Chapter I
Introduction

INTRODUCTION

1.1 DYES

A dye or dyestuff may be defined as a coloured organic compound which is used for imparting colour to a substrate. Usually, the substrate is the textile fibre or fibre or fabric. In addition to these, there are other substrates like as paper, leather, plastics, wax, cosmetic base, etc. the non-toxic dyes are used for colouring the food stuffs and drugs. The colour sensitive dyes are used in colour photography.

A dye is a coloured substance whereas all coloured substances are not dyes. Thus a dye should fix itself on the substrate to impart it a permanent coloured appearance. For example, azo benzene is not a dye even if it is red in colour, as it cannot be attached to substrate. However, Congo red is a dye because it can be applied on cotton and retained by it. Thus, the dyes should have certain groups which help the attachment of the fibre.

PIGMENT

It is the coloured substance which is insoluble in water or other solvents. It means that the application of dye and pigment will be different. A dye is applied in the form of a solution, while the pigment is applied in the form of a paste in a drying oil, in which it is insoluble. There are some colourless compounds which are used as the optical brighteners. They are also known as the white dyes. They have the special property of absorbing ultraviolet light and re-emitting the visible light so that the fabric appears bright.

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NOMENCLATURE

The chemical names of the dyes have been complex. Therefore trade names are now used. The letters following the name of the dye reveals the primary colour and its tone. These letters are derived from German words.

The numbers reveal the intensity of tone.

G= Gleb = yellow;   e.g. indanthrene yellow GK

R = Rot = red;   e.g. Acridine orange R

B = blue = blue;   e.g. Rhoda mine B

Similarly, other letters reveal the type of dye, fastness property, temperature of dyeing etc.

D = Direct dye for cotton

S = acid dye (German, Sauer = acid)

F = fastness to specific agencies

L = light fastness

C = cold brand reactive dye

H = hot brand reactive dye

IK, IN = dyeing in cold (kalt) and normal temperature.

PHOTOCHROMISM

Some dyes change colour reversibly upon exposure to light. This effect is known as photochromism (or phototropism) and is considered as a defect in textile dyes.

Textile Fibres – Types and Structures

Although dyes are used to colour substrates other than textile fibres, e.g. paper and plastics, textiles are still the principal outlet for dyes. Textiles fibres may be classified conveniently into three types.

1. Natural

2. Semi-synthetic,

3. Synthetic.

The early textile industry was based entirely on nature fibres. There were of animal origin (e.g. wool, silk, hair, etc.) and vegetable origin (e.g., cotton, linen, hemp, jute, flax, etc.)[1-5]. Even though the natural dyes had been totally replaced by superior synthetic dyes by the end of the nineteenth century, natural reigned supreme well into the twentieth century.

Early Theories

Chemists have long been intrigued by the relationship between the colour of a dye and its chemical constitution: to trace the unravelling of this relationship we have to go back over 100 years to the period when the dyestuffs industry was in its infancy.

Although investigations into the structure of the natural dye, alizarin and indigo, had begun, the only colored compound whose structure was known as p-benzoquinone.

It was during this period that Grebe and Liebermann, in 1867, undertook the first study of the known dyes destroyed the colour instantly and from this observation they inferred that dyes were chemically unsaturated compounds.

It was from a study of compounds like azo benzene and p-benzoquinone that led Witt, in 1876, to formulate his celebrated theory which proposed that dyes consist of unsaturated groups, the chromophores, and salt forming groups, the auxochromes.

Three years later Nietzki's stated that increasing the molecular weight of a dye by the introduction of substituent's such as methyl, ethyl, phenyl, ethoxy or bromo produced a bathochromic shift. Though Nietzki's Rule initially proved useful, its utility decreased as many exceptions were subsequently discovered.

The next major development was made by Armstrong who, in 1887, propounded the 'quinonid theory' of colour. He argued that only compounds which can be written in a quinonid form are colored. Since at that time the majority of dyes fell into this category the quinonid theory proved popular for many years[6].

The importance of conjugation was first realized by Hewitt and Mitchell in 1907. From a study of azo dyes, these workers observed that the bathochromicity of a dye was directly relates to the length of the conjugated chain of atoms in the chromogen- the longer the conjugated chain, the more bathochromic the dye – and this important

Observation became known as Hewitt's Rule. Although there are exceptions to this rule, as Broker and others later discovered, it remains one of the most valuable rules of thumb in colour chemistry.

Modern Theories

All the early theories had one thing on common -- they were qualitative. A completely new approach was required which would not only provide a new insight into colour structure relationships but would also allow quantitative assessments to be made. The Einstein-Planck quantum theory, which states that energy is not continuous but can only have certain discrete (quantized) values, constituted such a breakthrough. It was from this fundamental new theory that the two modern theories is that the former is based on the concept of bonding valence electron pairs being localized between specific atoms in a molecule, whereas the latter pictures electrons as being distributed among a set of molecular orbital's of discrete energies.

Using quantum theory, Schrodinger, in 1926, derived his new famous wave equation. Theoretically, solution of this equation enables the behaviour of atoms and molecules to be calculated without recourse to experimentation[7-11]. Unfortunately, the equation can only be solved exactly for one-electron systems such as a hydrogen atom or the hydrogen molecule ion, H_2^+. For polyelectronic systems the mathematical difficulties, due primarily to electron-electron interactions, are insurmountable at present.

VB theory was pioneered by Heitler, London, Pauling and Slater shortly after publication of the Schrodinger equation. Since it originated from a chemical point of view qualitative VB theory is similar to the resonance theory proposed by Bury. In contrast, quantitative VB theory is rarely used nowadays because it is unwieldy and for large molecules, it is virtually impossible to apply. Indeed, quantitative VB has never been applied to dyestuff.

Dyes as Ligand

It is also found that dyes act as Ligand and the studies on metallo dyes may throw much light on their characteristic properties. Hence, in addition to the studies of Schiff base complexes. Studies are also conducted on dyes and the same synthetic methodology is adopted to prepare their corresponding metallo dye.

1.2 SYNTHESIS AND CHARACTERIZATION OF METALLO DYES

From the olden days itself colour has been used for all manner of decorations. Colored paintings decorated the walls of caves in France, the earliest of which date back to c.a.30 000 years ago. Perhaps the most famous cave paintings are those of Lascaux in southwest France and Altamira in North West Spain. These date to around 17 000 years ago and the paints used for these creations were derived from natural earth pigments such as ochre and zinc oxides. Interestingly it has also become clear to obtain the exact colour of paint; the people of Lascaux must have heated the natural pigments to temperatures of more than 1000C.

Thousands of years, later natural dyes and pigments were still being used to dye clay pots and textiles. Amongst the most popular vegetable dyes were wood, saffron, madder and indigo, and examples of dyes from animal sources included cochineal of Tyrant purple. However, some of these dyes were difficult to prepare and gave poor colour value.

By the seventeenth century, the rise in scientific activity soon resulted in some well-known name applying them to explaining the mechanisms of dyeing and colour. Robert Boyle wrote Experimental considerations de colour bus in 1665 and William petty wrote an apparatus to the history of the common practices of colour included JR Glauber and Isaac Newton. It was not only the science of dyeing but also the aesthetics that were being pondered. In 1974, the Venetian dyer Gloachin Burain in his Tratto dellorate wrote from this fine art you can truly say that it is the soirit, which brings to life everything it, touches.

By the eighteenth century, France led the way in developing the theory of dyeing. Charles Francois Dufay de cistern classified dyeing as grant taint or petint. And the regulations did not permit grant teint dyers to have possession of the lesser the products required for the more economical 'petit teint' Du Fay also was to consider dyeing to be a chemical and not a physical phenomenon. Du Fay was followed as the guru of European dyeing by Jean Hellot (1685-1765) and Pierre Joseph Macquer (1718-1784). Helot (1685-1765) and Pierre Joseph Macquer (1718-1784).Hellot had propounded theories based on imprisonment of dyes in the pores of the fibre. Macquer realized this was not the whole story and developed du Fay's physical chemistry approach and suggested that dyeing was because of particular affinity between dye and fibre. Helot had written a definitive treatise on wool dyeing.

Macquer a similar work on silk and it was a third Frenchman, Le pileur who wrote "Traite Sur part de la teinture sur fil ET cotton".

During the nineteenth and twentieth centuries, there were many landmark discoveries in the world of chemistry, with the turning point for dyes coming in 1856. This is when an 18-year student, Hoffmann at the royal college of chemistry attempted, in his spare time, to synthetic dye, mauveine. This promising student then immediately gave up his studies and started up a factory to produce mauveine. His discovery changed history and over the next few decades immense number of new synthesized[12, 13]. This activity, mainly by British and German chemists, gave birth to the synthetic organic chemical industry (including pharmaceuticals) that we know today. This period may well have been just as world change as the first industrial Revolution of the late eighteenth and early nineteenth centuries.

Natural dye colours.

Dye	Colour
Cochineal	Scarlet
Fustic	Yellow
Logwood	Purple-Black
Madder	Red

Key developments in dye History

Year	Achievement
1825	Faraday Discovered Benzene

1828	Wohler synthesized urea (as organic chemical) from Inorganic Elements.
1845	Hoffman recognized the significance of coal tar as a rich Source for organic chemicals (Aniline purple) – the first synthetic dye .
1862	The First azo dye, Bismarck Brown, was made by Martius at Roberts, Dale and co.
1865	Kekule elucidated the structure of benzene.
1880	Bayer synthesized indigo.
1893	The first sulphur dyes were produced by Vidal.

THE DYEING PROCESS

Dyeing is not a purely physical process like painting or other colouring process involving the physical application of pigments. There are difficulties encountered in controlling the physicochemical changes that occur during dyeing, in order to maximize factors such as colour, yield, level dyeing, penetration, colourfastness etc. therefore, there is a vast sub-technology of specialty of chemical auxiliaries used in preparation for dyeing and in the process itself, such as additives and after treatments[14-21]. It is not simple impregnation of the textile fibre with the dye that occurs in the dying process. A fibre as result of the chemical reaction between them takes up a dye. A many dyes for the textiles are water- soluble and like simple electrolytes, their molecules split into positively and negatively charged ions. The uptake of dye by the fibre will depend on the nature and its chemical constituents. The strongest dye-fibre attachment is that of a covalent bond with another important interaction where the dye ion and the fibre have opposite charges. In all dying

processes Vanderwaals forces, hydrogen bonds and hydrophobic interactions are also involved. The combined strength of the molecular interactions is referrer to as the affinity of the dye for the substrate. The substantively of the dye is less specific term but can indicate the level of exhaustion. It is the attraction between the substrate and a dye under precise conditions where the dye is selectively attracted from the medium by the substrate.

Classes of Dyes

The appropriate dye class for the fibre in question must be used, along with specific dyeing conditions, in order to gain an optimum result. Some of the key steps in the development of dye synthesis are shown below. The ten major dye classes involve acid, metal complex, mordant, direct, vat, sculpture, reactive, basic, disperse and azo dyes. Some of these can be used to dye the same fibred type but varying conditions would be required. For example, acid, metal complex, mordent and dyes can all be used to dye wool. However, many dyes are preferred for a certain dyeing process, for examples disperse dyes for polyester fibres.
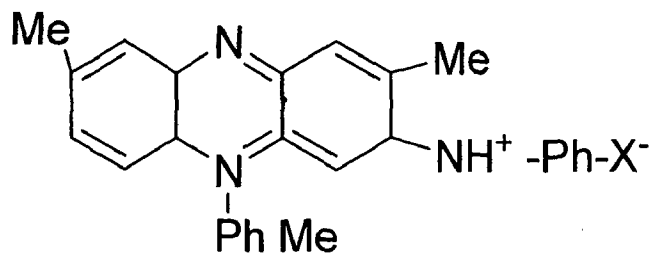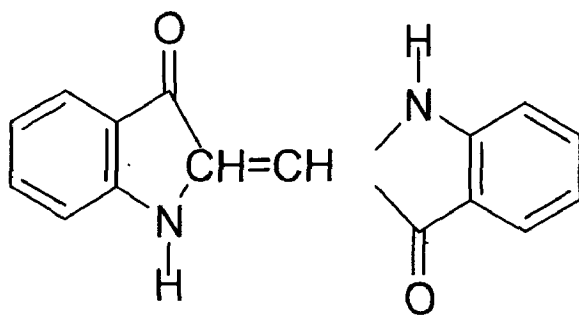
Mauveline
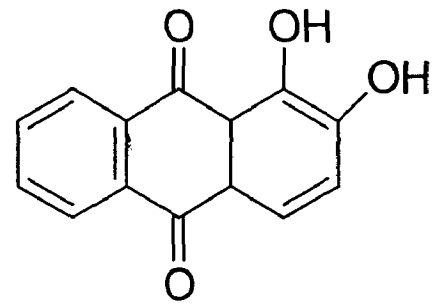
Alizarin
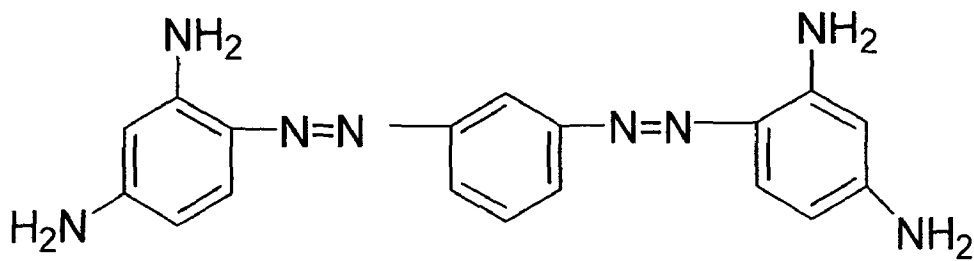
Bismark Brown

Indigo

Dying Theories

A successful dyeing process can be conveniently broken down into three principal stages: the diffusion of dye in the bath to the surface of the fibre; the adsorption of dye at the surface of the fibred and the diffusion of dye from the fibre surface to its interior. The theories below are a brief coverage of the dye adsorption stage[22].

It seems sensible to use percentage exhaustion as a measure of the substantively of a dye for a particular textile material (equation -1), where D is the amount of dye.

% Equation= D on fibre at dyeing end ×100/ D applied at dyeing start

SR = [D] on fibre at equilibrium / [D] in solution at equilibrium.

Because, as we have seen many dyeing processes are irreversible it is only possible to study the uptake of dye from the dye bath on those, which are reversible, even though the actual process is relevant to all dyeing systems.

It is very easy to be convinced by the Langmuir approach when dealing with acid dyes (negatively charged dye ions) on wool or nylon (with positively charged groups under acid conditions) or with basic dyes (positively charged) on acrylic (with negatively charged groups on the fibre). This concept of dye sites has been widely used to explain and predict dying behaviour. Dyeing is a very complex and large subject.

Decolonization and Degradation Kinetics

Dyestuffs widely employed in a variety of industries, particularly that of textile coloration. Effluent from dye house is not particularly toxic, but a large quantity of coloured wastewater is produced. As many dyeing factories now have insufficient space to house conventional biological wastewater treatment systems, alternative methods of decolorizing effluent are required.

Previous studies have shown that chemical coagulation and carbon adsorption are available for decolorizing textile wastewater, but these methods generate sludge bulking problems and have very high operating costs. UV photo-oxidation, combined with hydrogen peroxide or ozone dosing, have been found to be an effective treatment technology for colour removal. Haung et al, reported that ozonation treatment is more effective than the UV/ peroxide process, with the low yields using UV/peroxide (less than 50%. 1 hr treatment) probably using due to the short penetration of UV radiation blocked by the azo dye. Work then carried out by Fung and Tissue reported that decolonization of dyeing wastewater was enhanced when ultrasound was applied to the UV / peroxide treatment. Among the various dye classes, reactive dyes have lower rates of fixation in fabric and therefore contribute more significantly to the colour in textile wastewater.

The dosage of peroxide is the key parameter for the decolonization of dyeing wastewater, having direct on the treatment performance. Literature reports have stated that some oxidation processes can be enhanced by the use of ultrasonification to oxidize organic contaminants in water ultrasound may increase the uptake and

transfer rates. The hydroxyl radicals may react with the organic substrate via several mechanisms, most of which involve consumption of oxygen.

Properties of Anthraquinone Dyes

Anthraquinone derivatives have completed with monoazo and diazo compounds for use as disperse dyes. Anthraquinone dyes are capable of covering the gamut from greenish-yellow to bluish-green, but are particularly important for the production of bright red to blue dyes. Alkyl amino Anthraquinone in which the alkyl group is substituted or unsubstituted have been extensively used as dyes for synthetic fibres. Short chain alkyl (C_1-C_6) derivatives and 1-arylaminoanthraquinone have been reported to be more suitable for the colouration of polyester fibres. A range of substituted groups in the aryl amino residues has been described in the patent literature and these dyes have been introduced as industrial colourants. The influence of various electron donors and acceptor substituent's in the aryl amino residues has been assessed, and the dyeing and fastness properties of these dyes on polyester have been investigated. Colour and constitution relationships in dyes derived from 1, 8-dihydroxy-4, 5-dinitroanthraquinone have also been reported in the literature.

1.3 COLOUR AND DYES

Colour sensation

Colour always played an important role in the life of human beings. Dyes and pigments have been important articles of commerce since time immemorial. Let us understand how we get a sensation of colour.

White light is made of seven different colours. These are violet, indigo, blue, green, yellow, orange and red having wavelengths between 400nm and 750 nm. When white light falls on a substance,

It may be.....

Totally reflected,

Partially reflected,

Totally absorbed.

When the white light is totally reflected, the substance appears white and when it is very absorbed, the substance appears to be black. When a part of the incident light is absorbed and the rest reflected the colour of the substance is the colour of the reflected light. If only a single band is absorbed, the colour of the substance is the complementary colour of the absorbed light band. Relationship between the wavelengths of the light band absorbed and the visible colour of the substance is given in the table;

Wavelength Absorbed (nm)	Colour Abs Absorbed	Visible Colour (complementary)
400-435	Violet	Yellow-green
435-480	Blue	Yellow
480-490	Green-blue	Orange
490-500	Blue-green	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-blue
605-750	Red	Blue-green

If only one of the bands is reflected and all the rest are absorbed, the colour of the substance is that of the reflected band[23, 24]. For example, if a substance absorbs all the bands except blue, it will appear blue,

Thus the substance may appear blue.....

(i)   Either because it absorbs only the yellow band (wavelength 580-595 nm) of the incident white light and reflects all the rest,

(ii)   On the other hand, because it absorbs all the bands except blue (wavelength 435-480 nm) which it reflects.

In practice, substances do not reflect only one band of wavelengths but reflect a mixture of them,

For example,

Malachite green reflects in addition to green light, small amounts of red, blue and violet.

Dyes and dyeing,

Coloured substances used for colouring various fabrics are called dyes. Not all coloured substances, however, are dyes. Requisites of a true dye are...

(i)   It must have a suitable colour.

(ii)   It must be able to attach itself to the material from solution or to be capable of being fixed on it.

(iii)   When fixed it must be fast to light and washing. For this, it must be resistant to the action of water, acids and alkalis, particularly the latter due to the alkaline nature of washing soda and washing soap.

Previously, dyes were obtained from animal and vegetable sources. Today most of the available dyes are synthetic dyes prepared from aromatic compounds.

The mechanism of dyeing differs with the nature of the material whether it is protein, cellulose or synthetic fibre. Dyeing of wool and silk were once considered a chemical process. Herin the acidic or basic groups in a dye combined with basic or acidic groups in the protein. At present, it is believed that acidic or basic groups in the dye help in the initial adsorption of the dye on the surface of the fibre. This is followed by solution and diffusion of the dye into the fibre[25-29].

1.4 Colour and constitution

Grebe and Liebermann (1868) observed it that organic colouring mater on reduction gave colourless product, which regained original colour on oxidation[30].

The relationship between colour and constitution was however, pointed out for the first time in 1876 by the German chemist Otto Witt. He put forward his chromophores auxochromes theory of colour and constitution.

According to him......

(i)   Colour usually appeared in an organic compound when it contained certain unsaturated groups which should more appropriately be called groups with multiple bonds.........

Witt called these groups with multiple bonds as chromophores. A few important chromophores are,

$$-N\underset{O}{\overset{O}{\diagdown}}$$
Nitro

$$-N=N-$$
Azo
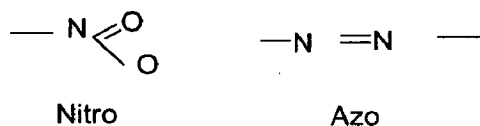
(ii)   The compound containing the chromophores group is called chromogen. It has been noticed that chromogen containing only one chromophores are usually yellow. Depth of the colour increases with the number of the chromophores.

A single C=C group, as in ethylene ($CH_2=CH_2$), does not produce any colour.

For example,

$CH_2-(CH=CH)_6-CH_3$ is yellow in colour.

(iii)   Certain groups, which could not cause any colour effects in the absence of chromophores groups, do have an important effect on the development of colour when

(iv)   They are introduced into a compound containing a chromophores group. Witt described such groups as auxochromes or colour augmenters or deepeners.
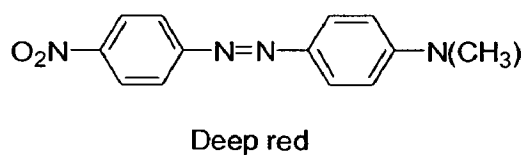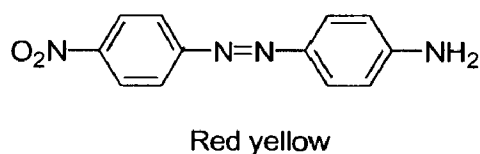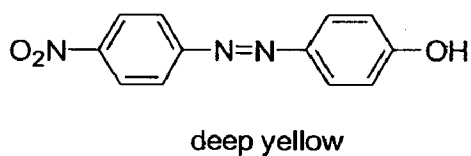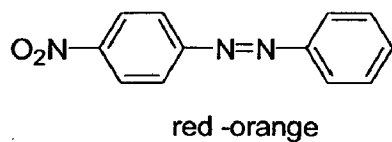
Some important auxochromes are…

-OH   ;   -OR   ;   -NH$_2$

Hydroxyl   Alkoxy   Amino
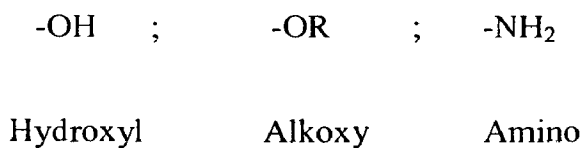
Auxochromes are salt- forming groups and perform two functions;

(a)   They deepen the colour of the chromogen.

(b)   Their presence is necessary to make the chromogen a dye.

An interesting example of the effect of auxochromes groups may be noted with the following compounds;

$$O_2N\text{---}\langle\bigcirc\rangle\text{---}N{=}N\text{---}\langle\bigcirc\rangle$$

red -orange

$$O_2N\text{---}\langle\bigcirc\rangle\text{---}N{=}N\text{---}\langle\bigcirc\rangle\text{---}OH$$

deep yellow

$$O_2N\text{---}\langle\bigcirc\rangle\text{---}N{=}N\text{---}\langle\bigcirc\rangle\text{---}NH_2$$

Red yellow

$$O_2N\text{---}\langle\bigcirc\rangle\text{---}N{=}N\text{---}\langle\bigcirc\rangle\text{---}N(CH_3)$$

Deep red

The sulphonic and carboxyl acid groups possess little auxochromes properties but their presence makes chromogen a dye presence of sulphonic acid group makes the dyes soluble in water. Due to the presence of carboxyl acid group several dyes form lakes[31-39].

From practical experience, several empirical observations have been made.

For example,

In the case of phenols, it has been observed that

(a)   Salt of phenols are more strongly coloured than free phenols from which they have been made.

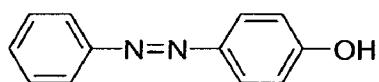(b)   Auxochromes do not affect the colour when present in the Meta position to the chromophores.

Thus according to Witt's theory of colour and constitution

Chromogen

Is chromophore –bearing compound and the dye can be considered to be equivalent to a chromogen containing an auxochromes?
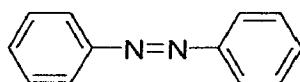
For example,

(i) In p- hydroxyazobenzene,

p-Hydroxyazobenzene
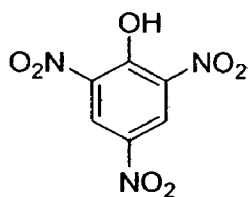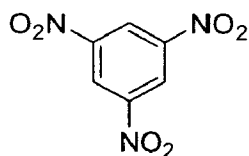
a bright red dye

(ii) In azobenzene

Azobenzene

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Is the chromogen, N=N, is the chromophores and −OH is an auxochromes.

Similarly, in picric acid (a yellow dye) tri nitrobenzene is the chromogen containing three NO2 groups (chromophores).

Picric acid (dye)

Trinitrobenzene
chromogen

Some other terms introduced later are called bathochromic and hypsochromic groups. The bathochromic groups bring about deepening of colour in a dye whereas the hypo chromic groups bring about the lightening of colour. The term deepening of colour in dye chemistry is being used for the following changes in colour;

Yellow → orange→ red→ purple→ blue→ green →black.

This is exactly the order of visible complementary colours of the colour absorbed with increase in the wavelength of the absorbed light. Thus, we have seen that longer the wavelength of the absorbed light, the deeper will be the colour of the dye.

Since visible colour is a complementary colour of the absorbed band, bathochromic groups (which bring about deepening of colour) will help absorption of longer wavelengths i.e., the colour absorbed will be one lying near the lower or red end of the column. The bathochromic groups are, therefore, said to have a red shift.

On the other hand, hypo chromic groups (which bring about lightening of colour) will help absorption of shorter wavelength i.e. The colour absorbed will be one lying near the upper or blue end of the colon. The hypo chromic groups are, therefore, said to hare a blue shift.

1.5 Valence bond theory of colour.

According to the valence bond theory, the electron pairs of a molecule in its ground state are in a state of oscillation. When this molecule is placed in the path of a beam of light, it absorbs a photon of appropriate energy and gets excited and the amplitude of oscillation of its electron pair is increased[40]. The wavelength of the photon absorbed depends on the energy difference between the excited and ground states of the molecule. The smaller difference between the two states, the longer is the wavelength of the photon absorbed. It further states that.....

(i) The energies of both the ground and excited states are lowered as a result of resonance among the charged structures

(ii) Charged structures contribute more to the excited state than the ground state.

(iii) The larger the number of electrons involved in resonance, the smaller is the energy difference between the excited state and the ground state.

Ethylene is colourless but a polygene is coloured[41-47]. In fact, intensity of colour increases as the number of double bonds in a molecule increases. Let us understand this fact in the light of valence bond theory.

Ethylene may be regarded as a resonance hybrid of (I) and (II)

$$+ \quad -$$

$$CH_2{=}CH_2 \quad CH_2{-}CH_2$$

(I)   (II)
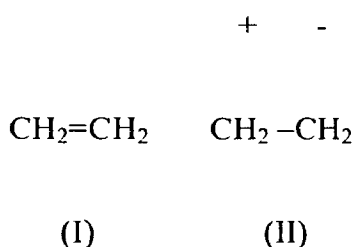
Ground state of ethylene is represented predominantly by (I) and the excited state by (II). The energy difference between the two beings very large, the energy of the photon required to excite ethylene is very high, i.e. its wavelength is very short. The colour produced by absorption of these very short wavelengths will be very light.

In 1, 3-butadinene and 1, 3, 5-hexatriene there is greater contribution of charged structures to the resonance hybrid due to extended conjugation in these molecules. Since large number of electrons are involved in resonance, the energy difference between the

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ground and excited states is smaller and longer wavelength of the photon is required to excite the molecule,

Ex Λ_{max} CH2= CH2

(175 nm)

$CH_2=CH-CH=CH_2$

(217 nm)

$CH_2=CH-CH=CH-CH=CH_2$

(258 nm)

The longer the wavelength of the photon required for excitation, the greater the tendency for colour.

Presence of groups with inductive and resonance effects at the ends of a conjugated system will extend the conjugation as well as increase the contribution of charged structures to the resonance hybrid. Because of it, the wavelengths of the photons required produce sensation of colour and become longer as illustrated by the following examples:

Benzene is a resonance hybrid of two Kekule structures and a small amount of charged canonical structures (dipolar ions)
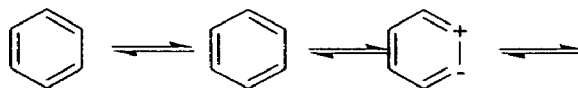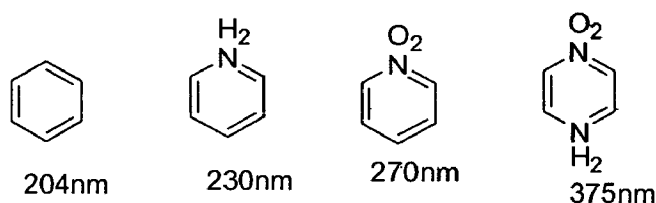

Thus benzene itself is chromophores. Presence of certain groups like NH_2,

t

NO$_2$, etc, Increases the wavelength of the photon required for excitation of the molecule

e.g....

204nm   230nm   270nm   375nm

Resonance in a conjugated system is maximum, when the system is completely planar or almost so. If resonance is inhibited due to some steric effect, the depth of colour, which depends on resonance, will diminish and the compound may even become colourless.

The valence bond theory of colour and constitution has now been modified by the molecular orbital theory which considers molecule as a whole for its contribution to the colour and it has been possible to theoretically calculate the ^ max of a dye from its structure. The detailed discussion of the molecular orbital theory of relationship of colour with constitution is outside the scope of the book.

1.6 CLASSIFICATION OF DYES.

Dyes are classified according to their chemical constitution or their application to the fibre. The chemist prefers to classify dyes according to its structure but the dyer is mainly concerned with the reaction of dye towards the fibre being dyed. Based on these two ways of classification, different forms of dyes have been described below;

(i)   **Direct or substantive dyes.**

A compound is classified as a direct dye if it can be applied directly by immersing the animal and vegetable fibres or cloth in a hot solution of the dye in water.

Dyes suitable for dyeing animal fibres directly are subdivided into acid dyes and basic dyes.

(a)   Acid dyes are sodium salts of sulphonic acids and nitro phenols and can readily dye animal fibres (wool and silk) but not vegetable fibres. Wool and silk are dyed by dipping in the solution of acid dyes after acidifying with sulphuric or acetic acid.

(b)   Basic dyes are the salts of colour bases with hydrochlorides acid or zinc chloride. Basic dyes can dye animal fibres directly and vegetable fibres after these have been mordant with tannin. Basic dyes are mostly used for dyeing silk and cotton.

(ii)   Mordant or adjective dyes. A mordant is any substance, which can be fixed to the fibre, and which can be dyed later on, commonly used mordents are hydroxides or basic salts of chromium, aluminium or iron. Tannic acid is used as mordent with basic dyes.

(iii)   The fabric is mordant by dipping in the solution of the metallic salt or tannin and then dipped into the solution of the dye when coloured lake is obtained which being insoluble is fast to washing. Alizarin and other Anthraquinone dyes are applied in this way.

(iv)   Ingrain dyes. These are dyes produced in the fibre itself during the process of dyeing. For example, a piece of cloth may be soaked in an alkaline solution of β-napthol

(v)   And then dipped into a diazonoum salt solution. Coupling takes place to produce an azo- dye in and on the fibre.

(vi)   Vat dyes. These are water insoluble coloured compounds, which can be reduced to colourless (leuco) derivatives, which are soluble in alkali and readily are deoxidized to the dye. After treatment in an alkaline bath, the cloth is subjected to air oxidation, which causes a return to the insoluble coloured form. Vat dyes in the leuco condition dye both animal and vegetable fibres directly but they are mostly used for cotton fibres. Indigo is an outstanding example of vat dye[48-51].

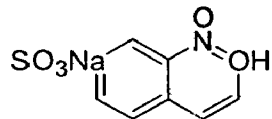**Classification of dyes according to chemical structure**

(i)   **Nitro and nitroso dyes.**

These dyes are among the oldest synthetic dyes but are not important commercially.

Example

$$O_2N \underset{\text{Picric acid}}{\overset{\overset{\displaystyle H}{\underset{|}{O}}}{\bigcirc}} NO_2$$
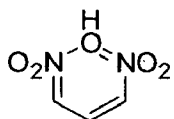
Picric acid
Nitrodye

$$SO_3Na \overset{\overset{\displaystyle O}{\underset{\|}{N}}}{\bigcirc} OH$$

Napthol greenB
Nitroso dye

(ii)   Triphenylmethane dyes.

Triphenylmethane dyes have brilliant colours but they fade with washing and on exposure to light .these are used for colouring paper and typewriter ribbons.

These dyes are obtained by introducing-NH_2,-NR_2, or-OH, groups (auxochromes). Into the Triphenylmethane, ring (chromogen) when the colourless leuco compound is obtained. The leuco compound on oxidation gives the corresponding tertiary alcohol called the colour base (colourless benzenoid compound). This in the presence of acid readily changes to the quinonid dye due to salt formation[52-66].
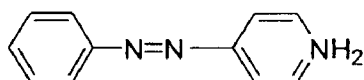
29

Example.
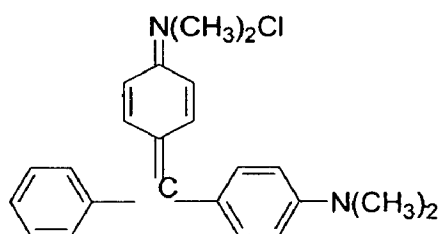
Malachite green.

Malachite green

(iii) Azo dyes.

All azo dyes have the same chromophores –N=N- , the azo group, but the auxochromes may be different. Common auxochromes are $-NH_2$,$-NR_2$, and $-OH$ groups

Example

p-Aminoazobenzene

1.7 Scope of the present investigation

Azo compounds and their complexes with transition metal have attracted much attention, in part because of their physico chemical properties and applications in many important areas. They are highly coloured and have been studied widely because of their excellent thermal and optical properties in applications such as optical data storage, photo switching, non-linear optics and photochromic materials, dyes, chemical analysis and pharmaceuticals

The present investigation describes the synthesis, spectroscopic characterization, of Amaranth, Methylene blue, Remazol red B and Golden yellow HER and its lead, cobalt, nickel and copper complexes. The ultrasonic technique has been used for studying the solute –solvent interactions in a number of systems, including organic low melting solids complex formation. The propagation of ultrasonic waves and the measurement of velocity and absorption in inorganic, organic and organo-metallic binary systems have been used to access the molecular interactions in these systems. The variation of ultrasonic velocity and other acoustic parameters with temperature has been studied using a diffraction technique. Several workers have used ultrasonic velocity measurements for studying ion-solvent interactions. Several workers to determine the solute-solvent interactions in aqueous solutions have used ultrasound. A number of workers have reported the ultrasonic studies on different types of dyes and its complexes. According to Eyring et al. molecules in liquid state are so loosely packed as to leave some free space in between them. This free space and its dependent properties are related to the molecular

structure and many show some interesting features about the interaction, which may occur among liquids.

This work deals with ultrasonic velocity and density measurements of solutions of various dyes namely Amaranth, Methylene blue, Remazol red B and Golden yellow HER and its metal complexes at various concentrations by keeping temperature constant. The dependence of these parameters is found to be useful in understanding the nature and extent of interaction between molecules. Physico-chemical properties can be understood among the interacting components from ultrasonic velocity measurements and it can be coupled with other experimental data such as density and viscosity to calculate various acoustical parameters such as adiabatic compressibility, free length, free volume and internal pressure, which are useful in understanding the molecular interactions of a binary and ternary mixtures.

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