SYNTHESIS AND CHARACTERIZATION OF SOME AMPHIPHILIC STYRYL DYES AND THEIR APPLICATION ON WOOL FABRIC

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MAY, 2016

DECLARATION

I, Reuben GANGAS, hereby declare that this dissertation contains no materials which have been accepted for the award of any degree or diploma in any university and that, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made or the source quoted in the work.

Signature……………………………..Date…………………………………..

CERTIFICATION

This dissertation titled "SYNTHESIS AND CHARACTERIZATION OF SOME AMPHIPHILIC STYRYL DYES AND THEIR APPLICATION ON WOOL FABRIC" by ReubenGANGAS meets the regulations governing the award of the degree of Master of Science in Colour Chemistry and Technology of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This research dissertation is dedicated to Almighty God.

In memories of:

My beloved father, Mr. Hassan B. Gangas

My beloved brother, Mr.Abdullahi Enoch Gangas

My beloved sister, Miss Esther Gangas

My beloved friend, Mr. Jerry Garba

May their gentle souls rest in perfect peace. (Amen)

ABSTRACT

Amphiphilicstyryl dyes were synthesized based on condensation of 2-methylbenzothiazolium salt of alkyl halide and 4-dimethylaminobenzaldehyde. The identity of the resultant dyes was investigated using FTIR, UV-Visible spectroscopy and Mass spectrometry. Two commercial dyes were compared with the synthesized dyes and all applied on to wool fabric. The surface tension of the dyes were determined and analysis showed that the surface tension of the synthesized dyes were far lower than that observed for the commercial dyes. This low surface tension of the synthesized dyes could be attributed to the fact that the synthesized dyes arepartly surfactant themselves.In fact, the synthesized dyes were found to have equal surface tension when compared to some industrial surfactants such ascetylpyridinium chloride and cetylpyridinium bromide at room temperature at a concentration of 0.3% w/v. This low surface tension imparted by the dyes on the dyeing liquor increased significantly the mobility of these dissolved dyes in water and thus was found to be very important in the exhaustion of the dyes. The percentage exhaustion of the dyes was determined and the results indicated that high% exhaustion was achieved at a limited time as a result of increase in the mobility of the dissolved dyes molecules, consequently increasing the absorption and adsorption of the dye molecules into the fibre. Levelled dyeing was achieved, though, with poor light fastness, good wash and perspiration fastness were observed.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Dyes

A dye is a coloured compound that has affinityand able to be retained on the substrateto which it is applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fibre.Both dyes and pigments appear to be coloured because they selectively absorb some wavelength of visible light. In contrast with a dye, a pigment is generally insoluble in the media in which they are applied. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments (Zollinger, 2003).

Dyed flax fibre has been found in the Republic of Georgia dated back in a prehistoric cave to 36,000 BC. Archaeological evidence shows that, particularly in India and Phoenicia, dyeing has been widely carried out for 5,000 years. The dyes were obtained from animal, vegetable or mineral origin, with none to very little processing. By far the greatest source of dyes has been from plant kingdom, notably roots, berries, bark, leaves and wood, but a few have ever been used on a commercial scale (Zollinger, 2003).

Dyes can be broadly divided into two major types i.e.

Natural and Synthetic dyes

1.1.1 Natural Dyes

The majority of natural dyes are from plant sources – roots, berries, bark, leaves wood, fungi and lichens. Throughout history, people have dyed their textiles using common, locally available materials. Scarce dyestuffs that produced brilliant and permanent colours such as the natural dye tyrian purple and crimson kermes were highly prized luxury items inthe ancient world. Plant-based dyes such as woad, indigo, saffron and madder were produced using resist dyeing techniques to control the absorption of colour in piece-dyed cloth. Dyes such as cochineal and logwood were introduced in Europe by the Spanish treasure fleets, and the dyestuffs of Europe were carried by colonists to America (Zollinger,2003).The use of natural dyes in textile application is gaining popularity because of the quality of the natural colour obtained as well as the environmental compatibility of the dyes. In addition, natural dyes can exhibit antimicrobial and deodorant properties. Nevertheless their inferior fastness compared to synthetic dyes is a deterrent to their use as there is difficulty in extracting and storing the colourant (Deo and Dasa, 1999). The discovery of man-made synthetic dyes late in the 19th century ended the large-scale market for natural dyes.

1.1.2 Synthetic Dyes

Synthetic dyes are coloured substances obtained by chemical transformation. They cost less to synthesize when compared to the highly expensive method of extracting natural dyes. They offer a vast range of new colours and impart better properties to the dyed materials. Synthetic dyes have quickly replaced the traditional natural dyes because they impart better properties to the dyed materials (Simon, 2000). Synthetic dyes have furnished the dye users with a colourful palette for over a century. Many different substrates which are either natural or synthetic polymer structures of all kinds can be dyed, printed or pigmented in virtually any colour to commercially acceptable standards of fastness, at an affordable price (Shore, 1990). Nearly all the synthetic dyes and those of natural origin are derived from one or otherof the following hydrocarbons such as benzene, toluene, naphthalene and anthracene. These hydrocarbons are contained together with a great variety of other substances, in coal-tar, the black viscid fluid obtained as a bye product in the manufacture of illuminating gas or of metallurgical coke. They are isolated from these materials by making use of their differences in their boiling points and other physical properties. Their development has been a notable achievement of organic chemists, who have had to overcome successive challenges due to their ingenuity (Shore, 1986).

Dyes suitable for use on textile must have the following desirable properties:

- Intense colour (tinctorial strength or colouring power). The minimum value of the molar extinction coefficient (i.e ε_{max}) must be greater than 10,000 $lmol^{-1}cm^{-1}$. Most textile dyes have ε_{max} values of around 40,000 $lmol^{-1}cm^{-1}$.
- Water solubility (either permanent or only during dyeing)
- Ability to be absorbed and retained by the fibre(substantivity) or to be chemically combined with it (reactivity).
- Fastness, i.e the ability of the dye on the fibre to be able to withstand the treatment which the fibre would undergo during processing and in normal use.
- The dye should be non- metameric, i.e its colour should not vary with light source and should be safe and economic to manufacture.

During the first decade of the 20^{th} century, organic chemistry and chemistry of dyes and intermediates developed together and could hardly be differentiated. The principal application of dyes is in the colouration of substrates, typically textiles. During the dyeing process, synthetic fibres require surfactants or organized assemblies such as micelles, vesicles or layers. Such auxiliary agents will probably continue to be important in the colouration of materials resulting from current and future development in fibre science and technology.

The application of binary dye-surfactant systems, together with an understanding of the interactions within them is also relevant to other scientific fields, including analytical chemistry, photography, luminescence and lasers. Of particular interest are amphiphilic dyes for which the concept of colour and surface-active properties coexist within the same molecular frame work.(Zollinger, 1987) and (Johnson,1989).

1.2 Statement of Research Problem

Conventionally, dyeing of wool and other similar fibres involve prolong periods at ornear boil that could degrade the fibre, it was our hope that these dyes would reduce dyeingtime and also give leveled dyeing.

1.3 Aim

The aim of this research is to synthesizeamphiphilicstyryl dyes based on 2-methylbenzothiazolium salt of alkyl halides and apply on wool fabric.

1.4 Objectives

- Synthesis of four (4) different 2-methylbenzothiazolium alkyl halides (inter-mediate)
- Synthesis of four (4) Amphiphilicstyryl dyes.
- Determination of the melting point and pH of the synthesized dyes.
- Characterization of each of the dyes.
- Determination of the surface tension of each dye and compare with two other commercial dyes (Malachite Green and Methylene Blue)
- Application of these dyes on wool fabric.
- Analysis of performance of the dyes on wool fabric.

1.5 Justification of the study

This research work is to synthesize amphiphilicstyryl dyes with surface active properties to reduce the dyeing time of wool thereby reducing also, the economiccost of its dyeing by saving energy.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Historical Development of Synthetic Dyes

Synthetic dyes were an early result of trial synthesis of quinine through the oxidation of a mixture of aniline bases by William H. Perkin in England(Allen, 1971). In the course of oxidation reaction, he accidentally obtained a black precipitate which after extraction with alcohol resulted in a purple dye called mauveine instead of the expected quinine. The brilliant violet of hue mauveine on silk immediately stimulated attention of many chemists. Vergum (1859) in Lyon discovered fuschine, whilst Peter Griess discovereddiazo compound in England then laid the foundation for the development of the currently largest class of synthetic dyes namely the azo compounds.

Perkin was able to prepare a relatively pure and technically interesting product which later resulted to large scale production in his industry set up by the following year after the discovery.

After the discovery of the quadrivalency of carbon by Kekule (1858) and the constitution of benzene (1865), a way was opened up for processes leading to the production of purely synthetic dyes, as well as for artificial production of natural dyes.The first success to be mentioned is the discovery of the synthesis immediately afterwards of alizarin (1, 2-dihydroxyanthraquinone) by Graebe and Libermann in 1868 by the fusion of sulphanatedanthraquinone with caustic alkali.

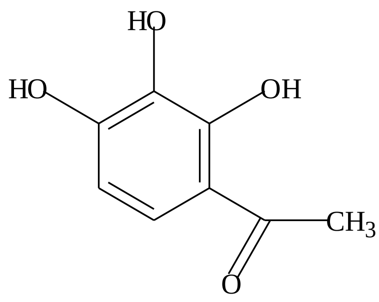
Vidal opens up the field of sulphur dyes whilst the year 1901 was characterized by the discovery ofindanthrone, the first anthraquinone vat dye discovery by R. Bohn. Other classes of dyes discovered in the 20th century includeNedan dyes (1915), phthalocyanine (1936) and metal complex dyes(irgalan dyes).Clavel and Dreffuss solved the problem of dyeing hydrophobic fibres by means of disperse dyes.

In 1951-1952, reactive dyes for wool were developed. Typical examples includeRemalan, produced by Ciba and Procion dye produced by ICI. These possess very brilliant shades on the substrate and the fastness characteristics are very excellent. The synthesis and the application of reactive dyes have further opened up ways for dyestuff research to graduate from purely empirical synthesis of coloured molecules to the study of the mechanism of interaction of substrate and dyes with which already known chromogenes such as azo, anthraquinone and cyclic azo compounds are associated.With these improvements and knowledge of synthesis, different types of dyes are now synthesized at various parts of the world.

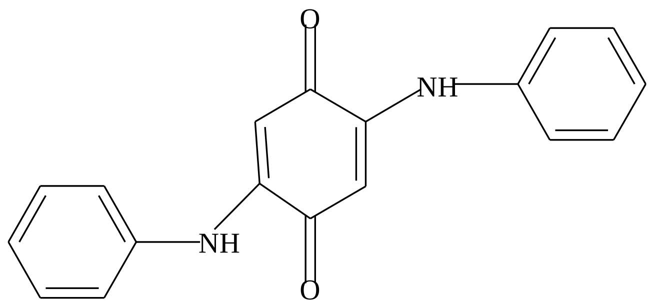
Dyes may be classified by fibre type, such as polyester, dyes for cotton, and dye for nylon or by their method of application to the substrate such a classification would include direct dyes, vat dyes, reactive dyes, disperse dyes and several more types. The most appropriate system for the classification of dyes is by chemical structure. This system has many advantages. First, it readily identifies dyes as belonging to a group which has characteristic properties, for example, azo dyes (strong and cost effective) and anthraquinone dye (weak and expensive). Second, it produces a manageable number of groups. Third, and most importantly, it is the classification used most widely by both the synthetic dye chemists and the dye technologists (Zollinger, 2003).

2.2 Classification of Dyes According to Chemical Structure

2.2.1Aminoketone and Hydroxyketone dyes

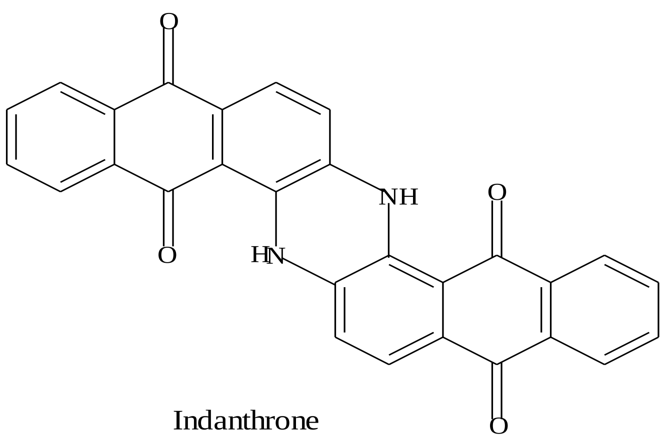


Hydroxyquinone



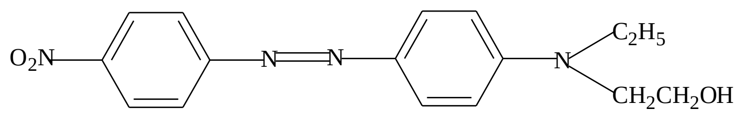
Arylaminoquinone

2.2.2 Anthraquinone Dyes



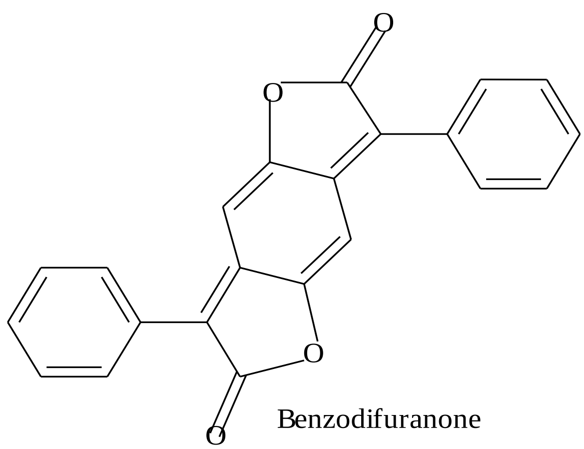
Indanthrone

2.2.3 Azo Dyes



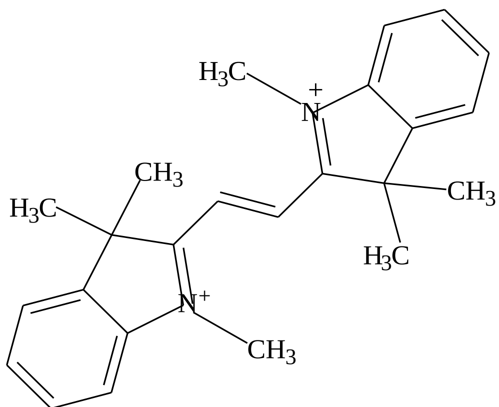
C. I Disperse Red 1

2.2.4Benzodifuranone Dyes



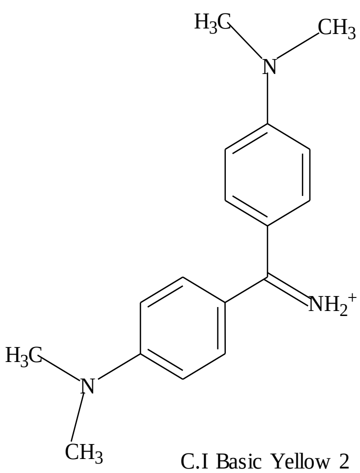
Benzodifuranone

2.2.5 Cyanine Dyes

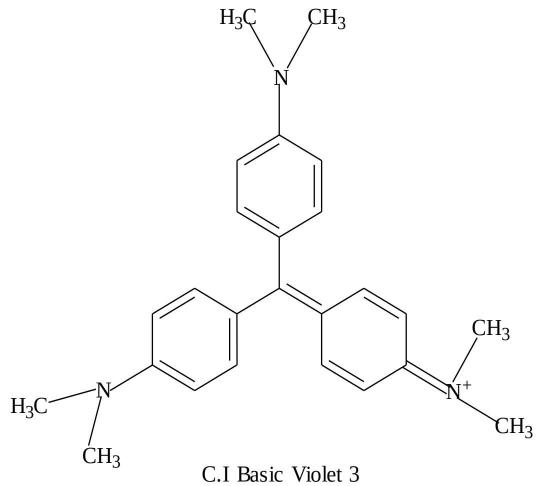


Polymethine

2.2.6Diphenylmethane and Triarymethane Dyes

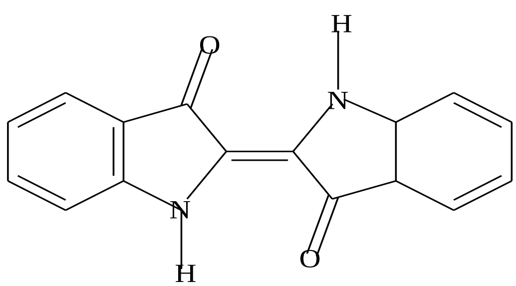


C.I Basic Yellow 2



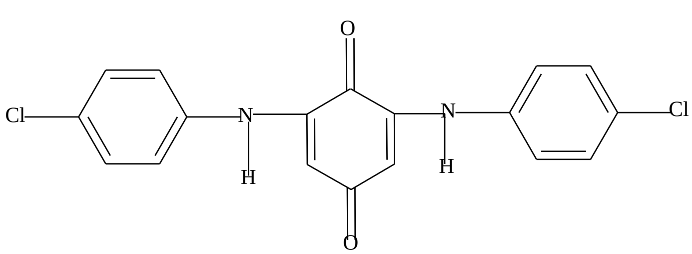
C.I Basic Violet 3

2.2.7 Indigoid Dyes



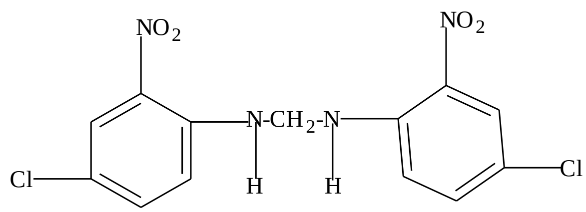
C.I Vat Blue 1

2.2.8 Lactone dyes (amino-ketone and hydroxyl-ketone dyes)



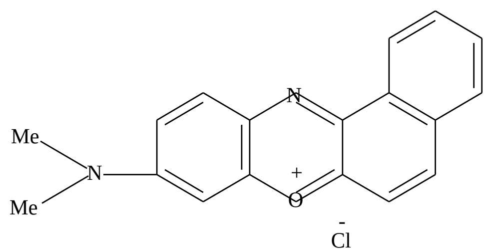
C. I Vat Yellow 5

2.2.9 Nitro dyes



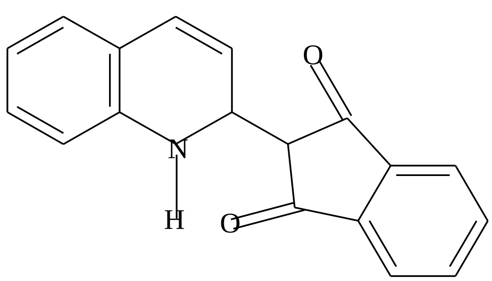
C.I Pigment Yellow 11

2.2.10 Oxazine dyes



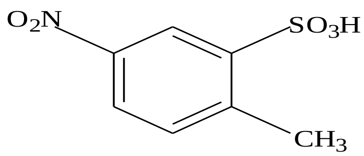
C. I Basic Blue 6

2.2.11Quinophthalone Dyes

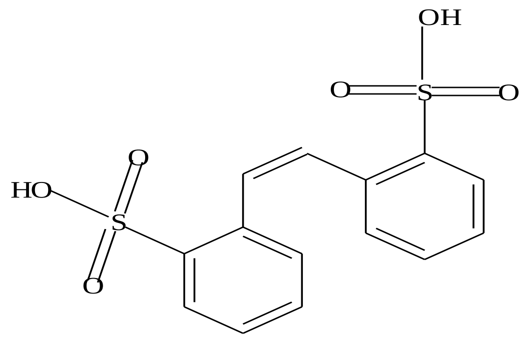


Quinophthalone

2.2.12 Stilbene Dyes

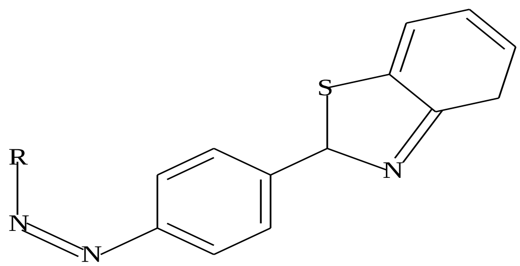


4-nitrotoluene-2-sulphonic acid

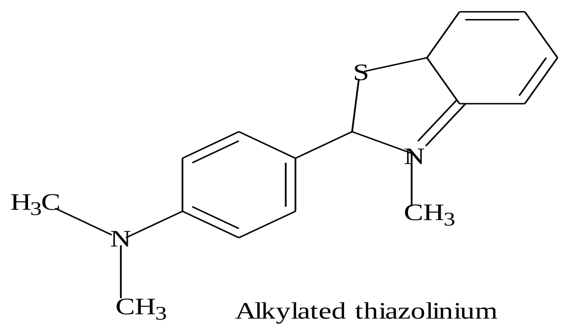


4,4-dinitrostilbene-2,2-disulphonic a

2.2.13 Thiazole Dyes

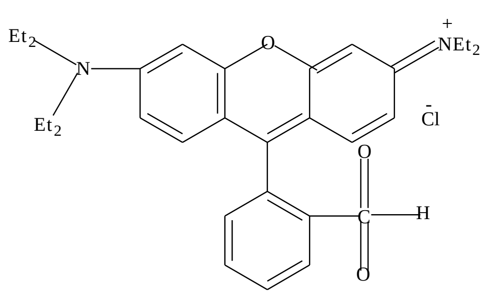


Azophenylthiazole



Alkylated thiazolinium

2.2.14 Xanthene dyes



C.I Basic Violet 10

2.3 Classification of Dyes According to Usage

Textile dyes are classified by the dyer according to their method of application to textile fibres, but the chemist uses a different method of classification based on their chemical constitution.

2.3.1 Direct Dyes

These are defined as anionic dyes with substantivity for cellulosic fibres, normally applied from an aqueous dye bath containing an electrolyte. The forces that operate between a direct dye and cellulose include hydrogen bonding, dipolar forces and nonspecific hydrophobic interaction, depending on the structural nature and polarity of the dye. Apparently multiple attachments are important, since linearity and planarity of molecular structure seem to be desirable features. The sorption process is reversible and numerous attempts have been made to minimize desorption by suitable after-treatment. The two most significant non textile outlets for direct dyes are the batchwise dyeing of leather and the continuous colouration of paper. Direct dyes are inexpensive and provide an outstanding wide range of hues. However, the fastness especially to washing, of dyeing on cellulosic fibres generally leaves much to be desired(Shore, 1990).

2.3.2 Vat Dyes

Vat dye is water- insoluble colorant containing two or more keto groups. It can be brought into aqueous solution by a reduction process (vatting) which converts the vat dye into alkali-soluble enolic (leuco) form. The application of vat dyes to cellulosic fibres (virtually the only fibre type on which their outstanding fastness properties can be exploited) thus proceeds in four stages:

(a) Reduction and dissolution

(b) Absorption

(c) Reoxidation

(d) Association of the vat dye molecules with the fibre.

About 80% of all vat dye belong to the anthraquinonoid class and this certainly includes the leading products in all sectors of the colour gamut (Shore, 1990).

2.3.3 Reactive Dyes

Reactive dyes are capable of reacting chemically with a substrate under suitable application conditions to form a covalent dye-substrate bond. The characteristic structural feature is thus the possession of one or more reactive groupings of various kinds, the most important being vinyl sulphone and severalhalotriazone and halopyrimidine systems. The introduction of these specific means of ensuring the fixation of the dye freed the colour chemist from many of the structural limitations implicit in the design of dyes, so that virtually any chemical class could be employed as a chromogen. In practice, however, the reactive dye chemist has relied heavily on the azochromophore usually unmetallised but sometimes as metal complexes in the duller hues,such as navy, brown and black. Anthraquinone, dioxazine, formazan and phthalocyaninechromophores in the bright blue-green sectors are the exceptions, but in every other hue sector azo hues account for over 95% of the reactive dye structures. The most important application segment for reactive dyes is the dyeing and printing of cellulosic fibres. Reactive dyes are suitable for dyeing glove leather and similar materials where resistance to water and dry-cleaning solvents is essential(Venkataraman, 1971).

2.3.4 Sulphur Dyes

These dyes are indeterminate in constitution and are usually mixtures of different chemical spices;they all contain the characteristics disulphide group in the insoluble form. A sulphur dye can therefore be brought into aqueous solution by reduction to the alkali – soluble (leuco) from (D-S). The soluble sodium thiolate form of the leucosulphur dye has substantivity for cellulose.

Thus the application of sulphur dye to cellulosic fibres is a three stage process broadly similar to that already outlined for vat dyes. Apart from their extensive contribution to the dyeing of cellulosic fibres, sulphur dyes are of little further interest. They have been applied to a limited extent on leather capable of resisting alkali (oil – tanned leather, for instance) but only the water – soluble brands are suitable (Abrahat, 1977).

2.3.5 Disperse Dyes

A disperse dye is defined as a sparingly water – soluble dye havingsubstantivity for one or more hydrophobic fibres, for example, cellulose acetate, and usually applied from fine aqueous dispersion. In addition to their use on acetate fibres, the dyes are used on polyester, polyamide and acrylic fibres.Due to the variety of the disperse dyes and their varied dyeing behavior on different fIbres, many dye makers have introduced system of classification for their products. For example, ICI (1973) classified their dyes into five groups according to dyeing behavior and fastness properties on polyester. According to (Bird,1964), the SDC proposed four tests by which the migration, buildup, temperature range, and rate of dyeing characteristics of disperse dyes on cellulose acetate under practical dyeing conditions can be determined. Tests for determining the same characteristics on triacetate were proposed in the following year. These tests permit individual dyes to be rated on an A to E scale for each characteristics property, where A represents the most satisfaction and E the least satisfactory performance (Abrahat, 1977).

2.3.6 Basic Dyes

These dyes are also known as cationic dyes.This a class of synthetic dyes, that act as bases and when made soluble in water, they form a coloured cationic salt, which can react with the anionic sites on the surface of the substrate. The society of Dyers and colourists defined a basic dye as ‘characteristics by its substantivity for acidic type of acryclicfibres and for tannin – mordanted cotton’, whereas a cationic dye is defined as one ‘that dissociate in aqueous solution to give a positively charged coloured ion’.Basic dyes dissociate in water to yield colouredcations and are characterized by their brilliance and very high tinctorial strength. This dye class, which includes some of the earliest synthetic dyes, was originally used for dyeing wool, silk and mordanted cotton, but generally poor light fastness of the dyes suppress their use until the introduction of acryclicfibre on which dyes exhibited higher light fastness and very good fastness to wet treatments. Apart from their primary use for dyeing acryclicfibres, basic dyes are used for dyeing acid modified polyamide and polyester fibre (Shore, 1990).

2.3.7 Acid Dyes

These are defined as anionic dyes characterized by substantivity for protein fibres. Leveling acid dyes and 1:1 metal – complex dyes are normally applied to wool from strongly acid solution but the 1:2 metal complexes and many milling acid dyes have considerable – substantivity even from neutral dyes baths. Wool, silk, and nylon contain basic groups and the uptake of leveling acid dyes by nylon at acid pH can usually be related to the amine end – group content of the fibre.

The first acid dyes, orange, I (Acid Orange 20), was discovered in 1876. All but a handful of the acid dyes develop since then were evaluated initially with wool dyeing in mind. In time of adaptability to the colouration of other substrates, however, acid dyes have proved pre-eminent. This is the main reason for their number and variety. As well as the dyeing and printing of nylon and protein fibres, acid dyes are important for the colouration of leather, paper, jute, wood and anodizealuminum(Shore, 1990).

2.3.8 Mordant Dyes

The term 'mordant dye' is defined as a dye that is fixed with a 'mordant'. A mordant is itself defined as 'a substance, usually a metallic compound, applied to a substance to form a complex with a dye which is retained by the substrate more firmly than the dye itself'. Unfortunately, the mordant dyes category in the *colour Index* follows the more restricted convention of excluding both chelatable direct dyes capable of complexing with copper salts and also those basic dyes that were formerly applied to tannin – mordanted cotton.

In all hue sectors except violet and blue, where triarylmethane, anthraquinone and oxazine dyes make notable contribution, 80% or more of chrome dyes are of the monoazo type. Although most chrome dyes are only of interest for wool dyeing (Hartley, 1979), minority are applicable to most of those substrates where acid dyes are found useful. Natural dyes and pigments occupy a separate section of the Colour Index but most of them are mordant dyes in the broader sense defined above (Thompson, 1971).

2.3.9 Leather Dyes

The application range designated by this name in the Colour*Index* incorporates those acid, direct and mordant dyes with substantivity for leather and satisfactory fastness on that substrate (Eitel – *et al.*, 1984). It is a commercially important sector, the number of products listed being exceeded only by the complete acid and direct ranges. As expected from the sources of this selection, about 85% of leather dyes are azo compounds (35% disazo, 30% monoazo, 20% metal – complex monoazo) and the remainder are mainly yellow – orange stilbenes and violet – blue – green anthaquinone or triarylmethane types (Eitel, et al., 1984).

2.3.10 Food Dyes

Food colouring, or colour additive, is any dye, pigment or substace that imparts colour when it is added to food or drink. They come in many forms consisting of liquids, powders, gels and pastes. The possibility that they may affect consumers adversely is causing increasing concern. Legislation over many years has increasingly restricted the usage of synthetic colourants to certain 'permitted' products that have shown no harmful effects when rigorously tested. There is yet no agreed international list of permitted food colours, however, only about forty long established colourants of relatively simple constitution, mostly monoazo yellows and reds appear on the permitted lists of the more legislatively critical countries. Triphenylmethanes and other chemical classes provide the few violets, blues and greens. The natural carotenoid dyes are of outstanding importance for colouring edible fats and oils (Meggos, 1995).

2.3.11 Solvent Dyes

These dyes are characterized by their solubility in one or more organic solvents. Numerous media are of interest in practice, the most significant being alcohols, esters, ketone, chlorinated solvents, hydrocarbons, oils, fats and waxes. More than half of the solvent dyes listed in the Colour Index are unsulphonatedazo compounds (27% monoazo, 18% monoazo metal – complex, 9% disazo) and a further 7% are complexes formed by co- precipitation of acid dyes and basicdyes, mostly yellows and reds. Unsulphonatedanthraquinones lead the field in the bright violet – blue – green sectors (17%). Xanthenes reds (5%) are the other noteworthy segments represented, together with a miscellany (12%) drawn from almost all other chemical classes (Shore, 1990).

2.4 Surface Tension

Surface tension is a property that arises from the mismatch in intermolecular forces experienced at a liquid/vapour interface. In the bulk portion of a liquid, a molecule experiences intermolecular forces from all directions around it. In water, these forces are predominately strong hydrogen bonds. Since the molecule is surrounded from all directions, all of the pair-wise intermolecular attractive forces cancel each other out and there is no net motion of the molecules other than random thermal motion. At the surface of the liquid, however, a very different situation is present. A water molecule at the surface will experience attractive hydrogen bonds back towards the bulk of the water, but there are no offsetting forces on the air side of the interface (or more accurately, the liquid-air intermolecular forces are much weaker than the liquid-liquid forces). This leads to a pulling in of the surface towards the bulk of the liquid. At liquid-air interfaces, surface tension results from the greater attraction of water molecules to each other (due to cohesion) than to the molecules in the air (due to adhesion). The net effect is an inward force at its surface that causes water to behave as if its surface were covered with a stretched elastic membrane.Because of this mismatch between intermolecular forces, energy in the form of work is required to expand the surface. The SI units for surface tension are N/m(or J/m^2). Surface tension is often listed, however, in cgs units of dynes/cm, but this can be translated to SI units according to 1 dyn/cm = 1mN/m. Surface tension affects a number of the handling and performance characteristics of a liquid.Examples include capillary action, wetting of surfaces, and drop formation. The latter is the effect that surface tension has on a liquid's "desire" to form spherical droplets in air. Since positive work is required to increase the surface area of a liquid, anything that can be done to reduce the surface area will lead to negative work, i.e. lower free energy. A sphere represents the geometry with the smallest possible surface area for a given volume. Wetting of a support surface is the opposite effect, where lower surface tensions mean that a liquid is more likely to spread and wet the entire surface of a supporting substrate like glass (Garland, et al.,2003) and (Somasundaran, 2006).

Surface tension can be seen in:

- Beading of rain water on waxy surface such as leaf
- Flotation of denser objects on water surface
- Separation of oil and water (interface tension) in a container
- Formation of water droplets

2.5 Surfactants

These are compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, dispersants and now auxiliaries in dyeing.There are usually organiccompounds that are amphiphilic, meaning they contain both hydrophobic groups (their *tails*) and hydrophilic groups (their *heads*). Therefore, a surfactant contains both a water insoluble (oil soluble) component and a water soluble component. Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The water-insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water-soluble head group remains in thewater phase. This alignment of surfactants at the surface modifies the surface properties of water at the water/air or water/oil interface (Rosen &Kunjappu, 2012).

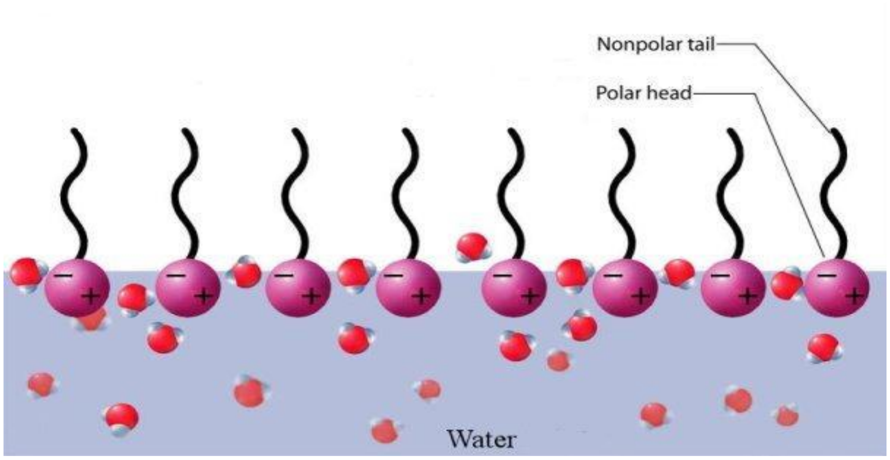


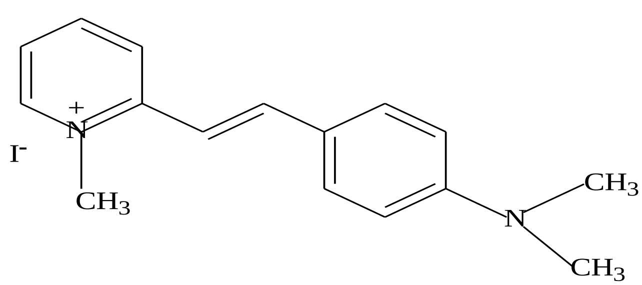
Figure 2.1: Surfactants at water/air interface

2.5.1Amphiphiles

Amphiphile is a Greekword; first, the prefix amphi means “double” and the root philo means “affinity”. Amphiphilic molecules are more or less surface-active agents or surfactants that exhibit a double affinity which can be defined from the chemical point of view as polar, non-polar duality. The polar portion exhibits a strong affinity for polar solvents particularly water, and it is often called hydrophilic part or hydrophile. The non-polar part is called hydrophobic part or lipophile from the Greek root Phobos (fear) and lipos (grease); because of its dual affinity, an amphiphilic molecule does not feel “at ease” in any solvents, be it polar or non-polar since there is always one of the groups which “does not like” the solvent environment. This is why amphiphilic molecules exhibit a very strong tendency to migrate to interface or surfaces and to orientate so that the polar group lies in water and the non-polar group is placed out of it and eventually in oil (Salager, 2002).Since Amphiphilic molecules are more or less surface-active agents or surfactants, thus they absorb at different interfaces. The dual nature of surface active agents lies in the possession ofboth polar and non-polar regions on thesame molecule. The latter is generally a hydrophobic flexible chain hydrocarbon, whereas the nature of the polar hydrophilic head is selected in respect to the surfactant classification.Negatively charged hydrophilic group results in anionic surfactants (anionics)e.g. Sodium dodecylsulphate (NaDs) $CH_3(CH_2)_{11}OSO^-{}_3Na$. Most nonionic surfactants (nonionics) carry an oligooxyethylene group bound to the hydrocarbon chain e.g. ethoxylated alcohol,C_nH_{2n-1} $(OCH_2CH_2)_nOH$. Most of the (cationics) contain a substituted ammonium group which can be attached to one or two hydrophobic chains. e.g. the distearyl ester of 2, 3-di- hydroxypropyl – trimethyl ammonium chloride.Amphoteric surfactants (amphoterics) bear both an anionic and cationic functional groups N-dodecyl – N, N–dimethyl betaine,$C_{12}H_{25}$-N^+ $(CH_3)_2$ CH_2COO^-.(Attowood and Florence, 1985).

2.6Styryl Dyes

These are cationic dyes with delocalized charge and have insertion of an aryl residue between the second nitrogen atom and the methine chain.Styryl dyes are one of the most important groups of dyes used in high-tech applications such as laser discs, flexible dyes, laser dyes and as optical sensitizers and in various other fields such as dye- sensitized solar cells and dyes with non-linear optical properties. Additionally, they are used for bio-labeling and medicinal analysis. Most importantly, styryl dyes are used for dyeing fibres (Tordor, et al.,2010).



2-[4-(Dimethylamino)styryl]-1-methylpyridinium ioc

2.7Wool

Wool is a protein fibre and it is formed in the skin of a sheep, hence, it is called animal fibre. It is produced from different types of sheep all over the world.Like all textile fibres, wool has its own physical and chemical properties which are required to be known for better processing in spinning, weaving, knitting, dyeing and printing as well as finishing (Leeder, 1984).

2.7.1 Physical Structure of Wool Fibre

Wool fibre has a very complex physical structure. A wool fibre can be considered as a biological composite consisting of regions that are both chemically and physically different. Australian merino wool fibre is an example. They are composed of two types of cells, the internal cells of the cortex and external cuticle cells that form a sheath around the fibre.Cuticle cells (or scales), which overlap like tiles on a roof, make wool unique amongst textile fibres. An important function of cuticle cells is to anchor wool fibres to the skin of sheep. The exposed edge of each cuticle cell points from the fibre root towards the tip. This gives rise to a larger surface frictional value when a fibre is drawn in the against-scale direction than in the with-scale direction. The frictional difference helps to expel dirt and other contaminants from the fleece, but it is also responsible for wool's property of felting when agitated in water. This characteristic, which is not shared by any other textile fibre, enables fabrics with very dense structures to be produced, such as blankets, felts and overcoat materials. When felting is regarded as undesirable (for example in knitted garments that will be machine-washed), processes are available to remove the frictional difference and make wool shrink resistant. The fibre surface is also largely responsible for the natural softness of wool and its property as one of the smoothest textile fibres. Even after the natural wool grease has been removed by scouring with a detergent, wool fibres are relatively difficult to wet compared with other textile materials. This natural water repellency makes wool fabrics 'shower-proof ' and able to resist water**.**The cortex of wool comprises approximately 90% of the fibre. It consists of overlapping spindle shaped cortical cells. Both the cuticle and cortical cells havehighly complex substructures. Cortical cells are held together by the cell membrane complex (CMC), which also separates cortical cells from those of the cuticle. The CMC is a continuous region, containing relatively lightlycross-linked proteins and waxy lipids that extend throughout the whole fibre. Although it comprisesonly around 5% of the total fibre mass, it plays an important role in the overall properties of wool. It is a region of relatively low mechanical strength in the fibre composite. When wool worsted fabrics are abraded during prolonged wear, breakdown tends to occur mainly by fracture along the boundaries between cortical cells, resulting in fibrillation. Because the CMC is only slightly cross-linked, it is also more susceptible to chemical attack than other regions of the fibre. Being the only continuous phase in the fibre, it also provides a channel by which dyes and chemicals can diffuse in and out of wool.The matrix proteins are also responsible for wool's property of absorbing and retaining large amounts of dyestuffs.Wool, a fibre that has evolved over thousands of years to insulate and protect sheep, is the most complex and versatile of all textile fibres. It can be used to make products as diverse as cloth for billiard tables to the finest woven and knitted fabrics. The insulating and moisture absorbing properties of thefibre make fine wool products extremely comfortable to wear. The chemical composition of wool enables it to be easily dyed to shades ranging from pastels to full, rich colours. It is indeed justified to call wool: “Natures Wonder Fibre”(Rippon, 1992) and (Leeder, 1984).

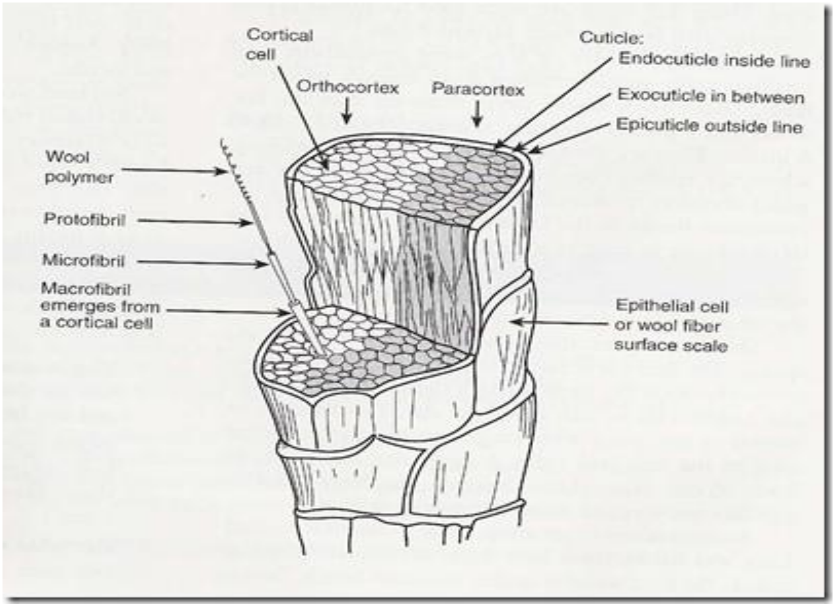
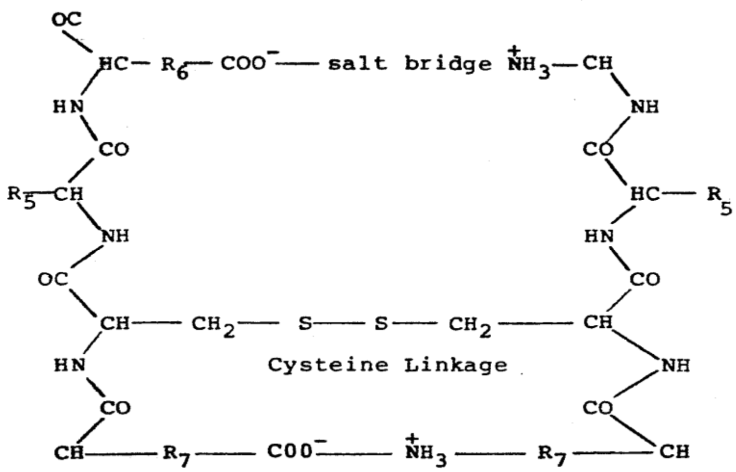


Figure 2.2: Physical Structure of Wool Fibre

2.7.2 Chemical Structure of Wool Fibre

It has been estimated that wool contains more than 170 different proteins. These are not uniformly distributed throughout the fibre; proteins of different structures are located in specific regions. This heterogeneous composition is responsible for the different physical and chemical properties of the various regions of wool. The proteins in wool are composed of amino acids; so called because they contain basic amino ($-NH_2$) and acidic carboxyl (-COOH) groups. Individual amino acids differ from each other in the nature of the side group. Of the 22 naturally-occurring amino acids, wool contains 18. The side groups of amino acids vary in size and can be grouped, according to their chemical properties: hydrocarbons which are hydrophobic (water-hating); hydrophilic (water-loving); acidic; basic; and amino acids that contain sulphur. In proteins, including wool, the amino acids are joined together to form long polymer chains. These compounds can be regarded as polyamides because each structural unit is joined by an amide group. When the polymer chain is a protein however, the amide repeat unit (-NHCHRCO-) is called a peptide group. In wool, individual polypeptide chains are joined together to form proteins by a variety of covalent (chemical bonds), called crosslinks, and non-covalent physical interactions. The most important crosslinks are the sulphurcontaining disulphide bonds, which are formed during fibre growth by a process called “keratinisation”. These make keratin fibres insoluble in water and more stable to chemical and physical attack than other types of proteins. Disulphide bonds are involved in the chemical reactions that occur in the 'setting' of fabrics during finishing. In this process, disulphide crosslinks are rearranged to give wool fabrics smooth-drying properties so that ironing is not required after laundering. Another type of crosslink is the isopeptide bond, formed between amino acids containing acidic or basic groups. In addition to the chemical crosslinks, some other types of interactions also help to stabilize the fibre under both wet and dry conditions. These arise from interactions between the side groups of the amino acids that constitute wool proteins. Thus, hydrophobic interactions occur between hydrocarbon side groups and ionic interactions occur between groups that can exchange protons. These ionic interactions or 'salt linkages' between acidic (carboxyl) and basic (amino) side chains are the most important of the non-covalent interactions. The carboxyl and amino groups in wool are also important because they give wool its amphoteric or pH buffering properties. This is its ability to absorb both acids and alkalis. The ionic groups also control the dyeing behaviour of the fibre (Rippon, 1992) and (Leeder, 1984).



Where R_5,R_6 and R_7 are amino acid side chains

Figure 2.3: Chemical Structure of Wool Fibre

2.7.3 Dyeing of Wool

2.7.3.1 Isoelectric Condition or Amphoteric Nature of Wool and Dyeing Behaviour

Isoelectric condition of wool means the wool fibre has equal numbers of positively and negatively charged sites upon which anions and cations respectively can be adsorbed.

$$\mathbf{H_3N^+\text{-wool-}COOH \longleftrightarrow H_3N^+\text{-wool-}COO^- \longleftrightarrow H_2N\text{-wool-}COO^-}$$

(acidic condition) (isoelectric condition) (basic condition)

(Choudhury, 2006)

Wool fibres are amphoteric because of the presence of acidic and basic side chains in some of the constituent proteins. These groups give wool a very large capacity for adsorbing acids and alkalis. This occurs as a result of adsorption or desorption of hydrogen ions by the carboxyl side chains of aspartic and glutamic acid residues, and the amino side chains of lysine, imidazoyl side chains of histidine and guanidinium side chains of arginine residues. As acid is added to the system, hydrogen ions react with the carboxylate anions to form carboxylic acid groups, leaving the positively charged ammonium groups available to act as sites for anions (including dye anions). Under alkaline conditions, hydrogen ions are abstracted from the positively charged amino groups. The carboxyl anions then confer a negative charge on the substrate. The maximum acid-binding capacity of wool is governed by the number of carboxyl groups present.

Thus, basic dyesare used on wool in a slightly weakbase dye-bath (Ion interaction) (Lewis, 1990).

CHAPTER THREE

3.0 MATERIALS & METHODS

The materials and methods used in this work are as follows

3.1 Chemicals Used

No.	Chemicals	% Purity	Source
1	1-Bromononane	98.0	Sigma-Aldrich
2	1-Bromoundecane	98.0	Sigma-Aldrich
3	1-Bromohexadecane	97.0	Sigma-Aldrich
4	1-Bromooctadecane	98.0	Sigma-Aldrich
5	4-Dimethylaminobenzaldehyde	99.0	Sigma-Aldrich
6	2-Methylbenzothiazole	99.0	Sigma-Aldrich
7	Piperidine	99.5	Sigma-Aldrich
8	Acetic Acid	97.0	Steve Moore Chemicals
9	Acetone	96.0	Steve Moore Chemicals
10	Ethanol	97.0	Steve Moore Chemicals
11	Diethyl-Ether	97.5	Steve Moore Chemicals
12	Methanol	98.0	Steve Moore Chemicals
13	Sodium carbonate	96.0	Steve Moore Chemicals
14	Toluene	98.0	Steve Moore Chemicals

3.2 Equipment/Instruments

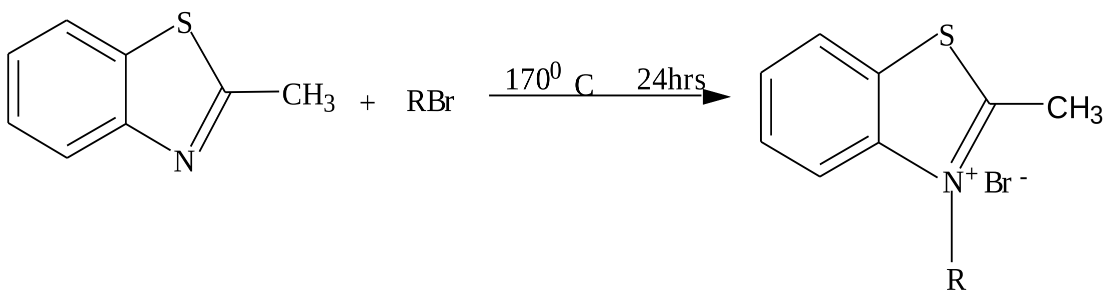
No.	Equipment/Instruments	Model	Supplier
1	FTIR Spectrophotometer	FTIR-8400S	Shimadzu, Japan
2	Mass Spectrometer	GCMS-QP2010	Shimadzu, Japan
3	UV-Visible Spectrophotometer	UV-1800 UV-Vis	Shimadzu, Japan

4	Reflux Condenser	-	Locally fabricated
5	Tensiometer	FT-9435	Paul N. Gardner Co., Inc, United States

3.3Methods

3.3.1 Preparation of 2-Methylbenzothiazolium Salt of Alkyl halides

2 – Methylbenzothiazole (19.39g, 0.13mole), was treated with 1-bromononane (8.49g, 0.041 mole)and stirred for 24hrs at 170^0C. The mixture was then cooled, filtered and the residue washed with diethyl-ether before recrystallizing from toluene. This process was carried out for the other three (3)alkyl halides to produce their respective intermediates.



Where R is:

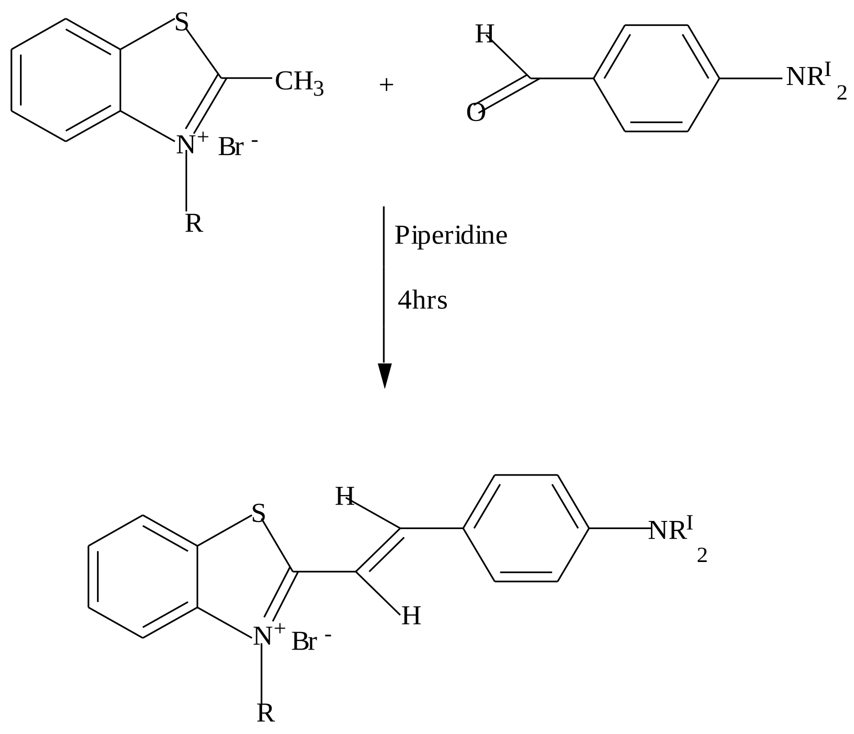
$CH_3(CH_2)_7CH_2Br$, $CH_3(CH_2)_9CH_2Br$, $CH_3(CH_2)_{14}CH_2Br$ and $CH_3(CH_2)_{16}CH_2Br$

Scheme 3.1-Synthesis of 2-methylbenzothiazolium salt of alkylhalides

3.3.2 Synthesis of the Styryl Dyes

3.3.2.1 Condensation Reaction

2-Methyl-N-nonylbenzothiazoliumbromide (17.90g, 0.05mole) prepared above was treated with 4-dimethylaminobenzaldehyde (7.45g,0.05mole) and 0.5ml of piperidine in 60ml of ethanol and thenrefluxed for 4 hrs. The reaction mixture was then cooled and the dye precipitated. The dye was collected by filtration, then dried and recrystallized from toluene. Using the same procedure, three (3) other styryl dyes were synthesized.



Where R^I is CH_3

+ H_2O

Scheme 3.2 - Synthesis of the styryl dyes

3.4Percentage Yield

The percentage yield was calculated using the formula below:

$$\% \, Yield = \frac{Actual \ yield}{Theoritical \ yield} \times 100$$

3.5Purification

The synthesized dyes were first washed in diethyl-ether then recrystallized using toluene by heating to boil, left for a while to cool gently and then filtered. Purity increased as this process was repeated but the quantity of the dyes keptdropping. Thin layer chromatography was used to determine the purity of the dyes before characterization.

3.6Determination of Molar Extinction Coefficient

The molar extinction coefficient (□), which is a constant for each molecule at any given wavelength represents the absorbance of 1cm thickness of a medium containing 1mole of the absorbing substance per litre (Giles, 1974).

□ was calculated using the relationship: A= □*cl*

□ extinction coefficient, A absorbance at λ_{max}, c concentration of dye in mol/dm^3 and *l* path length.

The absorbance was obtained from the UV-Visible spectrum, the concentration of the dye solution for each dye in mol/dm^3 was calculated and the path length of the cuvette (1 cm) were all substituted in the formula above then □ was calculated.

3.7 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR was determined using Nujol Mull method. A small quantity of each sample (5mg) of finely grounded dye was placed unto the face of a KBr plate and a small drop of mineral oil (Nujol) was added and the second window placed on top. The mixture was then evenly distributed between the plates with a gentle circular rubbing motion. The sandwiched plate was then placed in the spectrometer and the spectrum acquired from 4000-600cm^{-1}. The KBr plates were thoroughly washed in ethanol, cleaned and polished after every procedure to prevent contamination.

3.8 Gas Chromatography Mass Spectrometry (GC/MS) Analysis

Each sample was dissolved in methanol at a concentration of 0.5µg/ml in a 1.5ml GC autosample vial. The sample was vaporized at a temperature of 280^{0}C and results obtained from the visual display unit.

3.9Determination of Surface Tension

The surface tension of all the dyes was determined using Du Nouytensiometer (also known as the ring tensiometer). 0.03g of the dye was dissolved in 10ml distilled water and then placed in the tensiometer with the platinum-iridium ring fully immersed in the dye solution. As the ring is pulled out of the solution in vertical direction, the dye solution attempts to keep contact with the ring until the solution breaks away from the ring and restores back to the normal flat liquid surface.

The surface tension (γ) in the ring tensiometer is given by the expression:

$$\gamma = \frac{F}{4\pi R} \cdot Cf$$

Where F = maximum force (at breaking), R = radius of the ring. Cf is a correction factor based on the shape of the liquid being held in the air, and is normally close to 1.0(Somasundaran, 2006). The Du Nouytensiometer that was used had already been calibrated to compensate for this factor in dilute water solutions, and thus gives a direct reading on the surface tension of the liquid (in mN/m).

3.10 Dyeing

This is the process of adding colour to textile products like fibre, yarn and fabrics. Dyeing is normally done in a special solution containing dyes and particular chemical material (Farlex, 2003)

3.10.1Dyeing Procedure

Each wool fabric was dyedwith good stirring, in a dye-bath of 2% depth. 0.01% sodium carbonate $Na_2CO_3$was added to raise the pH to 5, and at intervals of 3min, 1% acetic acid was added to drop the pH again to 3.5, all in 50:1 liquor at 80^0C. The dyeingwas done for 15, 30 and 45min for each dye. Using a pH meter, the pH of the dye-bath was consistently monitored to ensure that dyeing took place only within the isoelectric region of wool (3.5-5.0). Thereafter, each dyed wool fabric was rinsed and dried. This procedure is a little modification from the dyeing of wool with nonmetallized acid colours (Harry& Miles, 1944).

3.11Measurement of Exhaustion

This was determined by measuring the optical densities of the dye solution before and after dyeing, after making the necessary dilution with distilled water. The instrument was set at the wavelength of maximum absorption of the dyes. However, before taking the absorbance after dyeing, the dye solution was cooled to room temperature. The percentage exhaustion was estimated using the relationship:

Exhaustion (%) = $\frac{OD1-OD2}{OD1} \times 100$

Where OD1 and OD2 being the optical densities of the solution before and after dyeing respectively (Erik,1977).

3.12Determination of Fastness Properties

Colour fastness is a term used in the dyeing of textile materials, meaning resistance of the material's colour to fading and running(Oger, 1996).

3.12.1 Determination of Wash Fastness

The wool samples, 3×5cm were required; one specimen was placed between two pieces of cotton, and then sewn together each set around its four sides to form composites. 5.0g of sodium laurylsulphate was dissolved in 200mls hot distilled water and diluted to 1 litre which served as washing liquor. Each composite specimen was washed at 40 ± 2^{0}C for 30min and stirred in a beaker containing the wash liquor. The liquor was poured off, and specimens rinsed twice for 5min in cold distilled water, finally squeezed and the stitches on both long sides were removed. The composite was dried at room temperature and the colour change of the wool fabric assessed and the staining examined with a grey scale.

3.12.2 Determination of Light Fastness

An area of the dyed wool fabric 1×4.5cm was used; the side to be exposed to light from a xenon arc along with the eight dyed blue wool standards for 72 hours. The fastness was assessed by comparing the fading of the dyed wool with that of the standards visually, based on the fading behavior of standard dyed materials exposed alongside the sample under test, under the same condition.

3.12.3 Determination of Perspiration Fastness

Resistance of perspiration was assessed using two artificial perspiration solutions, one at pH of 5.5and the other at pH 8.0. After separate drying of the wool samples and the undyed fabrics, the change in colour of the wool and the staining of the undyed fabric were assessed with the grey scale.

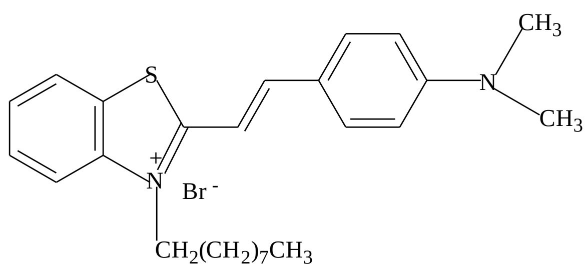
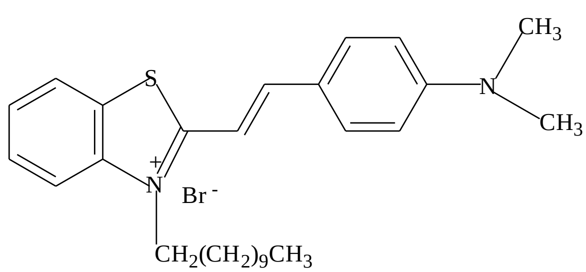
Solutions:

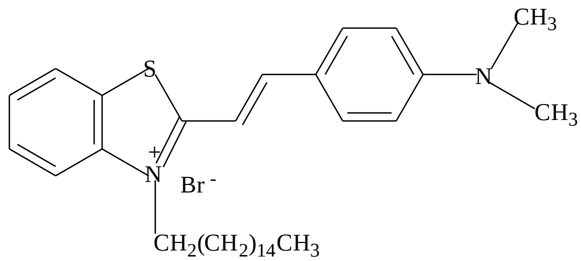
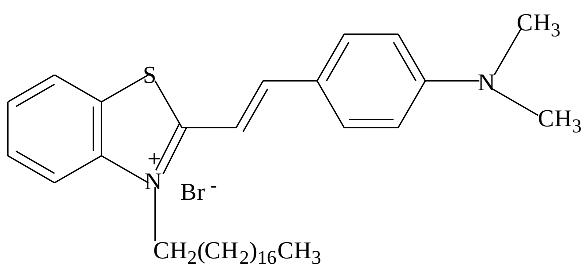
- Alkaline solution, freshly prepared, containing 0.5g histidinemonohydrochloride monohydrate, 5g sodium chloride and 2.5g disodium hydrogen orthophosphate ($Na_2HPO_4.H_2O$) per liter, brought to pH 8 with 0.1 M sodium hydroxide.
- Acid solution, freshly prepared, containing 0.5g histidinemonohydrochloride monohydrate, 5g sodium chloride and 2.2g sodium dihydrogen orthophosphate (NaH_2PO_4-$2H_2O$) per liter, brought to pH 5.5 with 0.1 M sodium hydroxide (Saville, 2002).

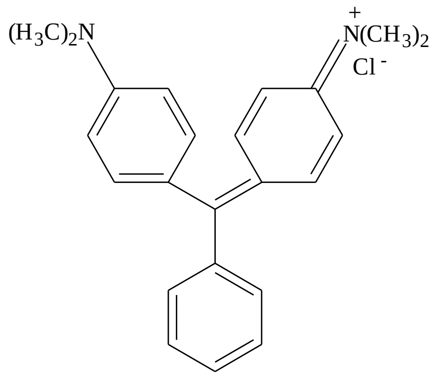
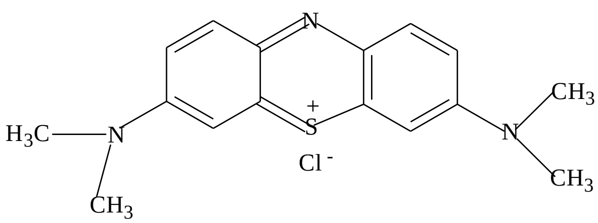
CHAPTER FOUR

4.0 RESULTS

Table 4.1: Dye Structures,Molecular Weight & Percentage Yield

Dye No.	Structures	Alkyl Halide	Cal.Mol. Wt (g/mol)	Exptal. Yield (%)
1.	 2-[4-(Dimethylamino)styryl]-N-nonylbenzothiazolium bromide	1-bromononane	487.53	33.79
2.	 2-[4-(Dimethylamino)styryl]-N-undecylbenzothiazolium bromide	1-bromoundecane	501.59	40.54

3.	 2-[4-(Dimethylamino)styryl]-N-hexadecylbenzothiazolium bromide	1-bromo hexadecane	585.72	50.06
4.	 2-[4-(Dimethylamino)styryl]-N-octadecylbenzothiazolium bromide	1-bromo octadecane	613.77	53.85

5.	 Malachite Green	-	364.91	-
6.	 Methylene Blue	-	319.85	-

Dyes 1 –4 are the synthesized dyes while dyes 5 and 6 are known commercial dyes; Malachite green and Methylene blue respectively.

Table 4.2: FTIRAbsorption Frequency of the Dyes

Dye No.	C-Br stretch (cm^{-1})	C-H bending (cm^{-1})	C-N stretch (cm^{-1})	C=C stretch (cm^{-1})	N-H stretch (cm^{-1})	C-Cl stretch (cm^{-1})
1	651.00	1165.04	1270.17, 1368.54	1448.59	3312.85	-
2	644.25	822.67, 952.87, 1291.39, 1364.68, 2831.60	1164.08	1526.71	3302.24	-
3	646.17	759.01, 1446.66, 2357.09, 2926.09	1269.20, 1364.68,	1535.39	3418.94	-
4	501.51	1362.75, 3077.53	1154.43, 1266.31	1539.25	3400.62	-
5	-	1370.47, 2930.93	1170.83	-	3430.51	821.70
6	-	1396.51, 2926.11	1138.04, 1343.46	1601.93	-	537.19

Table 4.3: GC/MS of the Dyes

Dye 2		Dye 3	
Fragments	m/z	Fragments	m/z
$C_3H_3^+$	39	$C_3H_3^+$	39
$C_5H_9^+$	69	$C_5H_9^+$	69
$C\text{-}Br^+$	77	$C\text{-}Br^+$	77
$C_3H_7COO^+$	89	$C_3H_7COO^+$	89
$C_8H_7NS^+$	139	$C_{11}H_{13}NS^+$	191
$M^+\text{-}C_{11}H_{22}O_2$	186	$M^+\text{-}C_{16}H_{32}O_2$	256
$M^+\text{-}C_{17}H_{16}N_2S$	279	$M^+\text{-}C_{17}H_{16}N_2S$	279

Table 4.4: Physical and UV-Visible Spectroscopic Properties

Dye No.	Cal.Mol. Wt (g/mol)	Melting point(^{0}C)	pH	εmax X10^4 (Lmol^{-1} cm^{-1})	Ethanol λmax (nm)	Methanol λmax (nm) a	Methanol + HClλmax (nm) b	Change in λmax (nm) b-a	Colour of Crystals
1	487.53	255	2.5	4.09	401.0	402.0	338.0	-64	Yellowish brown
2	515.59	261	3.3	6.59	400.5	402.0	338.5	-63.5	Yellowish brown
3	585.72	283	3.1	6.25	401.5	403.0	383.0	-20	Yellowish brown
4	613.77	301	3.0	6.24	401.5	406.0	397.0	-9	Yellowish brown
5	364.91	112	3.5	5.03	621.5	618.5	618.0	-0.5	Greenish blue
6	319.85	190	6.8	5.89	654.0	650.5	650.5	0	Blue powder

Table 4.5: Solubility Behaviour of the Dyes in Some Solvents

Dye No.	Water	Methanol	Ethanol	Acetone	Acetone + heat
1	Very soluble	Very soluble	Soluble	Sparingly soluble	Soluble
2	Very soluble	Very soluble	Soluble	Sparingly soluble	Soluble
3	Very soluble	Very soluble	Soluble	Sparingly soluble	Soluble
4	Very soluble	Very soluble	Soluble	Sparingly soluble	Soluble
5	Very soluble	Very soluble	Soluble	Soluble	-
6	Very soluble	Very soluble	Soluble	Soluble	-

Table 4.6: Surface Tension and Percentage Exhaustion of the Dyes

Dye No.	Concentration (%)	Surface Tension (mN/m)	Exhaustion (%)		
			15min	**30min**	**45min**
1	0.3	44.01	5.7	18.1	47.1
2	0.3	42.27	17.4	31.3	60.5
3	0.3	41.83	27.5	42.0	71.4
4	0.3	34.73	30.4	53.1	84.9
5	0.3	62.37	5.2	14.5	44.1
6	0.3	51.14	16.1	19.4	50.3

Table 4.7: Surface Tension of Some Industrial Surfactants

Concentration (%)	Surface Tension (mN/m)					
	SLS	**CPC**	**CTAB**	**CPB**	**TX-100**	**BRIJ 35**
0.21	47.5	41.2	49.6	32.2	31.9	45.6
0.32	49.2	42.3	50.3	33.0	32.5	48.3
0.44	50.2	45.6	52.3	34.2	33.6	49.6
0.58	51.2	48.2	55.3	35.2	34.2	51.2
0.68	55.6	49.2	56.8	35.6	34.5	55.6
0.72	56.5	51.6	59.0	36.6	34.8	56.3
0.8	57.5	58.6	65.2	41.0	35.1	58.9
1.5	55.9	60.3	66.3	41.9	35.4	59.3
2.5	53.7	67.5	67.5	42.9	36.1	61.2

Source: (Rashmi, 2011)

SLS – Sodium lauryl sulphate

CPC – Cetylpyridinium chloride

CTAB- Cetyltrimethylammonium bromide

CPB- Cetylpyridinium bromide

TX-100- Triton X-100

Brij 35- Ethoxylated fatty alcohol

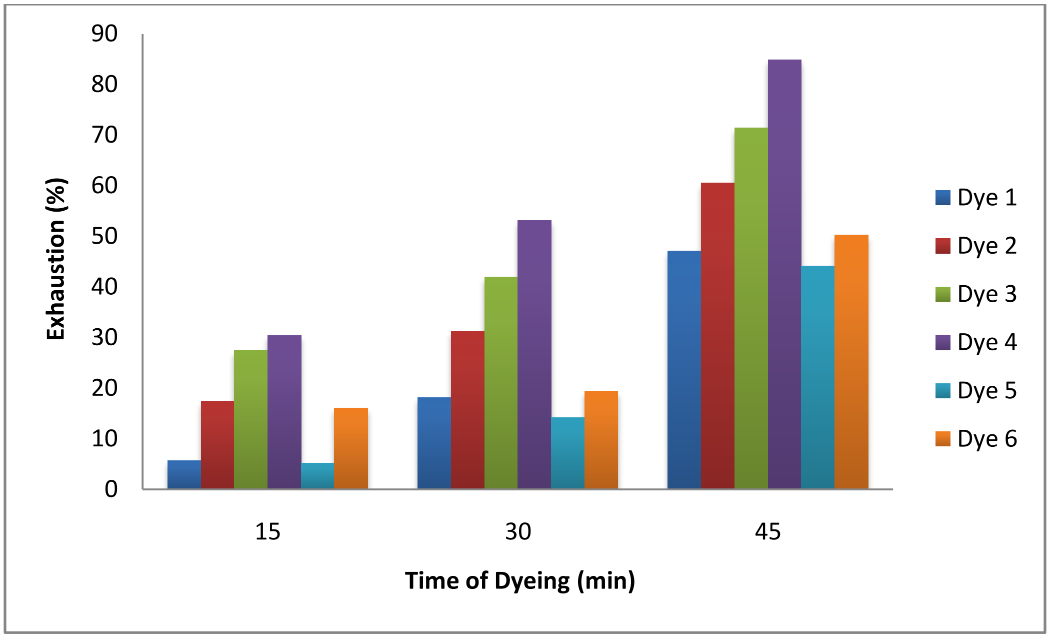


Figure 4.1: Histogram of Exhaustions (%) at 15, 30 and 45min of Dyeing

Table 4.8: Wash, Light and Perspiration Fastness of the Dyes

Dye No.	Wash Fastness		Light Fastness	Perspiration Fastness			
	Colour change	Staining		Acidic	Staining	Alkaline	Staining
1	3-4	3	3	3	3-4	3-4	3-4
2	3	3-4	4	3	3-4	3-4	3-4
3	4	4	4	3-4	3-4	3-4	3-4
4	3-4	3	3	4	4	3-4	3-4
5	3-4	3	4	3	3-4	4	4
6	3-4	3	3	3	3-4	3-4	3-4

CHAPTER FIVE

5.0 DISCUSSION OF RESULTS

5.1 Experimental Percentage Yield

The experimental percentage yield for all the synthesized dyes was calculated just immediately after the synthesis and the dyes completely dried. The actual yield was divided by the theoretical yield and then multiplied by 100. The experimental percentage yield for dyes 1, 2, 3 and 4 are33.79, 40.54, 50.06 and 53.85 respectively. The experimental percentage yield was found to increase as the molecular weight and the alkyl chain length of each dye increases.

5.2Fourier Transform Infrared Spectroscopy (FTIR)

The absorption of infrared radiation resulting from the vibration of atoms constituting the molecules showed the functional groups present in the molecules of compounds synthesized (Silvestein, 1997).Identification of an organic compound from a spectrum is a two-step process. The first step involves determining what functional groups are most likely present by examining the functional group frequency region which encompasses radiation from about 4000 to approximately 1500cm^{-1}. The second step is the finger print region from 1500 to 600cm^{-1} which is particularly useful because of small differences in the structure and constitution of a molecule resulting in the appearance and distribution of absorption peaks in the region (Roberts et al, 1985). Each of the synthesized dyes gave characteristic absorption peaks in the group frequency region and the relatively few peaks appeared at the finger print region as can be seen on the infra-red spectrum results in Table 4.2. C - Br stretching vibration bands appeared in the region 690 – 515cm^{-1} for dyes number 1 to 4. C-Cl stretching vibration bands appeared in the region 850 – 530cm^{-1} for the dyes numbers 5 and 6. =C - H Bending vibration bands appeared in the region 1000 - 675 cm^{-1}, C – N stretching vibration bands appeared in the region 1360 – 1080cm^{-1}, C = C stretching vibration bands of aromatic group appeared in the region 1600 –1400cm^{-1}, N – H stretching vibration bands appeared in the region 3500 – 3300cm^{-1} and –C – H bending vibration of alkanes group appeared in the region 1480 – 1350cm^{-1}. All of these functional groups corresponded to those found on the structures of the dyes.

5.3Gas Chromatography Mass Spectrometry (GC/MS)

The spectra showed the structures of the specimens in a suitable solvent (methanol) in this experiment. For the result to be interpreted this important point has to be taken into consideration: The molecular weight of the combined structure of each dye goes beyond the calibrated range of the GC/ MS machine, thus, the results are in segments, then segments have to be combined to have full structure of the samples (dyes). Furthermore, the structures obtained are a representation of the chemical composition of the samples under study, providing the basic points and fragments as above. The molecular weight of the dyes went beyond the calibrated range of the GC/MS machine, so, for each dye it broke the structure into two i.e. the parent structure (styryl part) and the alkyl chain.

5.3.1 GC/MS for Dye 2

The identified mass spectra with mass-to-charge ratio (m/z) are 39, 69, 77, 89, 139, 186 and 279 representing the corresponding positive charge fragments of $C_3H_3^+$, $C_5H_9^+$, $C\text{-}Br^+$, $C_3H_7COO^+$, $C_8H_7NS^+$, $M^+\text{-}C_{11}H_{22}O_2$ and $M^+\text{-}C_{17}H_{16}N_2S$ respectively. All the fragments from the styrylpart of the dyes are the same for dyes 1, 2, 3 and 4 because they have the same styrylstructure but theydiffer in the fragments ofthe alkyl chains which are different for each dye.

5.3.2 GC/MS for Dye 3

The same as dye 2, the identified mass-to-charge ratio (m/z) here are 39, 69, 77, 89, 191, 256 and 279 representing the corresponding positive charge fragments of $C_3H_3^+$, $C_5H_9^+$, $C\text{-}Br^+$, $C_3H_7COO^+$, $C_{11}H_{13}NS^+$, $M^+\text{-}C_{16}H_{32}O_2$ and $M^+\text{-}C_{17}H_{16}N_2S$ respectively.

The carboxylic fragments observed were due to the breakdown of the alkyl halide substituted fatty acid to their respective parent carboxylic acid.

5.4UV-Visible Spectroscopic Properties of the Dyes

The Ultraviolet-Visible absorption spectra of all the dyes were analysed in methanol and ethanol. The wavelengths of maximum absorption were mostly highest in methanol which is because methanol is more polar, and thus the molar extinction coefficient (□) was calculated using that of methanol. Subsequently, absorbance of each dye in methanol plus a drop of HCl was also analysed. The results of the Ultraviolet-visible spectra are summarized in Table 4.4.

Ultraviolet-visible absorption is indicative of electron transition between the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). All the dyes showed absorption in the visible region of (380 – 800nm). From the results on Table 4.4, dyes 1 – 4 absorbed maximally in methanol at 402nm, 402nm, 403nm and 406nm respectively while dyes 5 and 6 absorbed maximally at 618.5nm and 650.5nm respectively. Dyes 5 and 6 are much more bathochromic compared to dyes 1, 2, 3 and 4; this is because the degree of conjugation is higher in dyes 5 and 6. Dyes 1, 2, 3 and 4 showed very slight bathochromic shift progressively as the alkyl chain length increases. While absorbance of the dyes in ethanol have largely remain virtually the same for dyes 1, 2, 3 and 4 at 401nm, 400.5nm, 401.5nm and 401.5nm respectively, there was a bathochromic shift when compared to absorbance of dyes 5 and 6 in ethanol which absorbed at 621.5nm and 654nm respectively. Conclusively, the bathochromic shifts were due to an increase in polarity when the dyes were dissolved in methanol and also as conjugation increases in the individual dyes.

5.4.1 Effect of Acid on Visible Absorption Band (Halochromism)

The increase of maximum absorption wavelength in acidic medium shows a positive halochromism while a decrease will mean a negative halochromism. With a drop of HCl in methanol solutions of the dyes, dyes 1, 2, 3 and 4 exhibited negative halochromism as they absorbed at 402nm, 402nm, 403nm and 406 respectively in methanol and absorbed maximally at 338nm, 338.5nm, 383nm and 397nm respectively in acidic solution of methanol. This is indicating a hypsochromic shift (blue shift) of -64nm, -63.5nm, -20nm and -9nm respectively. However, Dye 5 showed a little negative halochromism of -0.5 from 618.5nm in methanol to 618nm in acidic solution of methanol while dye 6 showed no halochromism effect as it absorbed maximally at 650.5nm in both methanol and acidic solution of methanol.

5.4.2 Hyperchromism

Hyperchromicity is the increase of absorbance (optical density) of a material. The most famous example is the hyperchromicity of DNA that occurs when the DNA duplex is denatured. The UV absorption is increased when the two single DNA strands are being separated, either by heat or by addition of denaturant or by increasing the pH level. The opposite, a decrease of absorbance is called hypochromicity (Campbell, 2006).

Optical shifts in dyes can therefore be used to detect even a small amount of oligomers or polymers in the presence of relatively large amount of monomeric organic compounds (Colin, 1966). From Table 4.4, it could be seen that there was an increase in □max from 4.09×10^4 of dye 1 to 6.59 x 10^4, 6.25 x 10^4, 6.24 x 10^4($Lmol^{-1}cm^{-1}$) of dyes 2,3 and 4 respectively. From the knowledge above, this increase in optical shift could be attributed to the small change in the molecule of the dyes by the alkylhalides incorporated in the dyes.

5.5Solubility Behaviour of the Dyes

The solubility of the dyes was assessed using some common laboratory solvents such as water, methanol, ethanol and acetone. The results are shown on Table 4.5.

All the dyes were very soluble in water and methanol but were simply soluble in ethanol. Dyes 1-4 were however sparingly soluble in acetone but became soluble with a little application ofheat. Dyes 5 and 6 were also soluble in acetone. The order of decreasing solubility is water, methanol, ethanol and acetone. This could be attributed to decreasing polarity of the solvents.

5.6Surface Tension of the Dyes

A substance is referred to as a wetting agent if it lowers the surface tension of a liquid and thus allows it to spread more easily. To explain this better, two forces need to be taken into consideration:

- Cohesive forces: The forces exerted between the same molecules holding them together. If cohesive forces are strong, a liquid tends to form droplets on a surface.
- Adhesive forces: These are forces between liquid molecules and a surface. If adhesive forces are strong, a liquid tends to spread across a surface.

Lowering the surface tension lowers the energy required to spread drops on a film, thus, weakening the cohesive properties of the liquid and strengthening its adhesive properties (Petrucci, 2007).

Table 4.6 shows the surface tension of the dyes while Table 4.7 shows the surface tensionof some known industrial surfactants. It could be seen that there is a marked correlation between the surface tension of the synthesized dyes and of the surfactants at virtually the same concentration and all at room temperature. Dyes1 to 4 showed a marked reduction in the surface tension of water from 72.80 mN/m to 44.01mN/m, 42.27mN/m, 41.83mN/m and 34.73mN/m respectively while a relatively less reduction is noticed in those of dyes 5 and 6 which are 62.37mN/m and 51.14mN/m respectively. Comparing the dyes to the surfactants, the second row with 0.32% concentration on Table 4.7 is considered since the surface tension of the dyes was taken at 0.30% concentration.Dyes 1, 2 and 3 with values 44.01mN/m, 42.27mN/m and 41.83mN/m respectively showed similar values as surfactant CPC with surface tension of 42.30mN/m. Dye 4 (34.73mN/m) showed a similar value with surfactant CPB (33.00mN/m) while dyes 5 and 6 with 62.37mN/m and 51.14mN/m respectively, were not as effective. From above, lower surface tension was observed for all the synthesized dyes and this could be attributed to the fact that they are also surfactants. These dyes reduce significantly; the cohesive forces between water moleculesand thus increases the mobility of the dissolved dyes in water.

5.7Percentage Exhaustion of the Dyes

All dyeing took place at a temperature of 80 ^{0}C. From Table 4.6 it could be deduced that at 15min of dyeing, dyes 2, 3 and 4 showed better dye exhaustion of 17.4%, 27.5% and 30.4% respectively as against dyes 5 and 6 showing exhaustion of 5.2% and 16.1% respectively. The same trend was also observed in 30min of dyeing. Dyes 1, 2 and 3 showed exhaustion of 47.1%, 60.5% and 71.4% respectively at 45min of dyeing, dye 4 showed the best exhaustion of 84.9% while dyes 5 and 6 didn’t show as much exhaustion with % exhaustion of 44.1% and 50.3% respectively. From above, it could be deduced that if at 45min of dyeing, dyes 3and 4 showed exhaustions of 71.4% and84.9% respectively, then, dyes 5 and 6 would require more dyeing time to get such high % exhaustion exhibited by dyes 3 and 4.These high % exhaustions of the synthesized dyes as against the commercial dyes within all the dyeing times or durations could be attributed to increased mobility of the dissolved dye molecules in water due to a drop in the cohesive forcesbetween the water molecules (drop in surface tension) and hence high rate of absorption and adsorption from the dye-bath into the fibre. A levelled dyeing was observed for all thedyeings at all dyeing times.

5.8Wash Fastness

Colour fastness is a term used in the dyeing of textile materials, meaning resistance of the material's colour to fading or running (Oger, 1996). This is very important and there are several washing test that are applied according to the purpose for which the material is intended. Using ISO wash test No.3, it can be observed on Table 4.8 that the wash fastness is generally good without much stain on the adjacent white fabric. For instance, the rating is good for dyes 1, 2, 4, 5and 6 while it is very good for dye 3. Comparing dyes synthesized no. 1-4 to commercial dyes 5 and 6, one can say they have relatively equal rating of wash fastness which is generally good.

5.9Light Fastness

Light fastness is the property of a dye, pigment or paint that describes how resistant to fading it is when exposed to light. The fastness assessment can be done using daylight which takes a long period or by a xenon arc, which is the accelerated version of the test (Marsh, 1966). In the present studies, for achieving quick result, xenon arc lamp was used and the evaluation of result based on the eight blue wool standard 1-8.

Fading on exposure to light is undoubtedly the most complex of the reactions which dyes undergo on a substrate and much research has been devoted to discovering its causes. Energy in the form of light is absorbed by the dye and causes some of its molecules to become unstable, they are then in a so called excited state and, under these conditions, the dye may react with some surrounding materials such as oxygen in the air and sometimes with the fibre itself. It thus decomposes and loses its colour (Giles, 1974).

Table 4.8 shows dyes 1, 4 and 6 having the same light fastness rating of 3 which is moderate on a scale of 1-8 of the eight blue wool standards. Dyes 2, 3, and 5 also showed the same rating of 4 which is fair on the 8 blue wool standard. The general poor light fastness of these dyes can be attributed to the breakdown of basic dyes into much simpler form by sunlight or xenon arc light which was used in this test. The same phenomenon was reported in the photodecomposition of malachite green to benzophenone, 4-methylamino benzophenone, 4-dimethylaminobenzophenone and p-dimethylaminophenol by carbon arc light (Porter et al, 1970).

5.10Perspiration Fastness

Perspiration fastness test was done to assess the resistance of the dyed wool fabric to perspiration which could be acidic or alkaline. In the present study, the test was done in acidic and alkaline media and the results were assessed on change of shade using grey scale as well as the degree of staining of the adjacent white fabric using grey scale. The results are shown on Table 4.8.

The fastness to perspiration was generally good both in acidic and alkaline media for all the dyes with virtually all of them showing a change in shade of 3-4 rating on the grey scale in both acidic and alkaline media.

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

The synthesis and characterization of some amphiphilicsytryl dyes and their application on wool fabric was done successfully. The aim of the research was to synthesize amphiphilicstyryl dyes based on 2-methylbenzothiazolium salt of alkyl halides and apply on wool fabric. A total of four (4) different amphiphilicstyryl dyes were synthesized. Other objectives achieved weredetermination of the melting point and pH of the synthesized dyes, characterization of each of the dyes, determination of the surface tension of each dye and compared with two other commercial dyes (Malachite Green and Methylene Blue). Also, the surface tension of the synthesized dyes was compared with the surface tension of some industrial surfactants which showed that the dyes were able to drop the surface tension of water just as low as the industrial surfactants did. The dyes were applied onto 100% wool fabric, their percentage exhaustion determined and the synthesized dyes showed higher percentage exhaustion at a limited time of dyeing as compared to the commercial dyes.

The fastness properties were also analysed and it was found that the dyes exhibited poor light fastness but good wash and perspiration fastness.

6.2Conclusions

This research work has been able to achieve its objectives in terms of synthesis of the intermediates and then condensing them into the desired dyes. The dyes were characterized using FT-IR, Mass spectrometry and UV-Visible spectroscopyto determine their chemical and physical properties. Furthermore, the surface tension of the dyes was assessed with dyes 1,2,3 and 4 having 44.01,42.27,41.83 and 34.73mN/mrespectively and compared to two commercial dyes, dyes 5 and 6 having 62.37 and 51.14mN/m respectively. They were all applied on to wool fabric, their dyeing properties and exhaustion analysed for three different dyeing durations. All the synthesized dyes 1, 2, 3 and 4 showed good leveled dyeing and good exhaustions of 47.1,60.5,71.4 and 84.9 % respectively while dyes 5 and 6 had 44.1 and 50.3% at 45min of dyeing and same temperature (80^0C). The high % exhaustion of the synthesized dyes could be attributed to increased diffusion of the dye moleculesinto the fibre as a result of the reduced surface tension of water. The fastness properties of the dyes especially washing and perspiration were found to be good on the substrate.

6.3Recommendations

For further research on this thesis, it is recommended that more work should be done on the following areas:

1. ^{1}HNMR, ^{13}C NMR, COSY, DEPT should be carried out to further confirm the structures of the synthesized dyes.
2. Subsequent work on this research could be done to improve the light fastness properties of the dyes.

REFERENCES

Abrahat, E.N. (1977). Colour Chemistry.*Dyes and their Intermediates*. Edward AQrnold (Publishers) Ltd; London pp. 1-7, 13-17.

Allen, R.L.M. (1971). Colour chemistry.*Studies in Modern Chemistry*.Imperial Chemical Industries LTD (ICI), London. Pp. 5-25.

Attowood, D, and Florence, A.T. (1985).*Surfactant Systems*, Chapman and Hall, London and New York, Ch. 1.pp 1140

Basic Dyes/Cationic Dyes/properties of Basic Dyes/dyeing of Acrylic with Basic Dyes. Retrieved July 27, 2015 from textilelearner.blogspot.com.

Bird, C. L. and Harris, M.P. (1964).*The dyeing of Cellulose acetate with disperse dyes, VI – affinities*. Journal of the Society of Dyers and Colourist. Pp. 600-604.

Campbell, M. K., Farrell, S.O. (2006). Biochemistry, *Cengage learning*. Published by Brooks Cole 7th ed. United States, pp 249.

Choudhury, A.K.R. (2006).Man-made fibres.*Textile Preparation and Dyeing,*Science Publishers, Enfield, NH, U.S.A. Handbook of Textile Fibres: Vol II. Man-Made Fibres pp. 643

Colin, S. P., Vishnaic, W., Pearman, J. P.T. (1966). Biology and Exploration of Mars: *Report of a study held under the auspices of the Space science board.* Published by National Academy of Science National Research Council, Washington D.C, pp 402.

Deo, H.T. and Dasa, B.K. (1999).Colour Gamut produced by applying mixtures of natural dyes on de-inked mechanical pulp. *Journal of Society of Dyers and Colourist* (JSDC), 115:224.

Eitel, K. Rau, E. and Westphal, J. (1984). Colour Chemistry: Synthesis, Properties and Application of Dyes.*Review of Progress in Colouration*.Vol.14:119.

Erik, K (1977) in Venkataraman, K (ed); The analytical chemistry of synthetic dyes. Wiley, New York.Pp 524.

Farlex. (2003). *Dyeing*. Free online dictionary by Farlex Inc. Retrieved May 16, 2016 from http://en.wikipedia.org/wiki/Dyeing

Garland, C.W., Nibler, W.J. and Shoemaker, D.P. (2003). Physical Chemistry:*Experiments in Physical Chemistry, 7th ed*., McGraw Hill, NewYork.Pp 145.

Giles, C.H. (1974). Laboratory Course in Dyeing.*The Society of Dyers and Colourist:* Bradford. Pp. 36 – 37.

Harley, D. (1979).Lost Country Life New York, Pantheon Books Hewitt and Mitchell.*Journal of Chemical Society* 91,1251.

Harry, F. C. and Miles, A., D. (1944). *Dyeing of Wool with Nonmetallized Acid Colours.* Wilmington, Del., Assignors to E.I du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware No Drawing, U.S. Patent Serial No. 419,716.

Johnson, A. (1989). The Theory of Colouration of Textiles; *Society of Dyers and Colourist:* Bradford. Ch. 6 pp 428

Leeder, J. D. (1984). Structure of wool fibre.In*Wool -Nature's Wonder Fibre.* Ocean Groove, Victoria: Australasian Textile Publishers. Pp. 8-12.

Lewis, D.M. (1990). The Colouration of Wool and other Keratin fibres.*Proceedings of the 8th International Wool Textile Research Conference,* Handbook of Textile and Industrial Dyeing,Christchurch.Part 1:4,1.

Marsh, J.T. (1966).An Introduction to Textile Finishing.Chapman and Hall, London 2nd Ed .pp 38.

Meggos, H. (1995). Food Colours: an international perspective. *Themanufacturing Confectioner*.Pp. 59-65.

Oger, B. (1996).Fastness to Light and Washing of Direct Dyes for Cellulosic Textiles. Studies in Conservation, Maney Publishing, London. Vol. 41, No. 3 (1996), pp. 129 Retrieved July 28, 2015 from http://en.wikipedia.org/wiki/Colourfastness

Petrucci, F., Ralph, H., et al. (2007). General Chemistry: *Principles and Modern Applications.* Upper Saddle River, NJ: Prentice Hall. Retrieved September 13, 2015 from http://chemwiki/Wettingagent

Porter, J.J., Spears, Jr and Scott, B. (1970).The Photodecomposition of Malachite Green.*Textile Chemist & Colourist*, vol. 2 Issue 11, pp 33-37.

Rashmi, M. K. (2011).PhD Thesis.*Kinetic studies of some Esters and Amides in the presence of micelles*. Raipur (CG), India. Ch. 2. pp. 92.

Rippon, J. A. (1992) The Structure of Wool. *Wool Dyeing*, Lewis, D.M. (Ed.), Chapter 1 Bradford (UK): Society of Dyers and Colourists.

Roberts, R.M., Gilbert, J.C., Rodewald, L. B. and Wingrove, A.S. (1985).*Modern Experimental Organic Chemistry,* 4th Ed, Philadelphia; Saunders College Publishing pp 184.

Rosen, M.J. and Kunjappu, J.T (2012).*Surfactants and Interfacial Phenomena* (4th ed.). Hoboken, New Jersey: John Wiley & Sons. pp. 1.ISBN 1-118-22902-9.

Salager, J. (2002). FIRP Booklet.*Surfactant Types and Uses*.Second Edition, Merida, Venezuela.Pp 129-139.

Saville, B.P. (2002). Physical Testing of Textile. Textile Institute, Wood Head Publishing Limited Cambridge, England pp 244-255

Shore, J. (1986).Indian Journal of Fibre and Textile Research.*Colour Removal in Textile effluents*.New Delhi Vol. 29 pp. 239

Shore, J. (1990).*Colourant and Auxilliaries* Vol.1 Colourants Edited by John Shore BTTG, Shirley, Manchester, England. pp.1

Silverstein, R.M. and Webster, F.X. (1997).*Spectrometric Identification of organic compound.* John Wiley and Sons 6th Ed. PP 12-20.

Simon, G. (2000). *Mauve: How one man invented a colour that changed the world.* Faber and Faber.ISBN 0.393-02005-3.

Somasundaran P, ed. (CRC Press), (2006). *Encyclopedia of Surface and Colloid Science.*,2nd Ed. New York. PP. 391-394.

Thompson, R.H. (1971). The Biochemistry of Natural Pigments.*Naturally occurring quinines*. 2nd Ed. London Academic Press, London, PP. 734

Tordor, D., Aleksey, V., Stefka, K. and Juan, J. (2010). Colouration Technology.*Society of Dyers and Colourist*, Vol. 126 issue 2.

Venkataraman, K. (1971).Chemistry and Application of Dyes.*The Chemistry of synthetic dyes*. London Academic press, Vol 5 PP 3-5.

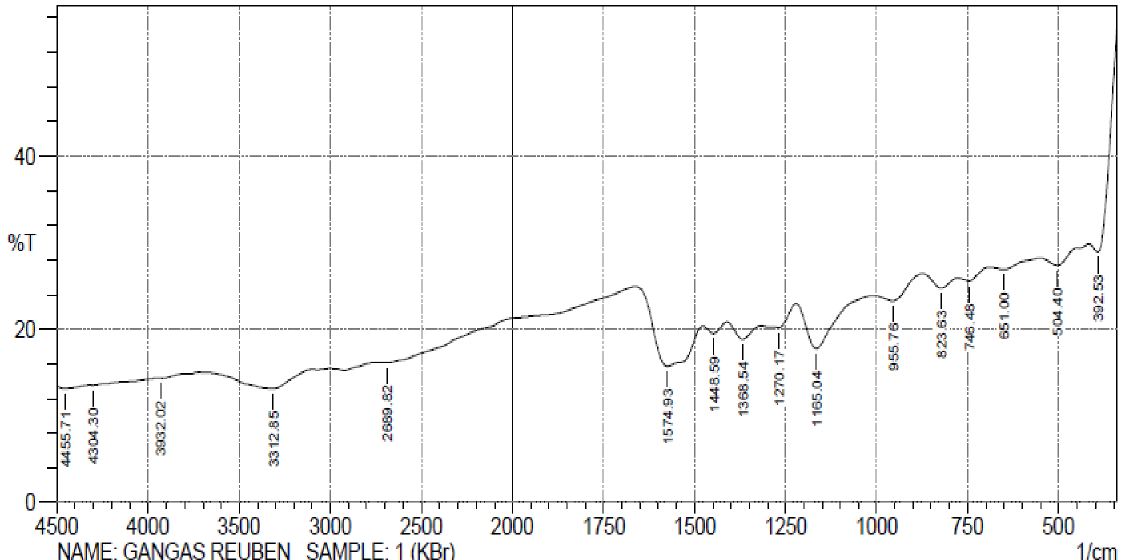
Zollinger, H. (1987). Synthesis, properties and applications of Organic Dyes and Pigments, *Colour Chemistry*,New York, USA: VCH Publishers;3rd edWeinheim, pp 92-103

Zollinger, H. (2003). Color Chemistry. *Synthesis, Properties and Applications of Organic Dyes and Pigments*, 3rd ed. Weinheim: Wiley-VCH. Retrieved July 28, 2015 from http://en.wikipedia.org/wiki/Dye

SHIMADZU

FTIR ANALYSIS RESULT NARICT,ZARIA

FTIR- 8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER



	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	392.53	28.928	9.08	417.6	339.48	35.549	4.98
2	504.4	27.37	1.402	551.66	450.39	55.814	1.077
3	651	26.895	0.567	690.54	551.66	77.926	0.466
4	746.48	25.589	0.78	777.34	690.54	50.492	0.485
5	823.63	24.756	1.403	874.75	777.34	57.802	1.09
6	955.76	23.272	1.582	1007.84	874.75	81.621	1.718
7	1165.04	17.772	5.432	1220.98	1007.84	143.254	8.843
8	1270.17	20.208	1.46	1317.43	1220.98	65.652	1.572
9	1368.54	18.83	1.805	1410.98	1317.43	65.927	1.769
10	1448.59	19.517	1.041	1476.56	1410.98	45.767	0.755
11	1574.93	15.731	7.051	1662.69	1476.56	135.719	15.264
12	2689.82	16.106	0.571	2753.48	1662.69	773.831	13.245
13	3312.85	13.145	2.052	3656.19	3100.67	473.184	17.96
14	3932.02	14.324	0.004	3941.67	3929.13	10.579	0.001
15	4304.3	13.527	0.053	4322.62	3954.2	315.65	0.34
16	4455.71	13.113	0.344	4500.08	4323.58	154.621	1.042