The chemical principles of coloration

Introduction

Although dyeing is a chemical operation, most of the simpler processes may be carried out on the small scale by sensible people who have very little chemical knowledge. Nevertheless, following a set of instructions in ignorance of the reasons behind their formulation is unlikely to lead to the deeper understanding of textile coloration that is needed by professional people in the coloration industry. Consequently this chapter has been included for the benefit of those with little working knowledge of chemistry. It contains a brief description of some of the chemical principles involved in coloration processes, as a supplement to more rigorous chemical studies that may be pursued elsewhere.

Modern chemistry is based on the belief that all matter is built from a combination of exceedingly minute particles (*atoms*) of the various chemical elements. Many different elements are found in nature, each possessing characteristic properties; the atoms of any one element are all chemically identical. Atoms combine together to form *molecules* of chemical compounds.

A single atom consists of a central core or *nucleus*, which contains numbers of positively charged particles (*protons*) and uncharged particles (*neutrons*), together accounting for almost all the mass of the atom. Numbers of very small negatively charged particles or *electrons* circulate around the nucleus in fixed orbits or 'shells', each corresponding to a certain level of energy of the electrons it holds. The number of electrons in an atom is equal to the number of protons in its nucleus, so that the atom is electrically neutral. The total number of electrons within a given atom is a characteristic of the element from which it originates.

The ways in which atoms of different elements combine to give molecules determine both the physical properties of the molecule and its chemical reactions with other molecules. These facts are as significant for the reaction of a dye molecule with a fibre molecule as they are for any other reaction. Dyeing reactions are also influenced by additives used in a dyebath and therefore some preliminary explanations of their chemical nature will be relevant for the later chapters of this book.

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Electrolytes

An *electrolyte* is a substance that, because of its chemical nature, conducts electricity in solution. The addition of electrolyte to the dyebath is frequently recommended in textile coloration, common salt being the most often used; its function is discussed below.

The chemical name for common salt is sodium chloride, to signify that it is made up of sodium atoms and chlorine atoms. The reaction of a sodium atom with a chlorine atom is shown in Figure 3.1. In both atoms the shell (i.e. the energy level) closest to the nucleus contains only two electrons: this is the maximum number of electrons that can be accommodated in that orbit. (Hydrogen and helium atoms, the two smallest atoms, have only a single shell, and are never associated with more than two electrons each.) The next is filled by eight electrons. Although strictly speaking an oversimplification, it is convenient to assume from now on that eight electrons is the maximum number that can be accommodated in an outer shell. The significant feature that governs the way in which different atoms combine is the number of electrons in the outermost shell.

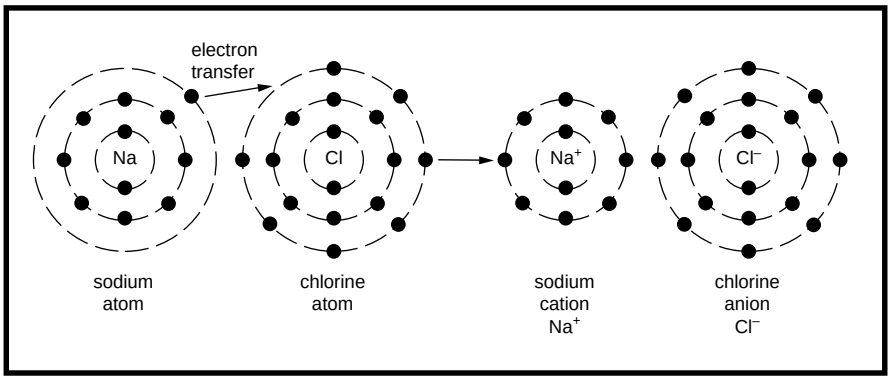

Figure 3.1 *The reaction between sodium and chlorine atoms*

The sodium atom has a single electron in the outermost shell, while the chlorine atom has seven. In the reaction between the two, one electron is transferred from the sodium atom (leaving the outermost shell with a complete octet of electrons) to the chlorine atom (making up an octet in its outermost shell). Since the atoms started out electrically neutral, the loss of one electron by sodium leaves the atom positively charged (it is now a positive *ion*, or *cation*) and the gain of one electron leaves the chlorine atom negatively charged (a negative ion or *anion*). The sodium chloride crystal is thus made up of equal numbers of sodium ions and chloride ions. Since opposite charges attract each other, there is a strong electrostatic attraction between the two kinds of ion, which makes sodium chloride a very stable compound.

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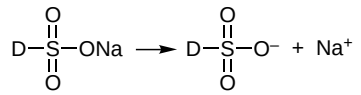
Electrolytes are compounds made up of ions, and are often referred to as ionic compounds. When simple electrolytes of this kind dissolve in water they split up (*dissociate*) into separate ions. It is for this reason that they will allow an electric current to pass through the water (an electric current may be regarded as a flow of negatively charged particles round a circuit). There are many simple electrolytes and the two most commonly used in coloration are sodium chloride (NaCl) and sodium sulphate (Na_2SO_4), the latter being known as Glauber's salt.

Water-soluble dyes are also electrolytes, but in this case the coloured part of the molecule is very large and usually an anion, whilst the cation, usually a sodium ion, is very small by comparison. In fact water-soluble dye molecules are all synthesised to contain at least one group of atoms known to confer water solubility on the dye molecule through the formation of ions. Very often this is the sulphonic acid group, —SO_3H, or the carboxylic acid group, —COOH, both of which form sodium salts which dissociate in water; Scheme 3.1, in which D represents the coloured part of the dye molecule, illustrates the dissociation of a sulphonate.



Scheme 3.1

Role of electrolyte in the dyebath

When a fibre is immersed in water, a negative electrostatic charge develops on its surface. This charge repels any dye anions present in the solution, so that the fibre cannot be dyed satisfactorily. If, however, the dyebath also contains an electrolyte such as sodium chloride or sodium sulphate, a diffuse layer of positive sodium ions forms at the fibre surface, neutralising its charge. The dye ions are then able to approach sufficiently closely to the fibre for the inherent attractive forces between the dye and the fibre to operate.

The covalent bond

A covalent bond differs from the bonding in a crystal of an ionic compound in that there is no transfer of electrons from one atom to another. Instead two atoms share two electrons, each atom providing one electron of the pair. Figure 3.2 represents the covalent bond in the simple inorganic molecule of chlorine (Cl_2) as an example. (In this diagram some of the electrons are represented by black circles and some by white. You should not be misled by this convention, which is introduced in the interests of comprehensibility: all electrons are alike, irrespective of the associated nucleus.)

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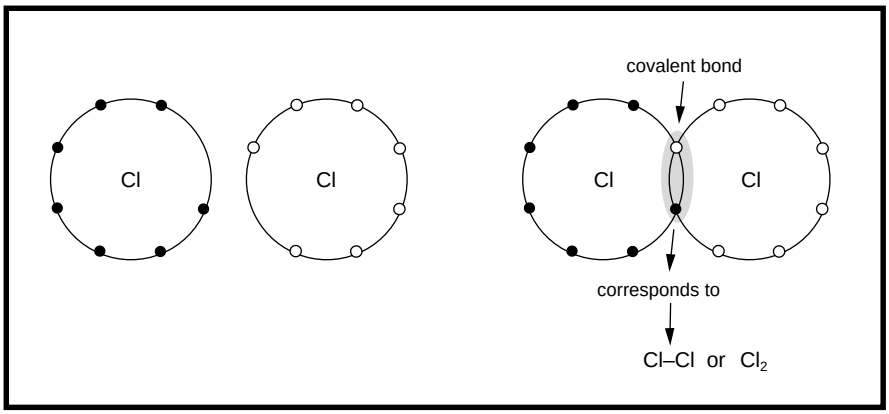

Figure 3.2 *The formation of the chlorine molecule*

The covalent bond is the most stable chemical linkage to operate between a dye and a fibre molecule, because the co-valently bound dye is an actual part of the fibre molecule. In effect the combination of the dye and fibre through a covalent bond is equivalent to forming a coloured derivative of the fibre molecule.

The structures of all organic molecules, including dye molecules, are based on carbon atoms linked by covalent bonds. The structure of carbon atoms acts as a scaffolding upon which other groups of atoms may be placed to provide the molecule with particular properties, which in the case of a dye may be a group of atoms that produce or modify the colour.

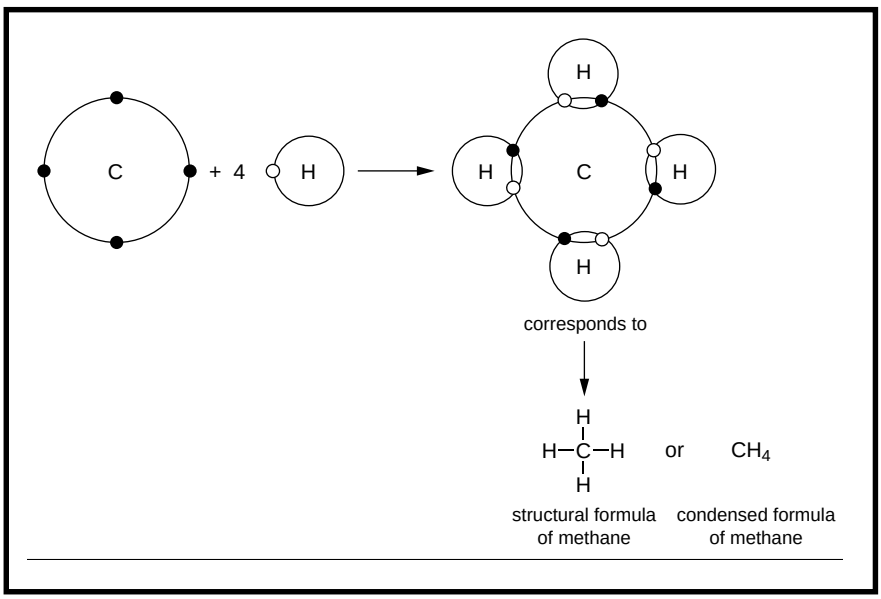

Figure 3.3 *The formation of methane (outer electron shells only are shown);*
● *electron from carbon,* ○ *electron from hydrogen*

The simplest organic compound is methane, CH_4 (Figure 3.3). In methane there are four covalent bonds from the carbon atom, one to each hydrogen atom, arranged in the form of a symmetrical tetrahedron with the carbon atom in the middle (Figure 3.4). The carbon atom thus has eight electrons in the outer shell and each hydrogen atom two. The electronic requirements of

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both carbon and hydrogen atoms are thus satisfied and the compound is very stable. Such bonds do not dissociate in water, and most covalent compounds are insoluble in water and do not conduct electricity. Covalent bonds are the most stable of all chemical bonds and they cannot be broken easily. The discovery of dyes that form covalent linkages with cellulosic fibres is the most recent major discovery in the field of textile dyes.

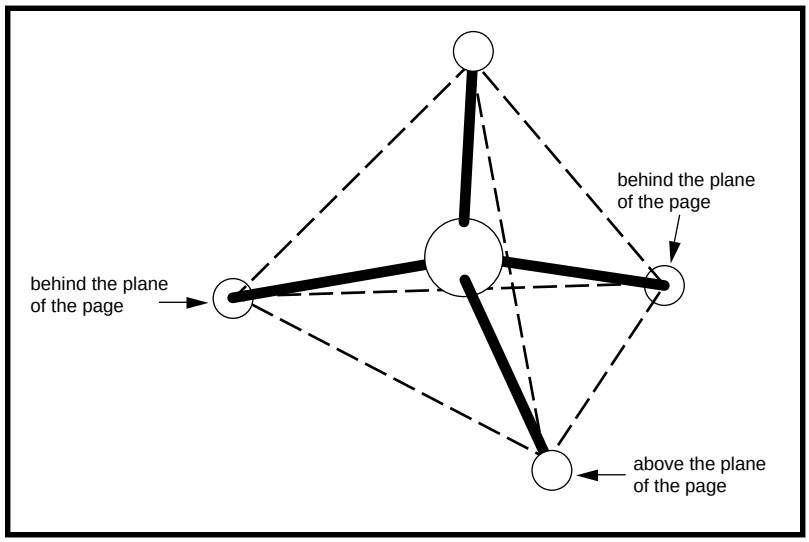
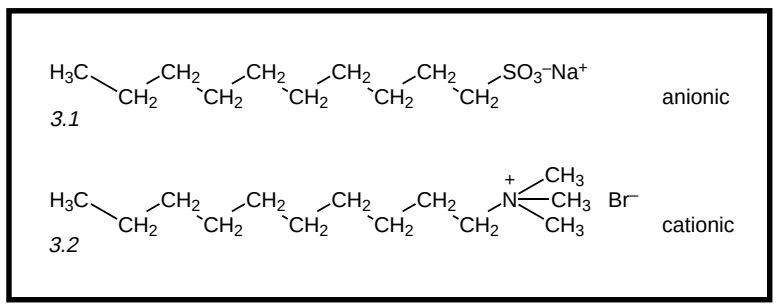


Figure 3.4 *The tetrahedral molecule of methane, CH_4*

Most organic molecules are more complicated than methane. For example, there are long chains of covalently linked carbon atoms in the molecules of the surface-active agents used as detergents for washing-off fabric or as dispersing agents for dispersing the sparingly soluble colorants in the dyeing of synthetic fibres; *3.1* and *3.2* are typical structures. They are good examples of how the properties of compounds may be modified by the introduction of specific chemical groups. The ionic group in the detergent molecule imparts water solubility to an otherwise insoluble chain of carbon atoms.



Carbon chains are often represented in the zig-zag fashion shown in Figure 3.5 (overleaf), which is a two-dimensional representation of the tetrahedral arrangement of the four bonds of the carbon atoms in space (Figure 3.4). Because the angles between the single bonds of a carbon atom are fixed, a chain of carbon atoms cannot lie flat in a straight line. Instead it is forced into a zig-zag arrangement. The arrangement of carbon atoms in space is important because it governs the three-

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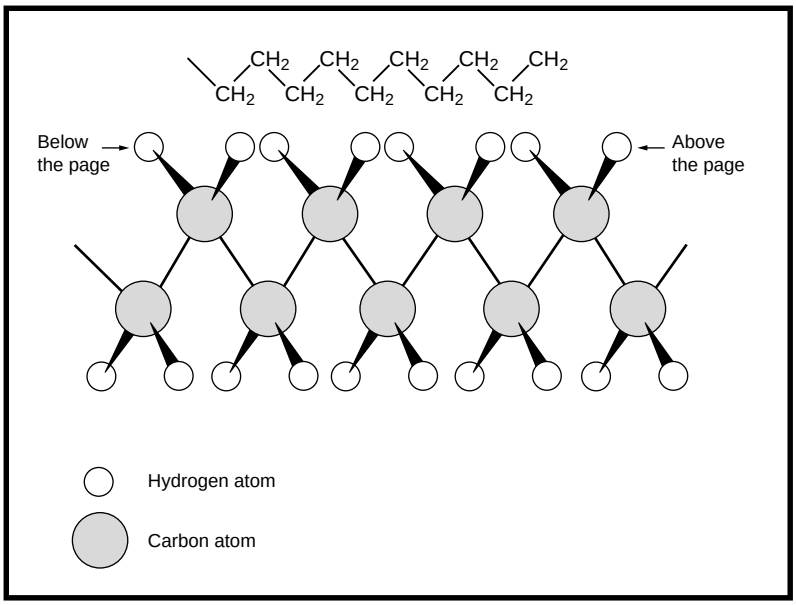

Figure 3.5 *The zig-zag conformation of a hydrocarbon chain*

dimensional shapes of organic molecules, which may in part determine their physical and chemical properties.

Fibres contain long chains of carbon atoms linked by single covalent bonds; each atom is able to rotate relative to its neighbour and this imparts great flexibility to the chain, a factor which is particularly relevant to the design of synthetic fibres (Chapter 4). For example, it can lead to the formation of long straight chains, as in polypropylene, or of chains with a helical configuration, like the keratin molecules of wool. With other more chunky molecules such as those of glucose or dyes, the configuration of the bonds of the constituent atoms gives a more bulky three-dimensional shape to the molecule.

Molecules containing only carbon and hydrogen atoms (*hydrocarbons*) are chemically unreactive and insoluble in water, but when ionic groups are added to large hydrocarbon molecules in order to make them soluble in the manner indicated above they may form a special kind of solution called a *colloidal electrolyte*. Like other ionic compounds, such a molecule dissociates in water, but the large ions do not remain separate. They cluster together to form special loosely knit spherical structures called *micelles*, in which the insoluble hydrocarbon chains (the 'tails') tend to associate together and form a hydrophobic (water-repelling) environment with the ionic 'heads' on the outer surface, keeping the micelle dissolved. Water-insoluble matter such as oil may dissolve within the micelle, suspended in the solution. This is the principle upon which detergents act. Similarly the micelles can engulf small colorant particles and keep them in a stable form of dispersion (Figure 3.6).

Methane is the simplest of a series of compounds called *alkanes*. They all have similar chemical properties, and differ only in the number and arrangement of the carbon atoms joined

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together by covalent bonds. After methane, the next member of the group is ethane, with two carbon atoms (*3.3*, overleaf), then propane with three (*3.4*). A series of compounds built up in this way is referred to as a *homologous series*. There are many such compounds in the alkane series, all with the general formula C_nH_{2n+2}, where n is the number of carbon atoms in the molecule. All the atoms of the compounds in this series are joined by single covalent bonds, and they are referred to as *saturated* compounds.

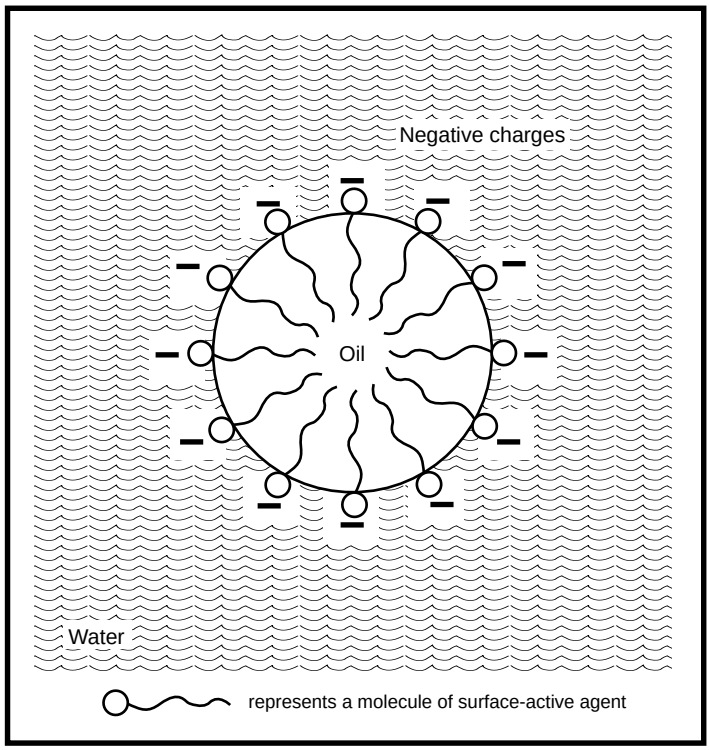

Figure 3.6 *Micelle formation by an anionic surface-active agent*

This distinguishes them from similar compounds in which some double bonds exist between the constituent atoms. Such compounds are known as *unsaturated* compounds, and their properties are different from those of saturated compounds because of the presence of the double bonds.

The double bond

A single covalent bond is formed by two atoms sharing a pair of electrons. The *double bond* is formed by two atoms sharing two pairs of electrons. The simplest homologous series of unsaturated hydrocarbons is the *alkenes*, of which the simplest is ethene (*3.5*, known as ethylene in the past), with two carbon atoms linked by a double bond.

The presence of a double bond does not double the strength of the bonding between the two carbon atoms. The second bond is much less chemically stable that the first, that is, it is more reactive. The first bond has true covalent character with one shared electron from each atom forming the bond. It is termed a σ (sigma) bond. The two electrons involved in the second bond are also shared but they are much less securely bound, and as a result are easily influenced by external

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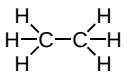
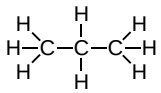


3.3



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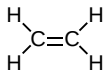
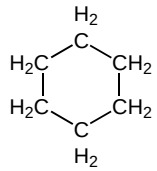


3.5

agencies. The second bond is referred to as a π (pi) bond, and it is this reactive bond that is responsible for the characteristic chemical reactions of double-bonded hydrocarbon compounds. The reactions of these unsaturated compounds include the polymerisation reactions used in the formation of synthetic fibres (Chapter 4) and the dye–fibre reactions of certain dyes.

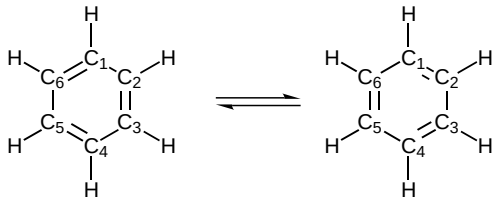
Aliphatic and aromatic compounds

Organic compounds based on hydrocarbon chains are classed as *aliphatic* compounds. In aliphatic compounds the chains of carbon atoms are linked together by single or double covalent bonds, and may be straight, branched or even linked into rings. Dyes, however, belong to a different group of compounds referred to as *aromatic* compounds.



cyclohexane
(aliphatic)

3.6



benzene (aromatic)
also represented as

3.7

The molecules of aromatic compounds contain ring structures of a special kind. The structural formulae of aromatic rings may be drawn as if alternating single and double bonds existed between adjacent carbon atoms. Compare, for example, the six-carbon aliphatic cyclic compound cyclohexane (*3.6*) and the six-carbon aromatic compound benzene (*3.7*). An arrangement of alternating single and double bonds is called a *conjugated system* and it is very important in the molecular structure of dyes.

The bonds in the benzene ring are of a very special kind, however, and do not form a conjugated system. All six bonds in the ring are exactly alike, and none of them undergo the characteristic reactions of the double bonds in, say, alkenes; they are in fact much more stable (unreactive) than double bonds. The π electrons are distributed above and below the ring, forming diffuse clouds of negative charge: they are said to be *delocalised*, and the phenomenon is known as *resonance*. The delocalising of electrons makes aromatic compounds different from aliphatic compounds. In recognition of the nature of the benzene ring, its structural formula is often

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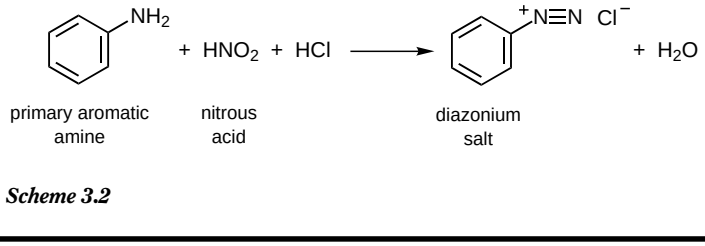
represented as a hexagon with a central circle rather than with alternating single and double bonds. Furthermore, for simplicity's sake the benzene ring is drawn without showing the individual carbon and hydrogen atoms, their presence being implied by the notation.

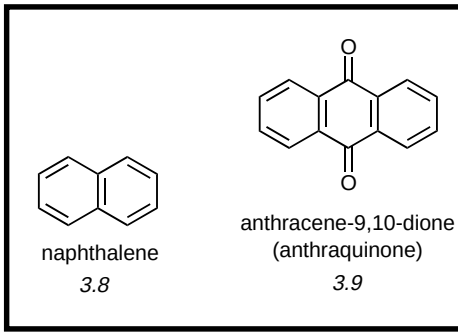
All dye molecules contain aromatic ring structures. The reactions of functional groups such as the carboxyl group or the amino group are noticeably different when they are linked to an aromatic ring and when they form part of an aliphatic molecule. For example, one particularly important reaction in dye synthesis is that carried out using the amino ($-NH_2$) group attached to a benzene ring in phenylamine (aniline), a primary aromatic amine. Scheme 3.2 shows this *diazotisation* reaction in which a colourless aromatic base (amine) is diazotised with nitrous acid to form a *diazonium* salt (no diazonium salt is formed if an aliphatic amine is used). These salts will react readily with an appropriate *coupling agent* to form a dye molecule.



Scheme 3.2

It is more usual in dye molecules to find fused rings, such as naphthalene (*3.8*), or rings joined through other groups, as in anthraquinone (*3.9*), on which many vat and disperse dyes are based.

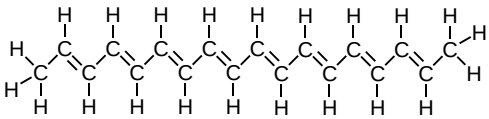
There are many possibilities for building dye molecules using such structures as a scaffolding to which functional groups of atoms may be joined to impart particular properties, and the fundamental features that allow this to be carried out systematically are outlined below.



Colour of dyes

The physiological sensation of colour arises when an object does not reflect all the incident white light falling on it. Some of the light energy is absorbed and the remainder is reflected and perceived as colour.

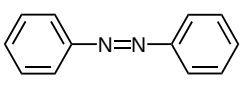
The absorption of light energy by an organic dye or inorganic pigment causes an electron to 'jump' into a higher energy level, thus bringing the dye molecule into an 'excited' state. It is easier for an electron to jump into an excited state from a double bond, where it exists as a π electron. Less energy still is required for the transition if alternate single and double bonds (i.e. conjugated double bonds) exist in the same molecule. Consequently, as the excitation of an electron becomes easier, the required spectral energy moves from the invisible ultraviolet into the longer wavelengths of the visible spectrum. For example, in structure *3.10* there are eight alternating single and double bonds. This compound absorbs violet light and as a result it is perceived as yellow in colour. Conjugated double bonds are present in the molecules of all dyes and many other coloured organic compounds.



3.10

Extended conjugated systems occur in several natural colouring matters, including carotene in carrots and fruit juices, and crocin which is found in saffron. Such compounds are not very substantive to fibres, however, and are unsuitable as starting points for dye synthesis. Structures containing benzene or naphthalene rings are of more use to dye chemists. Moreover, in aromatic rings the excitation of an electron is further aided by the enhanced delocalisation of the π electrons. Examples of such dyes and other dyes based on different chromophores (see below) of general commercial interest are given in Appendix 1.

One of the most widespread functional groups in coloured organic compounds is the azo group (—N=N—) mentioned earlier. It will react with other aromatic molecules to form the azo compounds that are widely distributed in several different classes of dye.



phenylazobenzene

3.11

The simplest azo molecule is phenylazobenzene (azobenzene), which has a weak yellow colour (*3.11*). Phenylazobenzene is called the *chromophore* (colour-bearing) group of azo dyes, and the colour of the molecule may be modified and increased in intensity of colour by introducing a variety of smaller groups into the molecule, examples of which are shown in Table 3.1. Such groups are called *auxochromes*. In addition, other groups can be added that have no influence on the colour, but change the insoluble molecule to a water-soluble dye. Thus compounds may be synthesised to produce all colours of the visible spectrum by suitable choice of auxochrome.

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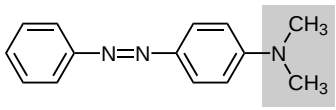
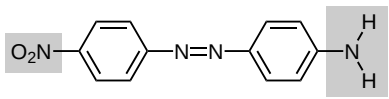
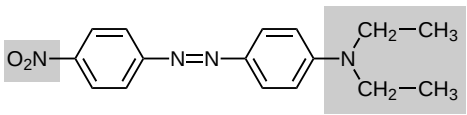
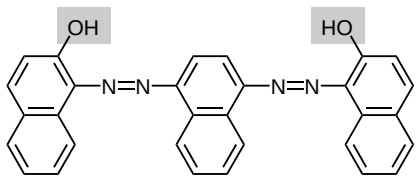
Approximately 50% of the available commercial dyes contain at least one azo chromophoric group.

Another important chromophore in dye chemistry is anthraquinone (*3.9*). Anthraquinone itself contains two carbonyl ($>$C=O) groups in a conjugated system; it absorbs ultraviolet light weakly and appears cream in colour, but replacement of hydrogen atoms in the outer rings by suitable auxochrome groups based on nitrogen, oxygen or sulphur brings about the development of strong colours. Such compounds are the basis of many vat and disperse dyes (Appendix 1) whilst other ranges of vat dyes are based on indigo (*3.12*; CI Vat Blue 1).

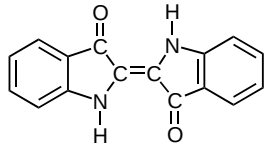
Table 3.1 Colour of some azo compounds

Structure	Colour observed
	Yellow-green
	Yellow
	Red
	Blue

– Auxochrome

The first chromophore to be synthesised for commercial use was Perkin's mauveine, but since that time many others have been produced. Unlike most water-soluble dyes, which are anionic, mauveine is cationic and is referred to as a basic dye. Other well-known examples of basic dyes are based on triphenylmethane, such as crystal violet (CI Basic Blue 11) (Appendix 1, examples 18–21). By modern standards their fastness is poor and they are of limited use on fibres other than acrylics.

One further chromophore deserves mention because of its high chemical stability and unique turquoise shades. This is copper phthalocyanine (*3.13*), which with appropriate auxochrome groups incorporated is used in several dye classes.



3.12 indigo

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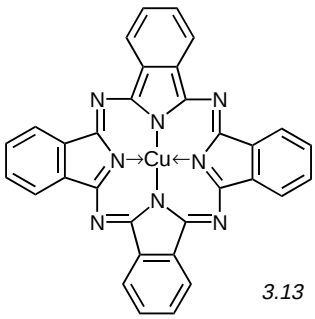


3.13

Role of intermolecular forces in coloration

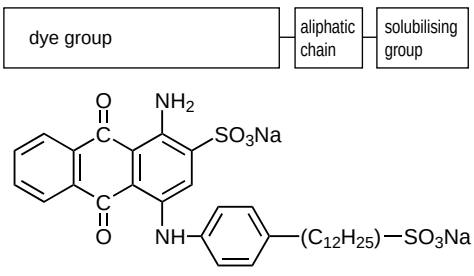
Various attractive forces have the potential of binding dyes to fibres, and often more than one type of chemical bonding can operate with the same dye–fibre combination. In any dye–fibre system the dominant force depends on the chemical character of the fibre and the chemical groups in the dye molecule. The relative strengths of different bonds is given in Table 3.2.

Table 3.2 Comparison of bond strengths

Bond type	Relative strength
Van der Waals	1.0
Hydrogen	3.0
Salt link	7.0
Covalent	30.0

Van der Waals forces and hydrophobic bonding

The large size of dye molecules contributes to the general attractive forces that they exert on surrounding molecules. The forces in question are called *van der Waals forces* after their discoverer. They are individually weak and are present in all organic compounds, but their collective effect in large organic molecules is considerable. They originate as weak interactions between the nuclei of the constituent atoms of one molecule with the electrons of another. They operate only when dye and fibre molecules are in close proximity to each other, when they can become the dominant force of attraction.



CI Acid Blue 138 (CI 62075) *3.14*

Sometimes the term 'hydrophobic bonding' is used to describe a situation in which hydrophobic groups in molecules tend to associate together and escape from an aqueous environment, i.e. from a dyebath to a fibre. For instance, the attraction of the molecules of simple acid dyes for wool fibres is greatly enhanced by the incorporation of a hydrocarbon chain in the molecule (*3.14*). This converts them to milling acid dyes (discussed in Chapter 5).

Hydrogen bonds

Hydrogen bonds are a further source of attraction between molecules, somewhat similar to van der Waals forces. The hydrogen atom is the smallest of all the atoms; in organic compounds it normally

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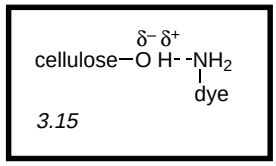
forms a single covalent bond only. Often, however, a neighbouring atom may have a higher affinity for electrons than does the hydrogen atom, causing a drift of the electrons shared by the hydrogen towards the larger atom. This leaves a slight positive charge on the hydrogen atom, which in turn encourages bond formation between it and nearby atoms such as nitrogen or oxygen (*3.15*). Such bonds are readily broken and re-formed and they are one of the factors involved when substances are dissolved by water. Most dye and fibre molecules possess groups with hydrogen-bonding capability. Consequently hydrogen bonds are often involved in dye–fibre attractions. One of the features of direct dyes that contributes to their attraction for cellulosic fibres is that their molecules are long and flat, and so can align themselves in close contact with the cellulose molecule, making it easy for hydrogen bonds to form.



3.15

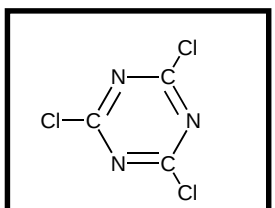
Dye aggregation

Individual dye molecules are also attracted to each other through van der Waals forces and hydrogen bonds, with the result that many dyes exist in solution as large molecular clusters called dye *aggregates*, which are colloidal electrolytes (page 32).

The large size of the dye aggregates can lead to a drastic reduction in the rate of fibre penetration, or in some cases to the precipitation (separation) of a dye from solution after prolonged storage. The addition of electrolyte to a dyebath can increase the degree of aggregation, but fortunately the aggregation process is reversible and may be decreased by a rise in temperature. A certain degree of aggregation can be beneficial since it tends to increase the attraction of the dye for the fibre (this is discussed further in Chapter 4). Adding salt and raising the temperature of the dyebath are both often used in the control of dyeing processes.

Covalent bonding

Covalent bonding between dye and cellulosic fibres is achieved nowadays by the incorporation in the dye molecule of special *reactive groups*, linked to the rest of the molecule through a *bridging group*. Many such groups can be used, but the first reactive dyes were based on cyanuric chloride (*3.16*, *3.17*).



3.16 cyanuric chloride

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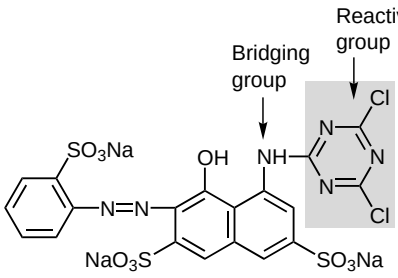

3.17 CI Reactive Red 1

Acid and basic groups in dyes and fibres

Reference is frequently made to acidic and basic groups when discussing coloration processes because in some dye–fibre systems they react together to form *salt links* (i.e. electrostatic links). For the purposes of understanding dye–fibre interactions, an *acid* may be regarded as a compound that will dissociate in solution to liberate hydrogen ions, H^+. For example, hydrogen ions are formed when hydrogen chloride dissolves in water, forming hydrochloric acid (Scheme 3.3).

$$HCl \longrightarrow \underset{\text{cation}}{H^+} + \underset{\text{anion}}{Cl^-}$$

Scheme 3.3

An acidic group in a dye molecule will dissociate similarly, and will react with a basic compound. For example, the sulphonic acid group in a dye molecule will react with sodium hydroxide to form the sodium salt of the dye, already mentioned (Scheme 3.4).

$$D{-}SO_3H + NaOH \longrightarrow D{-}SO_3Na + H_2O$$

Scheme 3.4

Likewise, a basic group in a large molecule, such as a fibre molecule, will react with an acidic group and form a salt. Once the basic group has been liberated from combination with other acidic groups in the fibre (for instance, by the addition of a simple acid such as hydrochloric acid), it can react with an acidic dye molecule to form a salt linkage between the dye and the fibre, as shown in Figure 3.7.

pH values

The *pH scale* is a convenient way of expressing the strength of solutions of acids or bases. It distinguishes between strongly acidic and strongly basic compounds, which are completely – or almost completely – dissociated in solution, and between weak acids and weak bases which dissociate only slightly. A solution with a pH of 7 is neutral; pH values of less than 7 represent acidity and values greater than 7 alkalinity (basicity), the full scale ranging from 0 to 14.

These figures are not arbitrary. They are derived from the concentration of hydrogen ions in the solution, written $[H^+]$. Consider first the case of water, H_2O. Even liquid water undergoes

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dissociation to some extent: about one water molecule in every 10 million molecules dissociates. Those molecules that dissociate do so according to Scheme 3.5. Each positively charged hydrogen ion is accompanied by a negative hydroxide ion, OH^-, so that the number of positive and negative charges in the solution are balanced.

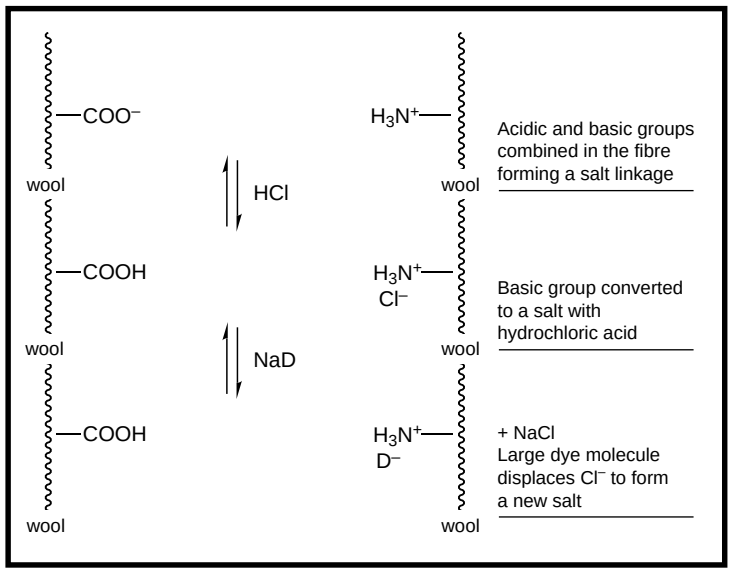

Figure 3.7 *The formation of salt linkages between a dye and a wool fibre: NaD represents the sodium salt of a large dye molecule*

A solution containing an excess of hydrogen ions, however, is acidic. Sulphuric acid, H_2SO_4, is an example of a *strong acid*, that is, one in which the acid is completely dissociated (Scheme 3.6).

Other acids, such as ethanoic acid (acetic acid, CH_3COOH), only partially dissociate in water and therefore are said to be *weak acids*. Even in weak acids, however, the number of hydrogen ions is very large, so the hydrogen ion concentration is more conveniently expressed on a logarithmic scale (Equation 3.1):

$$H_2O \longrightarrow H^+ + OH^-$$

Scheme 3.5

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

sulphuric acid — 2 protons (2 electrons lost) / sulphate ion (2 electrons gained)

Scheme 3.6

$$\text{pH} = -\log(\text{H}^+ \text{ concentration}) \qquad (3.1)$$

For pure water the pH = –log(1/10 000 000), i.e. $-\log(10^{-7}) = 7$. As the acidity increases the pH value diminishes, as shown in Table 3.3, overleaf.

In solutions where the pH is greater than 7, the concentration of hydrogen ions is less than in neutral water. In order that the numbers of positive and negative ions should be equal, the concentration of hydroxide ions (OH^-) has to be higher than in water. Such solutions are *alkaline* solutions. An example of a strong alkali is sodium hydroxide (caustic soda), which dissociates according to Scheme 3.7, overleaf.

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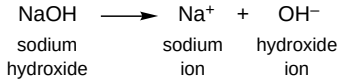
Table 3.3 Description of acidity in terms of pH

H^+ concentration (moles per litre)	pH units	Condition of solution
10^{-7}	7.0	Neutral
10^{-5}	5.0	Weakly acidic
10^{-3}	3.0	Strongly acidic
10^{-2}	2.0	Very strongly acidic
10^{-1}	1.0	Highest acidity

The pH of a solution can be monitored using special instruments called pH meters, or more simply (and less precisely) by putting a drop of the solution on an appropriate indicator paper. Indicator papers take on different colours at different pH values.



Scheme 3.7

Redox reactions

Oxidation–reduction reactions (*redox reactions*) are important in textile coloration because they are an essential part of the process of the application of vat and sulphur dyes. In rather oversimplified terms, when a compound is *oxidised* it gains oxygen; when something is *reduced* it loses oxygen. Reduction of a substance can also be thought of as gaining hydrogen atoms, and oxidation as losing hydrogen atoms. For example, when hydrogen reacts with oxygen to form water the hydrogen becomes oxidised and the oxygen is reduced. In a redox reaction there is always a compound acting as a *reducing agent* (hydrogen in this example). The reducing agent becomes oxidised during the reaction by the compound that is being reduced, which is acting as an *oxidising agent* (in this case oxygen).

In the water molecule, each hydrogen atom shares the only electron it possesses by pairing with one of the six electrons of the oxygen atom, to form a covalent bond. Thus the hydrogen atom has lost one electron to become oxidised and the oxygen atom is reduced by gaining electrons. This is a more general way of expressing the phenomena of oxidation and reduction:

– Oxidation – entails the loss of electrons by the oxidised compound and
– Reduction – entails a net gain of electrons by the reduced compound.

Vat dyes such as indigo and compounds derived from anthraquinone are applied after the temporary reduction of two carbonyl groups ($>C=O$) in a conjugated chain; this converts the dye into a colourless water-soluble form. The conversion is carried out using a strong reducing agent, and in the reaction the two oxygen atoms become reduced to $-O^-$ and the two hydrogen atoms are oxidised to H^+ (Scheme 3.8). The reduced (soluble) form is called the *leuco vat acid*, and is applied from an

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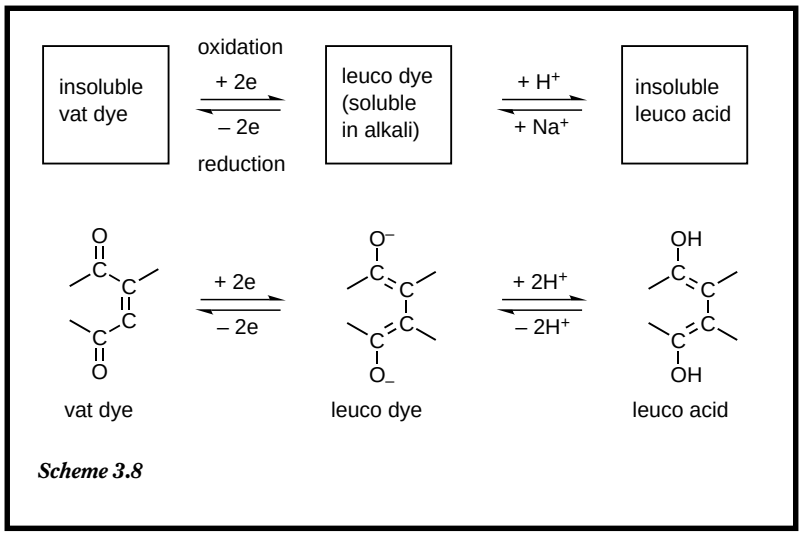
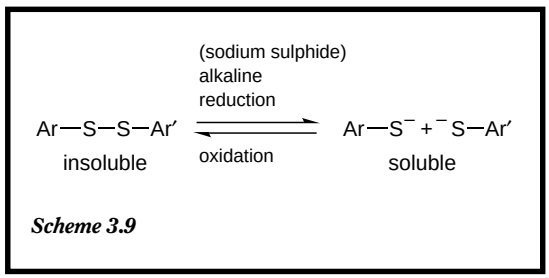
alkaline solution. Once on the fibre it can be re-oxidised back to the insoluble carbonyl form by air or by the use of an oxidising agent (that is, the redox reaction is reversed).

Sulphur dyes are also applied using a redox reaction mechanism, in which sodium sulphide is used as the reducing agent (Scheme 3.9).



Scheme 3.8



Scheme 3.9

Further reading

R Gallagher and P Ingram, *Chemistry made clear. GCSE edition* (Oxford: Oxford University Press, 1990).

R Hart, *Chemistry matters. GCSE edition* (Oxford: Oxford University Press, 1988).

E P G Gohl and L D Vilensky, *Textile science* (Harlow: Longman, 1990).

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