**Keywords:** Azo; Dyes; Coupling; Auxochrome; Chromophore

**Azo Compounds**

The history of dyeing can be divided into two great periods, the "pre-aniline," extending to 1856 and the "post-aniline" period. The former was characterized by a rather limited range of colors that were based on dye-producing animals and plants. The main vegetable dyes available were extracted from madder root (Asia and Europe), producing a brilliant red and leaves of the indigo plant (India), yielding the blue dye still used today in jeans. Among the most important animal based dyes is the famous and expensive "Tyrian Purple" which was obtained from the small shellfish nurez. We have the ancients' word that this dye was unbelievably beautiful, but evidence taken from ancient samples prove that it ranges through a rather uninspiring series of reds and purples. After seeing it, we wish that Homer had written about some of today's inexpensive coal-tar purples and reds. A far more beautiful natural color was introduced to Europe from Mexico in 1518, the brilliant scarlet dye cochineal, which purples and reds. A far more beautiful natural color was introduced to that Homer had written about some of today's inexpensive coal-tar purples and reds. A far more beautiful natural color was introduced to Europe from Mexico in 1518, the brilliant scarlet dye cochineal, which...
When the diazonium salt is reacted with a phenol, a yellow/orange azo compound is formed:

With an alkaline solution of naphthalein-2-ol, a red azo compound is formed:

**Coupling with Amines**

- A yellow dye is often formed when a diazonium salt is reacted with arylamines:

- Many different azo compounds can be formed by coupling different diazonium salts with phenols containing the azo group, \(-\text{N=N}\). For example, an alkaline solution of phenol (the coupling agent) reacts with benzene diazonium chloride (an electrophile) to form a yellow azo-dye. Coupled with naphthalen-2-ol a bright red precipitate is formed [9-11].

These particular dyes are of little practical value owing to their only slight solubility in water. However, azo-dyes containing one or more sulphonic acid groups are much more soluble and of considerable commercial importance in the dyestuffs industry [12-15].

In azo compounds the \(-\text{N=N}\) group is part of an extended delocalised electron system involving the aromatic rings, called a chromophore. The quantised molecular electronic energy levels are closer together in such delocalised systems and light from the visible region of the electromagnetic spectrum is absorbed (DE) when electrons are promoted from lower to higher levels. The azo compound then appears a colour corresponding to the unabsorbed visible light. Also, groups such as \(-\text{OH}\) and \(-\text{NH}_2\) are often attached to chromophores (also forming part of the extended delocalised electron system, so changing the DE values) to modify the colours of the molecules. Azo-dyes bind to fabrics in different ways. For cotton, many are insoluble and become trapped in the fibres. Others, called direct dyes, become attached to the fibres by hydrogen bonding and instantaneous dipole-induced dipole intermolecular bonding. Because intermolecular bonding is much weaker than covalent bonding, the dye molecules must be long and straight so that they can align closely with the cellulose fibres of cotton giving more opportunities for intermolecular attractions [16,17]. The structure of the dye Direct Blue 1 is illustrated below:

**Diazonium Salts**

- Both aliphatic and aromatic primary amines can form diazonium salts. They do this by reacting with Nitric(III) acid (nitrous acid), \(\text{HNO}_2\), at a temperature of 0-5°C.

- Owing to the instability of nitric(III) acid, it is always generated during a reaction, usually by the action of dilute sulphuric(VI) acid or hydrochloric acid on sodium nitrate(III) (sodium nitrite), \(\text{NaNO}_2\). The acid used to generate nitric(III) acid provides the anion of the diazonium salt.

\[
\text{R-NH}_2 + \text{NaNO}_2 + 2\text{HCl} \rightarrow \text{R-N}^+\text{N}:\text{Cl}^- + 2\text{NaCl} + 2\text{H}_2\text{O}
\]

\[
\text{Ph-NH}_2 + \text{NaNO}_2 + 2\text{HCl} \rightarrow \text{Ph-N}^+\text{N}:\text{Cl}^- + 2\text{NaCl} + 2\text{H}_2\text{O}
\]

- However, alkyl diazonium salts are extremely unstable and always decompose to evolve the colourless unreactive nitrogen gas, amongst other products.

- The diazoniocmations of aromatic diazonium salts are somewhat more stable than their aliphatic counterparts. With phenylamine the benzene diazonium ion is formed:

\[
\text{C}_6\text{H}_5 - \text{NH}_2 + \text{HNO}_2 + \text{H}^+ \rightarrow \text{C}_6\text{H}_5 - \text{N}^+\text{N}: + 2\text{H}_2\text{O}
\]

- Although benzene diazonium salts can be isolated in the crystalline form, they are usually retained in solution and used immediately as they decompose on standing even in the cold. In the solid state the salts are explosive and can be easily detonated by a slight shock or on mild warming.

A structure for benzene diazonium chloride is shown below:

The greater stability of the benzene diazoniumcation compared with the alkyl diazoniumcation is attributed to the diazo group being part of the delocalised system with the benzene ring and so the way in which the positive charge is distributed about the ring.

**Azo-dyes - Coupling Reactions**

- In practice, a solution of a benzene diazonium salt is added to an alkaline solution of a phenol (or aromatic amine, such as phenylamine). The benzene diazoniumcation behaves as an electrophile, but it is a
weak electrophile and so the aromatic ring which it attacks must have attached to it an activating group such as -OH or -NH₂. An electrophilic substitution reaction occurs to form an azo-dye.

• The electrophile chlorine activates the reaction and electrophilic substitution takes place on phenol.
• Substitution reaction takes place always in para position except when the position is already occupied.

The mechanism for p-mitrobenzenediazoniumtetrafluoroborate in azo coupling with benzene or nitrobenzene.

Aromatic diazonium ions acts as electrophiles in coupling reactions with activated aromatics such as anilines or phenols. The substitution normally occurs at the para position, except when this position is already occupied, in which case ortho position is favoured. The pH of solution is quite important; it must be mildly acidic or neutral, since no reaction takes place if the pH is too low [7,8].

Mechanism of Azo Coupling

Dr. Nagham synthesized manyazo groups linked with schiff base to produce various membered rings and formazane compounds [9].

Dr. Nagham et al. synthesized polymer containing azo groups [11].

Dr. Nagham synthesized azo groups linked with schiff base to produce formazane compounds from melamine compound [10].
Dr. Matelf et al. synthesized imidazole rings containing azo groups.

\[
\begin{array}{c}
\text{imidazole ring} \\
\text{with azo group}
\end{array}
\]

Dr. Hanser et al. synthesized imidazole azo complexes.

\[
\begin{array}{c}
\text{imidazole azo complex} \\
\text{structure}
\end{array}
\]

James prepared imidazole azo antibacterial and antifungal.

\[
\begin{array}{c}
\text{imidazole azo antibacterial} \\
\text{and antifungal}
\end{array}
\]

Alaa et al. prepared macroazo ligands.

\[
\begin{array}{c}
\text{macroazo ligands} \\
\text{structures}
\end{array}
\]

Dr. Nagham Aljamali synthesized formazane compounds containing azo groups linked with imine group.

\[
\begin{array}{c}
\text{formazane compounds} \\
\text{containing azo groups}
\end{array}
\]

Some azo compounds used as drugs like sulphadiazine derivatives.

\[
\begin{array}{c}
\text{sulphadiazine derivative} \\
\text{structure}
\end{array}
\]

References