs at 495nm in distilled water, 505 in ethanol and 535 in DMF. Also dye B_4 absorbs at 505nm,505nm, 520nm in distilled water, ethanol and DMF respectively. B_5 too absorbs at 505nm in both water and ethanol and 525 in DMF.

Although some of the dyes had negative solvatochromism, i.e a hypsochromic shift to lower wavelength in the visible absorption spectrum when the solvent was changed from ethanol to DMFe.g. dye A_1, A_5, B_1, B_3 changed from 510nm to 505nm, 510nm to 505nm, 510nm to 505nm and 510nm to 505nm respectively. Some of the dyes showed no change in wavelengths from ethanol to DMF, for example, dye A_3, A_4, A_7, A_8, B_1, B_6, B_7 and B_8.

Solvent polarity effects on visible absorption band of dyes have been thoroughly studied and well documented in literature (Venkatarama, 1972). The literature reported that $\pi \text{-----} \rightarrow \pi^*$ transition exhibits bathochromic effect when the polarity of the solvent is increased while $n \text{---} \rightarrow \pi^*$ transition shows hypsochromic effect with increase in solvent polarity. This is a clear

indication that in this study,the visible band is due to π----→π* transition since a positive solvatochromism occurred in some of the dyes and n----→π* transition since a negative solvatochromism also occurred in some of the dyes.

Solvatochromism is due to various solute-solvent interactions in both the ground and excited states. The red shift observed on changing to a polar solvent suggests that the dye molecules has a more polar excited state than the ground state and this will lower the energy of the π----→π* transition. Thus the energy difference between the ground and the excited state is reduced leading to a bathochromic shift of the visible band (Marini and Munoz, 2010).

4.9. HALOCHROMISM(EFFECT OF ACID ON VISIBLE ABSORPTION BAND)

The effect of few drops of acid (HCl) on the visible absorption band, which could decrease or increase the maximum absorption wavelengths, is referred to as halochromism. The increase of λ_{max} in acidic medium is referred to as positive halochromism while the decrease in λmax in same acidic medium is referred to as negative halochromism.

The effect of few drops of acid on ethanolic solution of the dyes was investigated and the results are summarized in table 4.4. Many (eight) of the synthesized dyes exhibit positive halochromism. For examples dyes A_1, A_2, A_3, A_6, B_3, B_5, B_6, in a neutral solution of ethanol absorbed at 510nm, 505nm, 505nm, 505nm, 510nm, 505nm and 510nm respectively but maximally absorbed at 515nm, 510nm, 510nm, 510nm, 515nm, 510nm, 515nm respectively in acidic ethanol solution,indicating a bathochromic shift of +5nm in the dyes above. Also dye B_7 in a neutral solution of ethanol absorbed at 505nm but maximally absorbed at 508nm in acidic ethanol solution,indicating a bathochromic shift of +3nm.

However, some of the dyes showed a negative halochromism. For example, dyes A_5 and A_7 absorbed in neutral ethanolic solution both at 510nm but absorbed maximally both at 505nm

in acidic solution of ethanol, indicating a hypsochromic shift of -5nm. The positive and negative halochromism is due to the protonation of the dye at β – nitrogen atom of the azo chromophoric group to form the azonium ion. Protonation has never been observed at α – azo nitrogen atom. The dyes that exhibited positive and negative halochromism can be used for acid-base titration.

4.10 APPLICATION OF THE DYES ON COTTON FABRIC.

The synthesized dyes were applied to cotton fabric. The dyed samples are shown in appendix 3

4.11EFFECT OF VARYING THE CONCENTRATION OF ELECTROLYTE

The effect of varying the salt/electrolyte concentration is shown in Table 4.5 and Figure 4.1

Table 4.5: Effect of varying electrolyte concentration on dye exhaustion.

DYE NO	Electrolyte concentration (%)					
	0	5	10	20	50	70
	Exhaustion (%)					
B_3	0	25	30	56	66	81
A_3	0	18	32	67	78	83
B_7	0	22	55	68	80	80
A_7	0	28	44	63	74	87

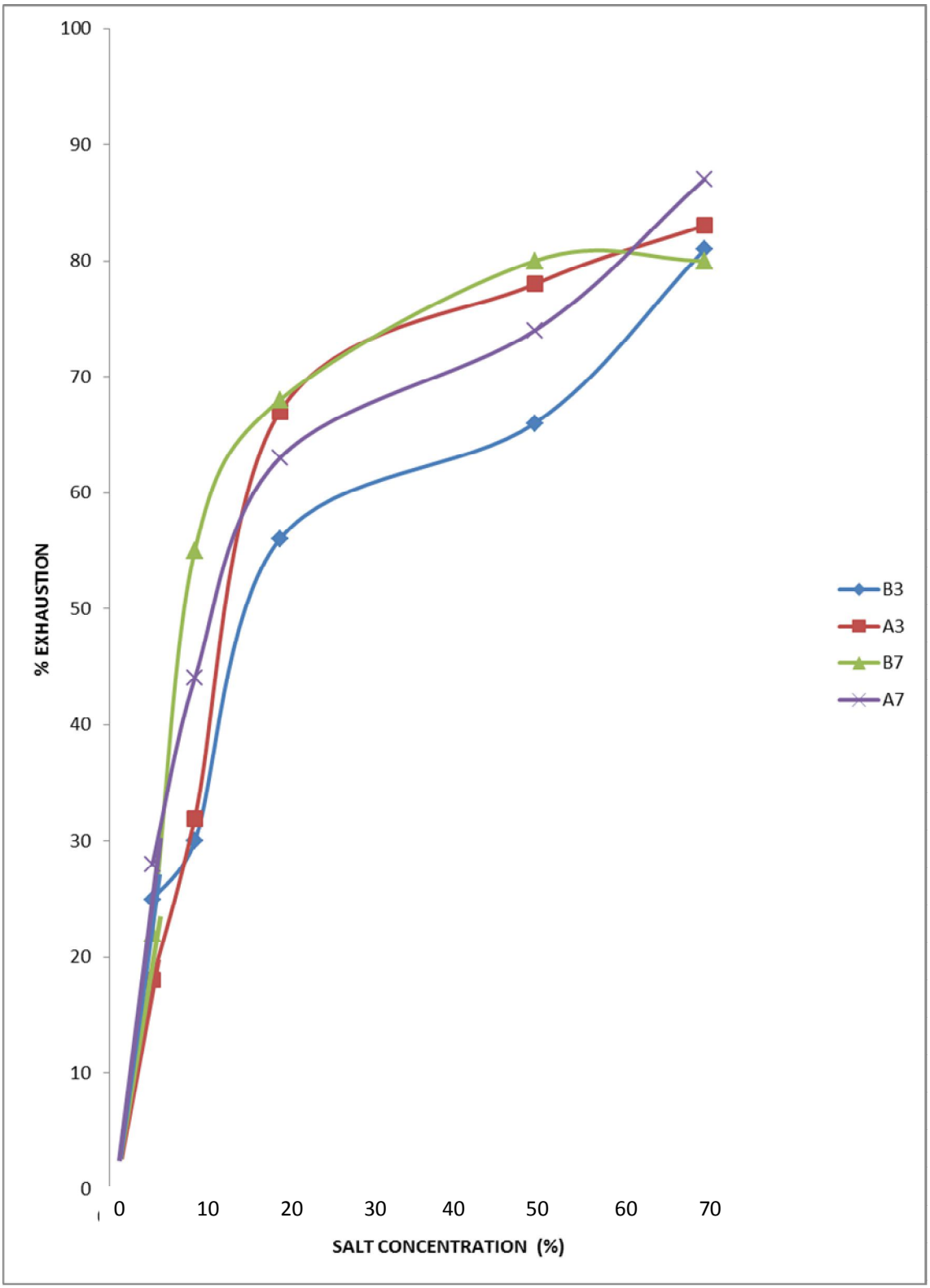


Fig 4.1: Effect of salt concentration on dye exhaustion

From the results summarized in Table 4.5 and graphically represented in Fig 4.1, increase in the concentration of the electrolyte led to an increase in the amount of dye absorbed and percentage exhaustion, which is typical of direct dyes. All these dyes (B_3, A_3, B_7, and A_7) adsorbed increased with electrolyte concentration, although, Dye A_7 had the highest exhaustion. This is because electrolyte in the dye bath promotes the exhaustion of direct dyes,as the sodium ions distribute between the external and internal solution so that the negative charge of the fibre is neutralised. This neutralisation allows more dye molecules to approach the fibre closely enough for the forces of attraction between the fibre and dye to take effect (Perkins, 1996).

The dyes generally contain two or more sulphonic acid groups and when absorbed on the pore surfaces they are still accompanied by attendant (usually Na^+) gegeions to preserve electrical neutrality. The diffusion of sodium cation is facilitated by mass action and the amount of dye anions adsorbed by the fibre is increased (Bird and Boston 1975).

4.12: Effect of time on dye exhaustion

Varying the dyeing time affects dye exhaustion as shown in Table 4.6 and graphically represented in Figure 4.2

Table 4.6: Effect of dyeing time on dye exhaustion.

DYE NO	Dyeing time (min)				
	0	15	30	45	60
	Exhaustion (%)				
A_1	0	42	59	68	72
B_1	0	33	52	64	75
A_5	0	44	52	59	75
B_5	0	42	58	65	73

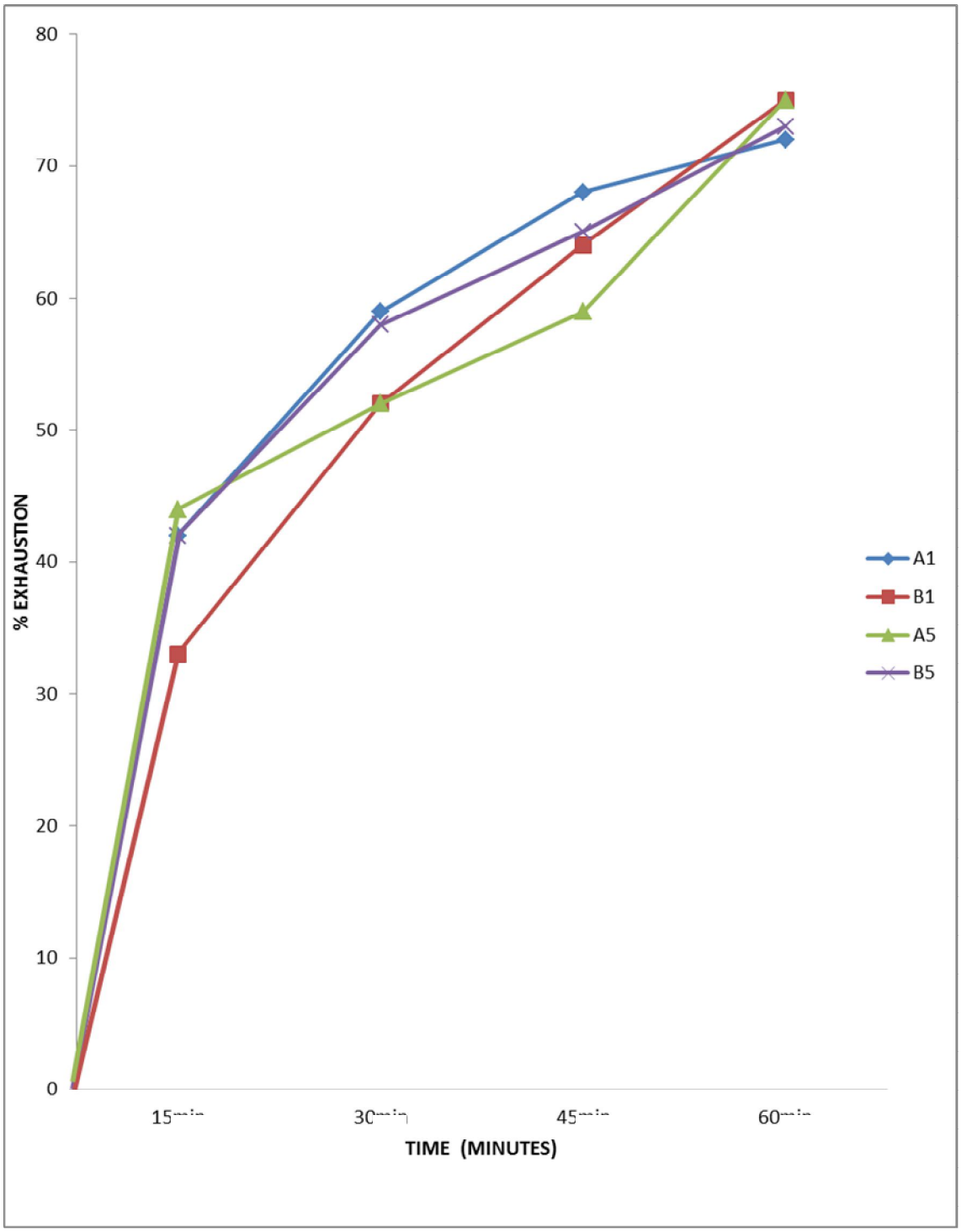


Fig 4.2: Effect of time on dye exhaustion

From Table 4.6 graphically represented in Fig 4.2, it can be seen that,for all the dyes as the dyeing time increases,the percentage exhaustion as well as the depth of shade on the fabric increased. This may be due to the fact that as the dye is initially absorbed on the surface of the fabric and with longer time it slowly diffuses into the fibre to give level dyeing. Thus,the longer the dyeing time the better the dye diffusion and consequently the higher the percentage exhaustion. The high percentage exhaustion with increased in dyeing time in the above listed dyes may be due to the presence of sulphonic groups which enhances the solubility of the dyes in solution thus making them available to the fibres (Aleem and Ahmed, 2005).

4.13 EFFECT OF TEMPERATURE ON DYEING AND PERCENTAGE EXHAUSTION

Table 4.7; Effect of temperature on dyeing and percentage exhaustion

	Dyeing temperature (^{o}C)			
DYE NO	0	40	70	100
	Exhaustion (%)			
A_2	0	21	51	76
B_2	0	26	43	75
A_6	0	24	58	81

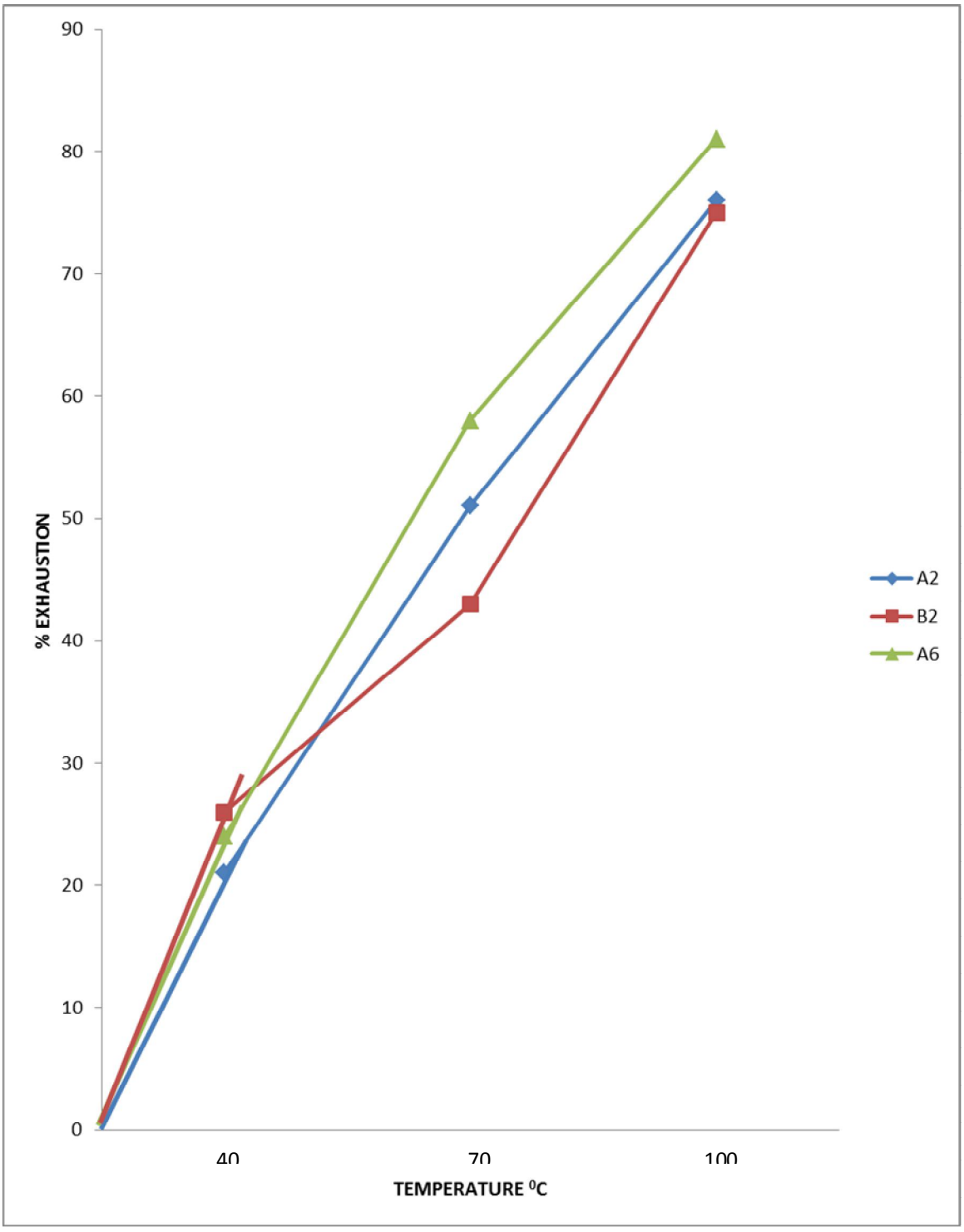


Fig 4.3: Effectof temperature on dye exhaustion

From the results in Table 4.7, graphically represented in Figure 4.3, it was observed that the rate of dye diffusion into the fibre increased with temperature. This is because increase in dyebath temperature increases the kinetic energy of the dye molecules in solution, and subsequently increased rate of dyeing leading to high exhaustion. In addition, the fibre swells and the pores open at high temperature thereby increasing the accessibility of the originally more difficult to penetrate region (Aleem and Ahmed, 2005). Therefore the optimum dyeing temperature was at the boil(100^{o}C).

4.14 EFFECT OF PERCENTAGE SHADE ON DYE EXHAUSTION

Table 4.8: Effect of percentage shade on dyeexhaustion

DYE NO	Percentage shade (%)					
	0	1	2	3	4	5
	Exhaustion (%)					
A_4	0	40	54	62	73	83
B_4	0	37	52	66	74	82
A_6	0	48	51	64	70	80
B_8	0	42	57	66	74	82

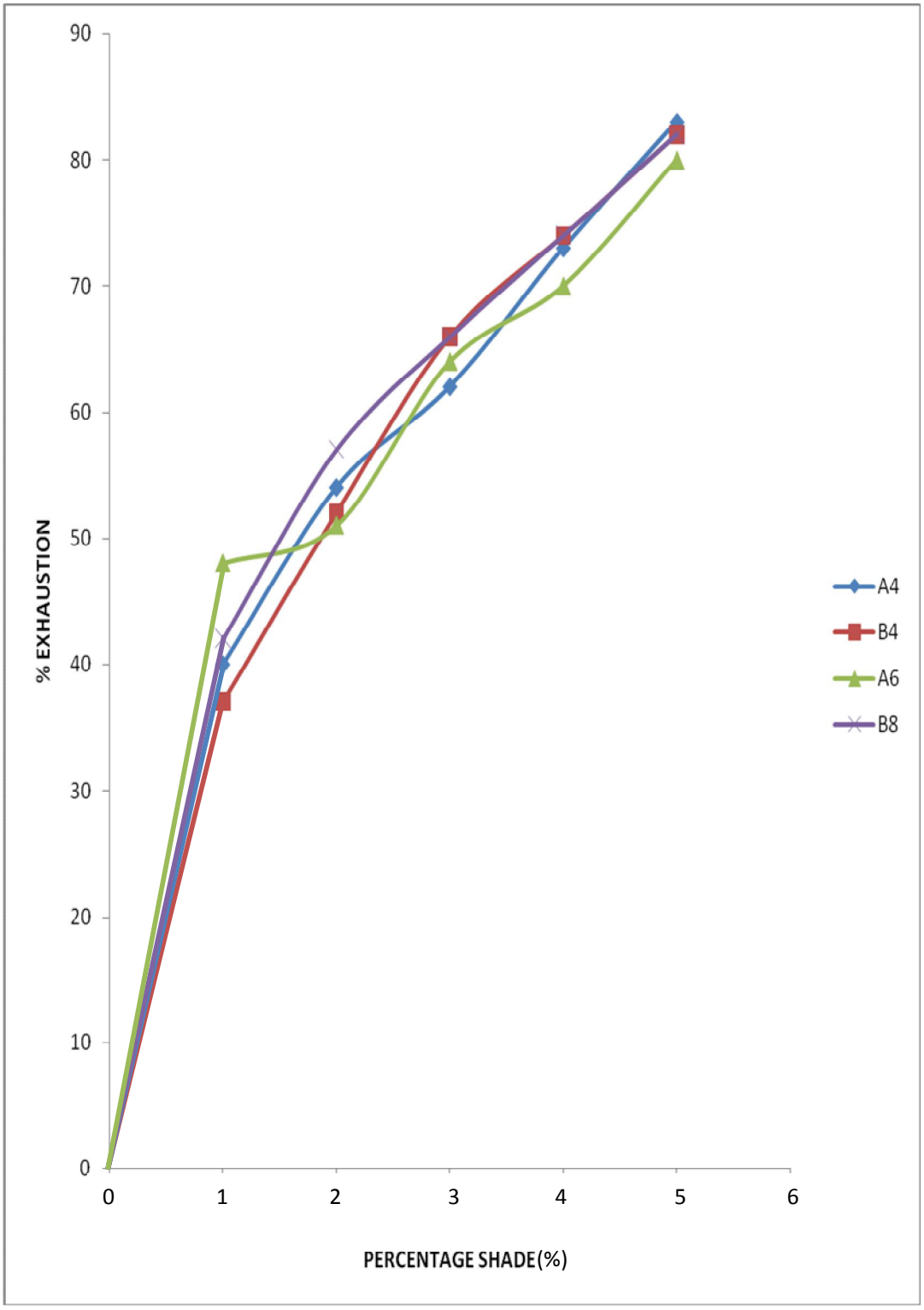


Fig 4.4: Effect of percentage shade on dye exhaustion

From the results in Table 4.8 graphically represented in Figure 4.4, It can be seen that increase in dye concentration and percentage shade led to a considerable increase in exhaustion of the dye,leading to deeper depth of shades for all the dyes used. This is because more dye molecules are present in the dye bathwhich are readily available to be accompanied in by the gegeions in the electrolyte and taken up by the fibre leading to deeper depth of shades and high exhaustion.

4.15 PERCENTAGE EXHAUSTION OF THE DYES

The percentage exhaustion of the dyes is shown graphically in Figure 4.5

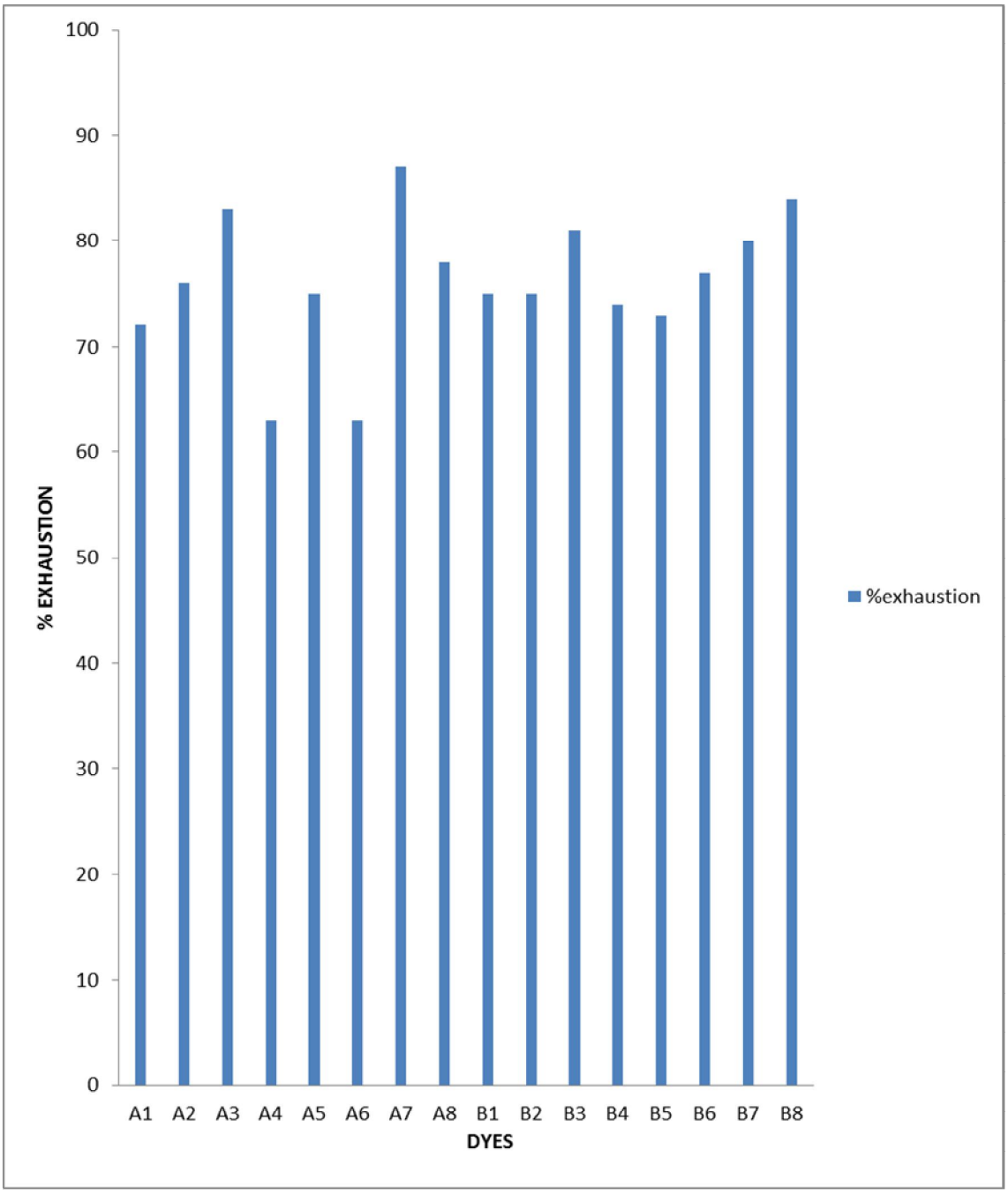


Fig 4.5: Percentage exhaustion of dyes

As shown graphically in Figure 4.5, all the dyes synthesized have good and high exhaustion ranging between 60 - 87%, whichare good properties of direct dyes.

4.16 FASTNESS PROPERTIES OF THE DYES

4.16.1 Wash fastness of the dyes

Table 4.9: Fastness to washing before aftertreatment

	FASTNESS RATING		
DYE NO	CHANGE IN COLOUR	STAINING ON COTTON	STAINING ON NYLON
A_1	3	4-5	4-5
A_2	2	3	4-5
A_3	3	3	4
A_4	3	3-4	4
A_5	2	3-4	4-5
A_6	2-3	3	4-5
A_7	3	3	4
A_8	2	3-4	4-5
B_1	3-4	4-5	4-5
B_2	2	4-5	4-5
B_3	2	4-5	4-5
B_4	2	4-5	4-5
B_5	3-4	4-5	4-5
B_6	2	4-5	5
B_7	1-2	4-5	4-5
B_8	3	4-5	4-5

Change in shade staining

5=no change 5 = no staining

4 = slight loss in depth	4 = very slight staining
3 = appreciable loss	3 = moderate staining
2 = significant loss	2 = significant staining
1 = great loss in depth	1 = deep staining

The resistance of a dye to water and detergent is an important feature in the use of a coloured textile material. The wash fastness results of the dyed fabric as shown in Table 4.9 were observed to be in the range of very poor to moderate, that is rating of between 1-3 on the grey scale except for dye B1 which had good fastness of 3-4. This poor wash fastness is as a result of the presence of two or more sulphonic acid groups present in high molecular weight direct dyes,which makes them too water-soluble in the dye bath and on the fibre. This accounts for the relative ease with which the dye is removed from the fibre on washing in water (Nkeonye,1993). The poor wash fastness is also attributed to the characteristics of direct dyes on cellulose when not aftertreated.

4.16.2 Fastness to washing upon the after-treatment process

As a result of the poor wash fastness properties obtained after washing the dyed fabrics,the original samples were subjected to an after treatment process using formaldehyde in order to improve the wash fastness results. The results obtained are shown in Table 4.10

Table 4.10; Fastness to washing upon after-treatment

DYE NO	CHANGE IN SHADE	STAINING ON COTTON
A_1	4-5	5
A_2	3-4	4
A_3	4	4
A_4	4-5	5
A_5	3-4	4-5
A_6	4	4-5
A_7	4	4-5
A_8	4-5	5
B_1	4-5	5
B_2	4-5	5
B_3	4	5
B_4	4	4
B_5	4-5	5
B_6	4	4-5
B_7	4	5
B_8	4-5	4-5

.Change in shade	staining
5 = no change	5 = no staining
4 = slight loss in depth	4 = very slight staining
3 = appreciable loss	3 = moderate staining
2 = significant loss	2 = significant staining
1 = great loss in depth	1 = deep staining

The results were greatly improved as all the dyes had good to moderate fastness to washing of between 3-4,4 and 4-5 as compared on the grey scale while staining on the adjacent fabric are from 4-5 indicating that they are rarely stained. This after-treatment worked on the principle of increasing the size of the dye molecule or decreasing the solubility in water by forming a methylene linkage between two of the dye molecule. Either of these effects restricts the ability of the dye to diffuse out of the fibre during washing (Perkins, 1996).

4.16.3 Fastness to light of the dyed samples

The fastness rating of the dyed samples are summarized in Table 4.11

Table 4.11: Light fastness rating of the dyed samples.

DYE NO	CHANGE IN SHADE
A_1	6
A_2	5
A_3	6
A_4	5
A_5	5
A_6	5
A_7	4
A_8	6
B_1	7
B_2	5
B_3	5
B_4	7
B_5	4
B_6	4
B_7	5
B_8	7

Fastness grade	degree of fading	Fastness grade	degree of fading
8	none	4	appreciable
7	very slight	3	significant
6	slight	2	extensive
5	moderate	1	very extensive

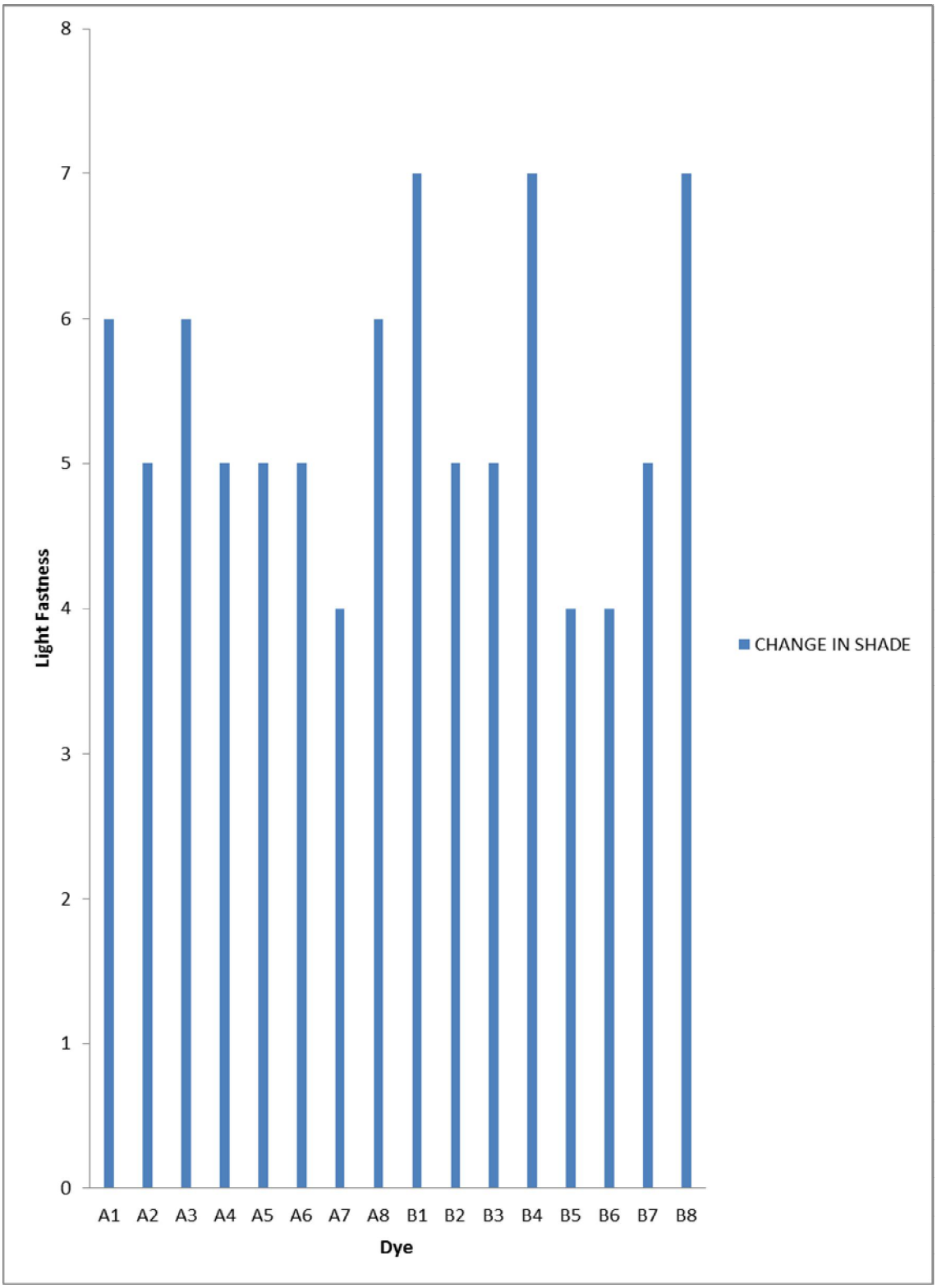


Fig 4.6: Light fastness rating of the dyes

The dyed samples were exposed to daylight along side with eight (8) blue wool standards. Their resistance to daylight are shown in Table 4.11and graphically represented in Figure 4.6.This shows that all the dyed samples had moderate to very good light fastness results of 4, 5, 6 and 7.

The poor light fastness of 2 may be due to poor planarity of the dye. There are many factors that affect light fastness. Some of them are depth of shade,the presence of foreign substances and inherent photostability of the dye chromophore and the way in which this stability is affected by the chemical nature of the fabrics.

4.16.4 Fastness to rubbing

The fastnesses to rubbing of both dry and wet dyed samples are summarized in Table 4.12

Table 4.12: Fastness to rubbing of the dyed samples.

DYE NO	CHANGE IN COLOUR-DRY	CHANGE IN COLOUR-WET	STAINING ON COTTON-DRY	STAINING ON COTTON-WET
A_1	4-5	5	4	5
A_2	5	4-5	5	4
A_3	5	4	5	4
A_4	5	4	5	4
A_5	5	4-5	5	4-5
A_6	4-5	4-5	4-5	4
A_7	5	4-5	5	4-5
A_8	5	4	5	4
B_1	5	4-5	5	4-5
B_2	5	4-5	5	4-5
B_3	4-5	4-5	4-5	4-5
B_4	5	4-5	5	4-5
B_5	4-5	4-5	4-5	4-5
B_6	5	4	5	4-5
B_7	5	4	4-5	4
B_8	4-5	4-5	4-5	4-5

.Change in shade
5 = no change
4 = slight loss in depth
3 = appreciable loss
2 = significant loss
1 = great loss in depth

staining
5 = no staining
4 = very slight staining
3 = moderate staining
2 = significant staining
1 = deep staining

The fastness to rubbing was carried out using both dry and wet dyed samples. The results as summarised in Table 4.12 shows that the dry samples had very good resistance to rubbing of values between 4-5,as eleven(11) of the dyed samples had no change in colour after rubbing and little or no staining on cotton and the wet samples also had good resistance to rubbing as well.

4.16.5FASTNESS TO PERSPIRATION OF THE DYED SAMPLES.

The fastness to perspiration carried out in both acidic and alkaline solution of histidine is summarized in Table 4.13

Table 4.13: Fastness to perspiration

	ALKALINE		ACID	
DYE NO	CHANGE IN SHADE	STAINING	CHANGE IN SHADE	STAINING
A_1	3	4	4	4
A_2	3	3	3	4
A_3	4	4	3	3
A_4	3	3	3	3
A_5	3	3	3	3
A_6	3	2	3-4	4
A_7	4	3	4	4
A_8	3	3	4	4
B_1	4	4	4	5
B_2	4	5	4	5
B_3	3	4	4	4
B_4	4	4	4	4
B_5	4	4	3	4
B_6	4	4	4	4
B_7	3	4	3	4
B_8	4	3	5	5

..Change in shade

5 = no change

4 = slight loss in depth

3 = appreciable loss

2 = significant loss

1 = great loss in depth

staining

5 = no staining

4 = very slight staining

3 = moderate staining

2 = significant staining

1 = deep staining

The perspiration produced by the human body is a chemical fluid that can have adverse effect on a coloured fabric in regular contact with it. All perspiration contains common salt which can affect some dyes but can vary in acidity or alkalinity according to a particular individual(S.D.C, 1991). Two chemical solutions which approximate to human perspiration were used,one being slightly acidic and the other slightly alkaline (Nkeonye, 1993). The results in Table 4.13 shows that the dyed samples in alkaline solution had good fastness properties to perspiration based on ratings between 3 and 4,with little and moderate staining on the adjacent fabric while the dyed samples in acidic solution had better resistance to perspiration based on rating of 3,4 and 5 mostly for all the dyes.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The synthesis of direct dyes from terephthalic and isophthalic acid using J-acid and H-acid was undertaken.The type of bridging group used affects λ_{max} only to a slight extent, which indicate the transition of conjugation by the diamidesystem. The chosen method of acid chloride synthesis in an organic solvent (chlorobenzene) allows one to prepare products in a simple way, preventing partial decomposition. The selected method for the synthesis of disazo dyes is simple and makes it possible to prepare dyes in high yield.

Generally, the exhaustion of the dyes were very good on cotton fabric with poor wash fastness properties.Though, improvement was observed upon after-treating the dyed samples with formaldehyde.They had good to moderate fastness to light,rubbing and perspiration. These dyes had bright and some deep shades on cotton due to high exhaustion and greater planarity of the dyes.

Based on the performance properties obtained,one can state that the obtained dyescan replace urea dyes and dyes derived from benzidine with similar structures.

Their practical properties such as light fastness,etc. especially those of the derivatives of J-acid are higher than those of the H-acid derivatives except for fastness to perspiration where the latter is better. The type of bridging group used in the dye synthesis plays an important part,with the best effect being obtained with the derivatives of isophthalic acid. They are observed to be relatively non-toxic and therefore can be used to dye apparels.

5.2 RECOMMENDATIONS

It is necessary to carry out further work on these dyes to enhance their application. It is in this regard that the following works are recommended.

(a) The dyes synthesized had high exhaustion on cotton but with high concentration of electrolyte. Therefore further studies should be carried out on how to obtain good exhaustion with low/minimum concentration of electrolyte.

(b) Determination of the carcinogenicity of the intermediates and dyes.

(c) Application of these dyes on rayon fabric.

(d) Total characterization using NMR and high resolution mass spectrometry.

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APPENDIX 3: SAMPLES OF DYED COTTON FABRIC

DYES	DYED SAMPLES
UNDYED COTTON	
A1	
A2	
A3	
A4	
A5	
A6	
A7	
A8	
B1	
B2	
B3	
B4	
B5	
B6	
B7	
B8	