Experiment 14

Chemistry of Blue Jeans: Indigo Synthesis and Dyeing

The task

The goal of this experiment is to synthesise the vat dye, indigo, and compare the properties of cloth that has been dyed with indigo and a mordant dye, alizarin red S.

Skills

At the end of this laboratory session you should be able to:

- vacuum filter,
- accurately weigh out samples.

Other outcomes

You will learn how to synthesise indigo.

You will learn how to dye cloth using a vat dye and a mordant dye.

You will observe the colours of different divalent metal ion complexes of a mordant dye.

You will test and compare dyed material for solubility and fading.

The Assessment

You will be assessed on your ability to isolate solid products using vacuum filtration. See Skill 6.2.

Introduction (History)

Indigo

The blue dye indigo has been used in India for about 4000 years. It can be extracted from the plant *Indigofera tinctoria*. Phoenician traders and migrating peoples gradually introduced this dye to the Mediterranean area and its use spread across Europe. In Northern Europe from the Bronze Age (2500 – 850 BC) onwards, people used a blue dye, woad, from the plant *Isatis tinctoria*. It has since been discovered that this plant contains the chemical indigo, but due to other compounds in the plant it is not as 'pure' blue as that from the plant *Indigofera*.

Indigo is termed a *vat dye*. Its preparation involved fermenting the juice of the crushed plant and then treatment with urine. (You will not have to do this today.) For dyeing, fibre was dipped into a bath (or vat) containing the initially colourless dye and then hung out in the sun to produce a blue insoluble dye on the fibre.

In 1865, the German chemist Johann Friedrich Wilhelm Adolf von Baeyer began working with indigo. In 1880, his work resulted in the first chemical synthesis of indigo and three years later the announcement of its chemical structure. BASF (***B****adische* ***A****nilin- und* ***S****oda-****F****abrik*) developed a viable manufacturing process that was in use by 1897, and by 1913 synthetic indigo had almost completely replaced natural indigo. In 2002, 17000 tons of synthetic indigo was produced worldwide.

Denim

Denim, a heavy woven cotton fabric, originated in the ancient textile centre of Nimes, France, and was called "serge de Nimes". Columbus is reported to have used denim for his sails on the Santa Maria. At approximately the same time in India, the sailors of Dhunga were using denim material for their pants, which became known as dungarees. Later on, the word "jeans" came into usage, because working men from Genoa, Italy, had adopted the practice of wearing denim trousers.

After the Californian gold rush of 1849, Levi Strauss, an unsuccessful miner, became rich by making denim pants for the more successful miners. The first Western "Levis" jeans were born. Over the next hundred years they remained working pants, but in the 1940's denim started to be used in sportswear and rainwear. Since 1960, the jeans business has undergone a transformation from tough, cheap clothing to a fashion conscious market. Around 1970, American youth adopted denim as their favourite material.

Alizarin

Alizarin was already used for dyeing cloth in Asia and Europe in ancient times. It has been found in the excavations at Pompeii and in Egyptian textiles from as early as 1567 BC and in Corinth from 146 BC. In 972 AD, alizarin was first used on paper in ink for a marriage certificate of Byzantine Empress Theophano, then later as a pigment in paint. In the Advocates Library in Edinburgh, alizarin paint has been identified in an illustrated book dated 1465-1489.

Alizarin is found in the root of the madder plant, or more precisely in the root of the Mediterranean and Asian plant *Rubia tinctorum*. The plant was usually harvested three years after planting for maximum dye yield. It was then uprooted and left to dry, put in larger piles for 2-3 days and then dried in warm-air drying houses. The dried roots were crushed and separated from the bark and ground into a fine powder. The juice of the roots of some species of the madder plant must be fermented for 1-2 years before it can be used. Other species, which have a significantly higher quality, can be used straight away, but in general it is better if stored first.

Sir William Henry Perkin (1838 – 1907), at 18 years of age, synthesised the first purely synthetic dyestuff (mauveine or aniline purple), from chemicals derived from coal tar, whilst trying to synthesise quinine. In 1869, Perkin also synthesised alizarin. Unfortunately for Perkin, the German company BASF beat him to the patenting process by one day! It was decided that Perkin would sell to Britain (400 tonnes a year) and BASF to the rest of the world.

The Birth of the Pharmaceutical Industry

A medical student, Paul Ehrlich (awarded the Nobel Prize for Medicine in 1908), had been impressed with the ability of certain dyes to stain tissues selectively. Ehrlich believed that staining was a result of a chemical reaction between the dye and the tissue. He therefore looked for dyes that had an affinity for micro-organisms, hoping that the dye could be modified to become specifically lethal to the micro-organisms.

Ehrlich's research was looking for "magic bullets" – chemicals that would be toxic to infectious micro-organisms, but harmless to humans. In 1907, he discovered the curative properties of the dye, Trypan Red I, when used against trypanosomiasis (of which African sleeping-sickness is one form), and in 1909 he discovered Salvarsan as a remedy for syphilis. Through these discoveries he ushered in the new field of "chemotherapy".

In 1935, the daughter of Gerhard Domagk, a doctor employed by the German dye conglomerate IG Farben (*Interessen-Gemeinschaft Farbenindustrie*), contracted a streptococcal infection from a pin prick. As his daughter neared death, her father decided to give her an oral dose of a dye called Prontosil, which had been developed in IG Farben's Bayer labs. Tests had shown that it inhibited the growth of streptococci in mice. Within a short time the little girl recovered. Domagk's gamble not only saved his daughter's life, but it initiated a new and wonderful productive phase in modern chemotherapy.

Introduction (Chemistry)

Indigo

Today you will be synthesising indigo using the Baeyer-Drewson reaction, as shown in Figure 1. In this and subsequent figures we have used stick notation, a shorthand method of drawing complex organic molecules. (See Skill 13 for a full description of stick notation.) The lines represent bonds and, unless otherwise specified, the atoms at the ends of all bonds are carbon. Whenever a carbon atom has fewer than 4 bonds, the number of hydrogens bonded to it can be calculated - carbon always has a valence of 4 and the undrawn bonds are assumed to be bonds to hydrogen.

The Baeyer-Drewson reaction was developed by von Baeyer in 1880 to produce the first synthetic indigo. It works well for small scale reactions, but is not used today in industry for producing large quantities of indigo.

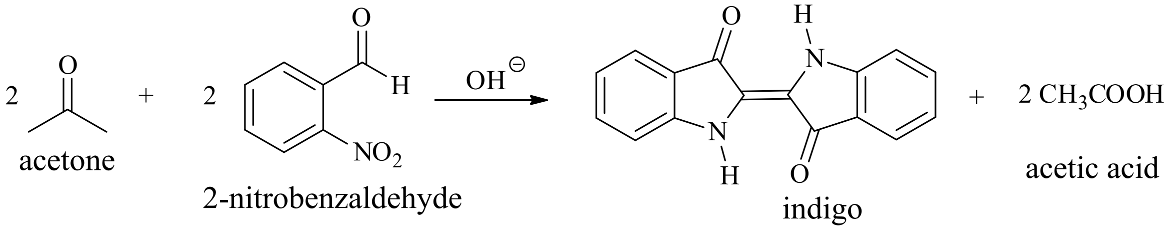

Figure 1: The Baeyer-Drewson reaction of 2-nitrobenzaldehyde with acetone in basic conditions to produce indigo.

Indigo is not soluble in water. Therefore, to dye cloth, the indigo needs to be first converted into a water soluble form. In this experiment, you will synthesize the insoluble indigo dye and then convert it (via a reduction reaction with sodium dithionite) to the colourless and water-soluble leucoindigo or indigo white, as shown in Figure 2. When the colourless leucoindigo comes into contact with air it oxidises back to the insoluble blue indigo compound.

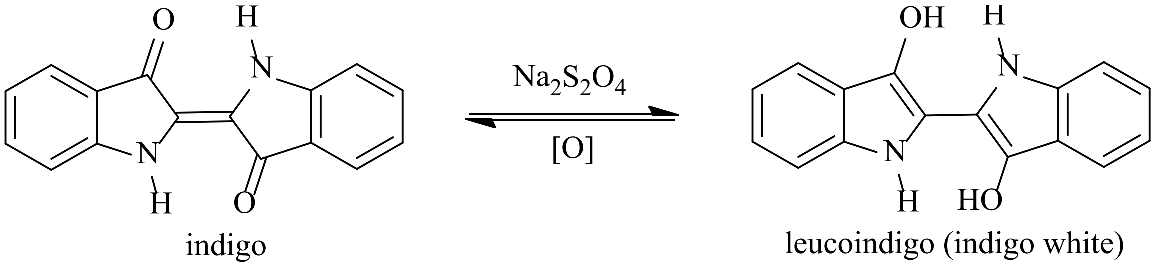

Figure. 2: The reaction showing the conversion of the insoluble blue indigo dye to the colourless water-soluble leucoindigo or indigo white.

Alizarin Red S

A *mordant dye* (*e.g* alizarin red S) cannot bond or be fixed directly to a fabric. Instead, the fibres of the fabric are first treated with a metal salt solution (*e.g.* aluminium, chromium and copper salts, *etc*) called a mordant. The metal ions in solution form strong bonds with the fibre and then subsequently with the applied dye, thus binding the dye indirectly to the fabric. The final colour of the dyed fabric is dependent on both the mordant (metal ion) and the dye.

Figure 3 shows the chemical structure of cellulose, a polymer made from D-glucose molecules. Cotton is essentially pure cellulose. When treated with a mordant, the hydroxyl groups on the cellulose bond to the metal ions, and then, when alizarin red S is added, it binds to the metal as shown in Figure 4, dyeing the cotton fabric.

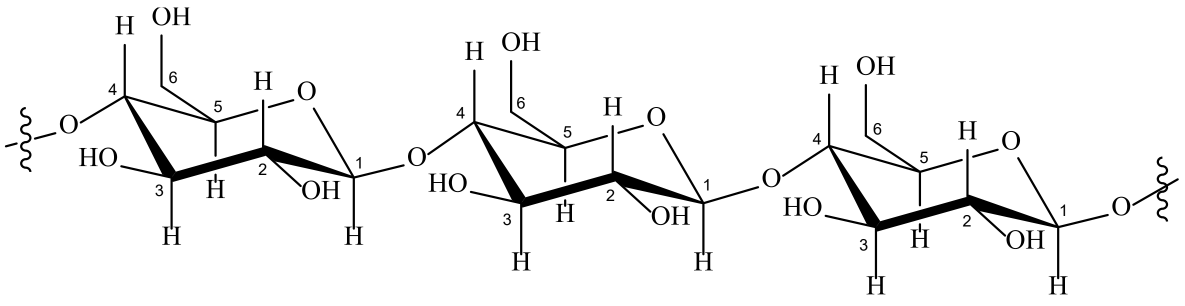

Figure 3: Structure of cellulose

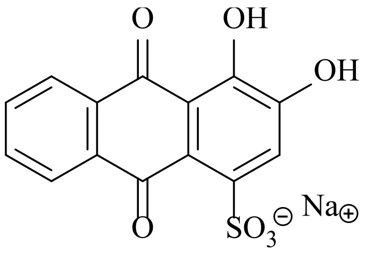

Figure 4(a): Structure of alizarin red S

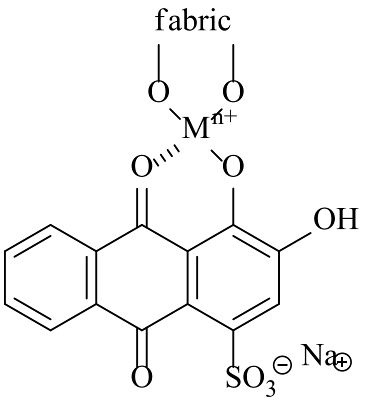

Figure 4(b): The metal ion bonds to alizarin red S and cellulose

Safety

Chemical Hazard Identification

2-nitrobenzaldehyde – hazardous. Irritant, moderate toxicity. Avoid eye or skin contact and dust generation or inhalation.

acetone – hazardous. Highly flammable, irritant, low to moderate toxicity.

ethanol – hazardous. Highly flammable, low to moderate toxicity, irritant.

sodium hydroxide – hazardous. Highly corrosive and hygroscopic, severe irritant.

sodium dithionite – hazardous. Moderate toxicity, slightly corrosive, irritant.

aluminium sulfate – hazardous. Slightly corrosive, irritant.

calcium chloride – non-hazardous, irritant.

copper(II) sulfate – hazardous. Toxic, irritant.

iron(II) sulfate – hazardous. Moderate toxicity, irritant.

cyclohexane – hazardous. Highly flammable, moderate toxicity, irritant.

diethyl ether (ether) – hazardous. Toxic, irritant. Avoid eye or skin contact and vapour inhalation. Highly flammable liquid and vapours.

5% v/v hydrogen peroxide – hazardous. Irritant.

alizarin red S – non hazardous.

indigo - non-hazardous. Low toxicity.

Risk Assessment and Control

Moderate risk.

Glass stirring rods are liable to break and cause serious cuts.

Organic solvents are a fire hazard and are easily absorbed through inhalation. They must be kept in the fumehood.

Waste Disposal

Any remaining iron and calcium solutions can be disposed of down the sink. Any remaining copper and aluminium solutions must be disposed of in the “Heavy Metal” waste container in the fumehood. Any remaining alizarin red S solution may be washed down the sink. The solid indigo waste is to be discarded in the “Indigo” waste container in the fume hood. Ether and cyclohexane waste is to go into the non-chlorinated organic waste container in the fume hood.

Experimental

This experiment is to be carried out in pairs.

Notes: All volumes of solutions should be measured in either a 10 mL or a 100 mL measuring cylinder as appropriate.

The pieces of cloth should be dried by leaving them on a piece of paper towel in the fume cupboard.

Part A Synthesis of indigo

(A1) Use a top loading balance (Skill 3.1) to weigh out 0.5 g of 2-nitrobenzaldehyde into a clean 100 mL beaker and dissolve it in 10 mL of acetone.

(A2) Dilute the solution with 20 mL of deionised water.

(A3) Measure out 2.5 mL of 2 M sodium hydroxide (NaOH).

(A4) Using a glass rod, stir the solution in the beaker vigorously and carefully pour in the sodium hydroxide. The solution should immediately turn a deep yellow, then become darker and within 20 seconds a dark precipitate of indigo should appear.

(A5) Continue to stir the mixture for 5 minutes.

(A6) Collect the purple-blue precipitate in a Büchner funnel (Skill 6.2).

(A7) Wash the product with deionised water until the washings are colourless (approx. 100 mL of water needed). Then wash with 20 mL of ethanol.

(A8) Take out ~100 mg of the indigo (about ½ the size of a pea) and place in a clean 100 mL beaker for vat dyeing the cotton.

Part B Vat dyeing of cotton

(B1) To the beaker with the indigo sample, add a few drops of ethanol and make a paste by rubbing the mixture with a glass rod.

(B2) Add 1 mL of deionised water to the paste and make a suspension by stirring with a glass rod.

(B3) Add 3 mL of 2 M sodium hydroxide solution to the suspension.

(B4) Use a top loading balance (Skill 3.1) to weigh out 0.6 g of sodium dithionite into another clean 100 mL beaker and then dissolve it in 20 mL of deionised water.

(B5) Add the sodium dithionite solution to the beaker that contains the indigo dye and then cover the beaker with a watchglass.

(B6) Heat the mixture to 50 °C on a magnetic stirrer hotplate, and as soon as a clear yellow or green solution is obtained, add 40 mL of deionised water.

(B7) Immerse five small pieces of cotton in the 'vat' and leave for 1 hour at 50 °C, occasionally moving the fabric to ensure even dyeing.

(B8) Proceed with Part C during this 1 hour waiting time.

(B9) Remove the cotton pieces with metal tongs and squeeze dry. Wait until it changes colour (< 30 s), then remove any residue of indigo which is not incorporated into the fibres of the cloth by rinsing the cotton under the tap until the washings are clear. Dry the pieces of cloth.

(B10) When the pieces of cloth are dry, **attach one to your logbook**. The remaining pieces will be used later for testing the colour fastness of the dye.

Part C Dyeing with the mordant dye alizarin red S

Do not touch the dye with your fingers.

In this part of the experiment you will discover how to use alizarin red S to dye pieces of material various colours by varying the mordant (metal ions).

(C1) Make up a series of stock solutions of the metal ions which will be used as the mordant. You will need four clean 100 mL beakers. Label each beaker appropriately.

- Cu^{2+}: Dissolve half a nickel spoonful of $CuSO_4$ in 40 mL of deionised water.
- Fe^{2+}: Dissolve half a nickel spoonful of $FeSO_4$ in 40 mL of deionised water.
- Al^{3+}: Dissolve half a nickel spoonful of $Al_2(SO_4)_3$ in 40 mL of deionised water and add 1 mL of 2 M NaOH.
- Ca^{2+}: Dissolve half a nickel spoonful of $CaCl_2$ in 40 mL of deionised water.

(C2) In a clean 100 mL conical flask, dissolve half a nickel spoonful of alizarin red S in 80 mL of deionised water.

(C3) Pour 10 mL of the alizarin red S solution into a clean 100 mL beaker.

(C4) Using metal tongs, take a new piece of cloth and dip it first into the copper mordant and then into the alizarin solution. Make sure that it is completely covered.

(C5) Using the tongs, squeeze as much solution as possible out of the material and blot dry.

(C6) Wash the remaining (now contaminated) alizarin red S solution down the sink. Rinse the 100 mL beaker using a small amount of deionised water.

(C7) Repeat steps (C3) - (C6) with the remaining mordants (Fe^{2+}, Al^{3+} and Ca^{2+}).

(C8) Repeat steps (C3) - (C6) using tap water as the mordant.

(C9) Repeat steps (C3) - (C6), but without using any mordant, to dye 5 pieces of cloth.

(C10) Repeat steps (C3) - (C6) with a mordant of your choice to dye 4 pieces of cloth. This is for testing the colour fastness of the dye later on.

(C11) When the cloth has dried, wash it with cold water until the water is clear. Dry the cloth again.

For your logbook:

Record your results in a table and attach your dyed cotton samples (that are not required for testing) in your logbook.

Include what ions you think, based on your results, are present in tap water.

Part D Testing the dyed cotton material

In this part of the experiment you will investigate how the dye can be removed from the material, *i.e.* which solvents can dissolve the dye. You will also investigate the resistance of the dye to fading.

Solubility of the Dye

(D1) On your bench, make a cold water bath. In the fumehood make up a cyclohexane bath and an ether bath as shown in Figure 5. (Ether and cyclohexane are non-polar organic solvents, water is a polar solvent.)

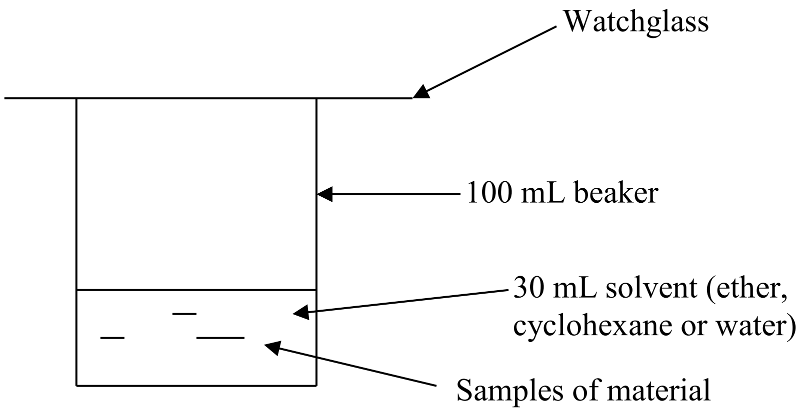

Figure 5: Diagram of a solvent bath.

(D2) Place one of each of the following dyed samples into each bath and leave for 10-15 minutes.

- cloth dyed with alizarin red S only (C9);
- cloth dyed with a single metal mordant (C10);
- cloth dyed with indigo (Part B).

(D3) Observe the colour of the solution around each piece of cloth, remove the pieces and dry them.

(D4) Dispose of the ether and cyclohexane baths in the non-chlorinated organic waste container.

For your logbook:

Compare the colour of the cloth that has been soaking in the solvent baths with the original piece of cloth, tabulate and record the results and attach the faded samples in your logbook. You should note whether the dye is soluble (most of the dye was removed from the cloth), slightly soluble (a little bit of the dye was removed from the cloth) or insoluble (no dye was removed from the cloth).

Fading

To test the dye for fading, we will speed up the process by using a mild bleach, dilute hydrogen peroxide solution.

(D5) On your bench make a solvent bath with 30 mL of 5 % v/v hydrogen peroxide.

(D6) Place one of each of the following dyed samples into the bath and leave for 10-15 minutes.

- cloth dyed with alizarin only (C9);
- cloth dyed with a single metal mordant (C10);
- cloth dyed with indigo (Part B).

(D7) Observe the colour of the solution around each piece of cloth, remove the pieces and dry them.

For your logbook:

Compare the colour of the cloth that has been soaking in the solvent bath with the original sample of cloth, tabulate and record the results and attach the faded samples in your logbook. You should note if the hydrogen peroxide has caused any fading. (Was there no fading, a little bit of fading or a lot of fading?)

Group Discussion

A dye is something that has the following properties:

- highly coloured, so that it can be used in small concentrations;
- capable of being attached strongly to the fabric, so that it won't wash out;
- resistant to fading and discolouring.

What other property should a commercially used dye possess?

Did the indigo and alizarin red S dyes fulfil these qualities? List the pros and cons for each of these dyes.

Was there a difference in the above qualities between the alizarin red S dye when there was mordant used and no mordant?

References

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