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SYNT
730

Dyes and Dyeing

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PURPOSE OF THE EXPERIMENT

Synthesize dyes and compare different methods used to dye cloth. Examine the bleaching effects of an oxidant and a reductant on dyes.

EXPERIMENTAL OPTIONS

BACKGROUND REQUIRED

You should be familiar with vacuum filtration.

BACKGROUND INFORMATION

Dyes were in use before recorded history. Indigo, a pigment extracted from the woad plant, was used to dye burial cloths for Egyptian mummies over 4,000 years ago. Indigo is used today to dye blue jeans. Tyrian purple was derived from Mediterranean mollusks. Approximately 9,000 mollusks were needed to give one gram of the dye.

American Indians used cochineal, a scarlet dye extracted from the dried bodies of insects, to color their baskets and clothing. The red dye alizarin, extracted from madder root, was known to the ancient Egyptians and Persians. Alizarin was used to dye the red coats of British soldiers in the American Revolution, the red caps and trousers of French soldiers in the French Revolution, and the violins of Antonio Stradivari. Structures for these dyes are shown in Figure 1 on the next page.

Colored compounds absorb some, but not all, wavelengths of visible light. When one looks at the light reflected from a colored object, the eye sees white light minus the wavelengths absorbed by the object. Therefore, a colored object appears as the color complementary to the wavelengths it absorbs. For example, if an old sheet becomes dingy and yellow, it is because substances on the surface are absorbing blue light. Some detergents contain bluing that absorbs yellow light and makes yellowed fabrics appear white again. Table 1 on the next page shows approximate wavelengths for colors and their complementary colors.

Dyes are compounds used to impart color to other substances. A dye is chosen for its color and for its ability to resist removal under the usual conditions expected for the dyed material. For example, a dye used for cotton should adhere to the cotton fibers well enough that the article can be washed repeatedly without fading.

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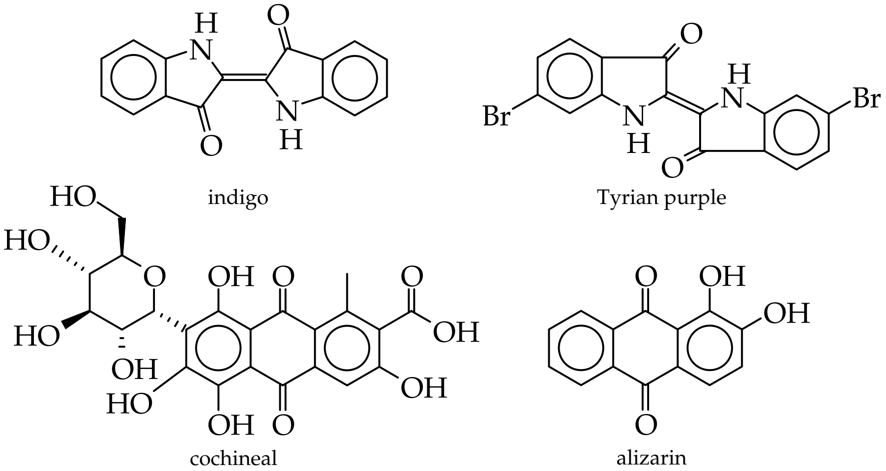
Figure 1 Structures for ancient dyes



indigo

Tyrian purple

cochineal

alizarin

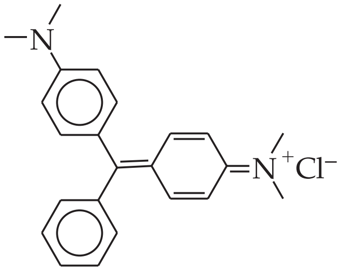
Table 1 Wavelengths and colors

wavelength absorbed	*apparent color*
700 nm (red)	green
590 nm (yellow)	blue
530 nm (green)	red
460 nm (blue)	yellow

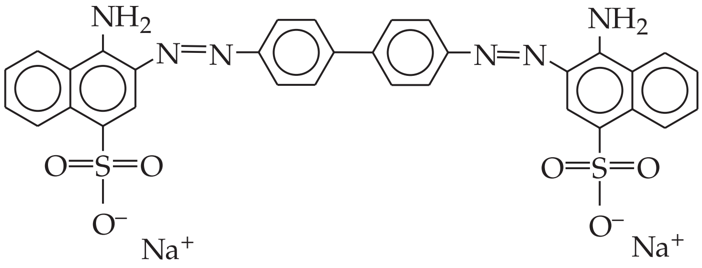
Functional groups that absorb light are called **chromophores**. Chromophores are typically highly conjugated systems containing several double bonds and one or more characteristic groups such as azo (–N=N–), nitro ($–NO_2$), and carbonyl (>C=O).

Auxochromes are groups that increase the wavelength and intensity of the color absorbed. Important auxochromes are hydroxyl (–OH), amino ($–NH_2$), sulfonate ($–SO_3^-$), and carboxylate ($–COO^-$). Large numbers of conjugated double bonds and auxochromes appear in the dyes shown in Figure 1 and in Malachite Green and Congo Red, shown in Figure 2.

Figure 2 Structures for Malachite green and Congo red

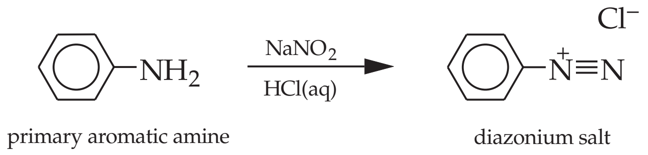


Malachite Green

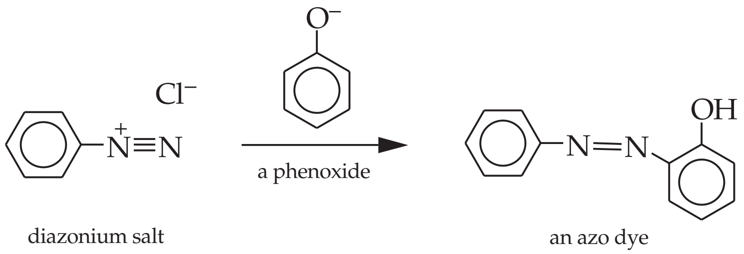


Congo Red

Azo dyes An azo dye is defined by having an azo linkage (–N=N–) as part of its chromophore. Azo dyes are made in two steps. First, a primary aromatic amine is reacted to give a diazonium salt, as shown in Equation 1. Second, the diazonium salt is reacted (coupled) with a strongly activated aromatic system, such as phenoxide, as shown in Equation 2.

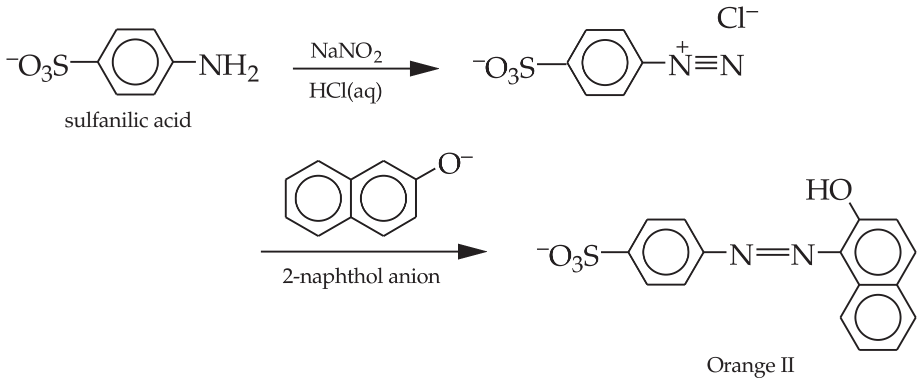


(Eq. 1)



(Eq. 2)

When sulfanilic acid and 2-naphthol are used, Orange II is formed, as shown in Equation 3.

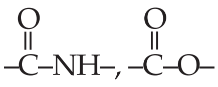
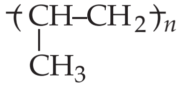


(Eq. 3)

Bonding of Dyes with Fabrics Dyes are bonded to fabrics in a variety of ways, depending on what functional groups are available on the fabric surface and how the auxochromes and other functional groups on the dye molecule interact with them. Hydrogen bonding is important if the dye or the fabric contains –OH or $-NH_2$ groups. Polar attractions occur if both the fabric and the dye have charged functional groups.

Some synthetic fabrics are so nonpolar they are difficult to dye. For example, dyes must be dissolved in molten polypropylene before the polypropylene is extruded into fibers. Table 2 gives a general indication of dyeing properties.

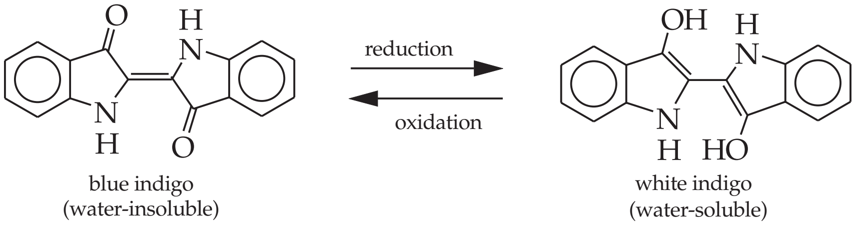
Table 2 Ease of dyeing

fabric	*functional groups*	*ease of dyeing*
wool, silk	$-OH, -SH, -{}^+NH_3, -COO^-$	very easy
cotton, linen	$-OH$	moderately easy
nylon, polyester	 $-\overset{\overset{O}{\|}}{C}-NH-,\ -\overset{\overset{O}{\|}}{C}-O-$	difficult
polypropylene	 $\left(\underset{\underset{CH_3}{\vert}}{CH}-CH_2\right)_n$	very difficult (requires dye dissolved in molten polymer)

For a dye to be permanent, or **fast**, it must penetrate the cloth fiber and bond strongly to the functional groups on the fiber molecules. Wool and silk are proteins with large numbers of highly polar functional groups and irregular, porous surfaces. These fabrics are most easily dyed and most easily stained. Cotton also has fibers with an irregular, porous surface, although its –OH groups do not bond to dyes as strongly as $–COO^-$ and $–^+NH_3$ groups on silk and wool.

Cloth can be dyed by either direct or ingrain dyeing. **Direct dyeing** occurs when a cloth strip is immersed into a solution of a dye and the dye adheres to the cloth. **Ingrain dyeing** occurs when the dye is synthesized in the presence of the cloth, so the dye is formed within the cloth.

When the most stable form of a dye is insoluble in water, but another form is soluble, the dye can be applied to cloth in its soluble form. After the water is removed, the soluble form is converted to the insoluble form to give the permanent color. For example, indigo exists in a soluble reduced form called white indigo because it lacks the intense blue color of indigo. Air oxidation converts white indigo to the insoluble blue form, as shown in Equation 4.



(Eq. 4)

In practice, the stable water-insoluble blue indigo is mixed with a reducing agent and converted to white indigo. White indigo dissolves in water and is easily applied to cloth. As the cloth dries, air oxidation converts white indigo to blue indigo, which is fast because it is insoluble in water. Rinsing the cloth with water when only part of the white indigo has been oxidized produces faded denim. The excess white indigo dissolves in the rinse water and is removed from the cloth.

Action of Bleaching Agents

Bleaching agents such as sodium hypochlorite (NaOCl) oxidize stains to lighten or remove them. Many dyes are also easily oxidized by NaOCl, destroying the chromophores. Reducing agents can also bleach some dyes. Sodium hydrosulfite ($Na_2S_2O_4$) reduces azo groups to two amino groups, thus disrupting the chromophore.

In this experiment, you will prepare Orange II, an azo dye. You will use Orange II, Malachite Green, and Congo Red to dye cotton cloth. You will treat the dyed cloths to determine the effect of bleaching agents. Finally, you will dye cotton cloth with a colorless reduced indigo and observe the effect as air oxidizes the dye to a colored compound.

Equipment

2 beakers, 50-mL
4 beakers, 100-mL
2 beakers, 150-mL
Büchner funnel, with adapter
clamp, three-fingered*
16 cotton cloth strips
25-mL Erlenmeyer flask
125-mL filter flask,
with vacuum tubing
filter paper, to fit Büchner funnel
forceps
glass rod*
glass stirring rod
10-mL graduated cylinder
100-mL graduated cylinder
hot plate
magnetic stirrer
magnetic stir bar
microspatula
Pasteur pipet, with latex bulb
4 Pasteur pipets[†][‡]
pneumatic trough[†][§]
support stand*
30 × 100-mm test tube
75 × 150-mm test tube
thermometer, –10 to 260 °C
1.0-mL transfer pipet

*for drying apparatus, Figure 3(a)
[†] for drying apparatus, Figure 3(b)
[‡] or glass tubing or glass rods
[§] or other deep tray

Reagents and Properties

substance	*quantity*	*molar mass (g/mol)*	*mp (°C)*
acetic acid, glacial	1 mL		
ammonium hydroxide, conc.	5 mL		
Congo Red	0.2 g	696.67	
hydrochloric acid, conc.	7 mL	36.46	
indigo, blue	0.1 g	262.27	
iron(II) sulfate $\cdot$ 7H_2O	0.5 g	278.02	
Malachite Green $\cdot$ HCl	0.1 g	382.94	
2-naphthol	0.35 g	144.17	122–123
Orange II*		350.33	
sodium carbonate	0.35 g		
sodium chloride	3.6 g		
sodium hydrosulfite	0.5	174.11	
sodium hydroxide, 10%	45 mL		
sodium hypochlorite, 5%	5 mL	74.44	
sodium nitrite	0.2 g	69.00	
sodium sulfate	0.2 g		
sulfanilic acid	0.4 g	173.19	

*product

Preview

- Prepare solutions of Malachite Green and Congo Red to direct-dye cotton cloth
- Diazotize sulfanilic acid with sodium nitrite and HCl for use in making Orange II
- Prepare a basic solution of 2-naphthol for use in making Orange II

- Ingrain dye cotton cloth by dipping cloth first in basic 2-naphthol, then in diazotized sulfanilic acid
- Prepare Orange II by mixing diazotized sulfanilic acid and basic 2-naphthol
- Direct-dye cotton cloth with Orange II using three methods
- Bleach dyed cotton using sodium hypochlorite
- Bleach dyed cotton using sodium hydrosulfite
- Direct-dye cotton cloth with reduced indigo
- Observe effects of air oxidation on indigo-treated cloth

PROCEDURE

Caution: Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

Always use caution in the laboratory. Many chemicals are potentially harmful. Follow safety precautions given for all reagents used in this experiment. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.

1. Direct Dyeing with Malachite Green and Congo Red

Caution: Malachite Green • HCl is toxic. Congo Red is toxic and irritating. Sodium carbonate (Na_2CO_3) is irritating.

Obtain six strips of cotton cloth from your laboratory instructor. Set up one of the drying apparatuses shown in Figure 3.

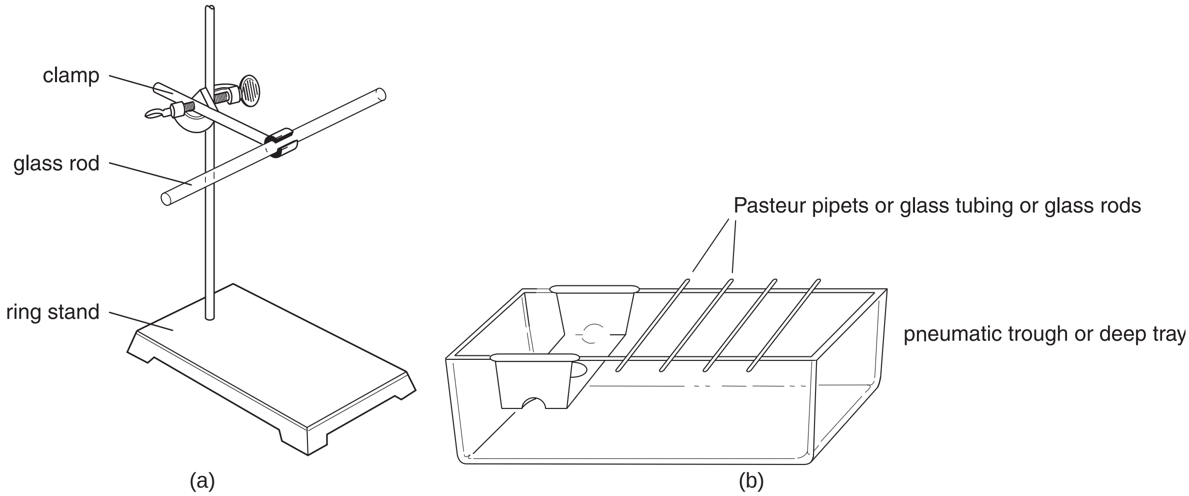


Figure 3 Drying apparatus for cotton strips (a) using a ring stand; (b) using a pneumatic trough

Label two 150-mL beakers “Malachite Green” and “Congo Red”, respectively. Add approximately 100 mg of Malachite Green and 75 mL of distilled or deionized water to the “Malachite Green” beaker. [NOTE 1] Mix to dissolve the dye.

NOTE 1: Do not weigh the dyes. Approximate the amounts from demonstration samples supplied by your laboratory instructor.

Add approximately 200 mg of Na_2CO_3 and 75 mL of water to the “Congo Red” beaker. Then add about 200 mg of Congo Red. Stir to dissolve the dye.

Use a hot plate to heat the solutions to boiling. Add 3 cotton strips to each beaker. Heat for 2 min.

Remove the strips. Rinse them in running water. Note the color retention of the cloth. Lay the wet strips over a horizontal glass rod to dry. Do not use aluminum rods because they will cause discoloration.

2. Synthesizing Orange II for Ingrain and Direct Dyeing

A. Diazotizating Sulfanilic Acid

Caution: Sulfanilic acid and sodium carbonate (Na_2CO_3) are irritating. Sodium nitrite ($NaNO_2$) is toxic and an oxidizer. Concentrated hydrochloric acid (HCl) is toxic.

Place 0.15 g of Na_2CO_3 and 0.40 g of sulfanilic acid into a 25-mL Erlenmeyer flask. Add 5.0 mL of distilled or deionized water. Warm the flask on a hot plate until the solids dissolve.

Prepare an ice-water bath using a 100-mL beaker. Cool the sulfanilic acid solution in the ice-water bath.

Place 0.2 g of $NaNO_2$ into a 30 × 100-mm test tube. Add 1 mL of water. Shake the tube to dissolve the $NaNO_2$.

Add the $NaNO_2$ solution to the cooled sulfanilic acid solution.

Place 3 g of crushed ice and 0.5 mL of concentrated HCl into a 50-mL beaker. Slowly add the sulfanilic acid/sodium nitrite solution with gentle stirring. [NOTE 2]

NOTE 2: The diazonium salt may stay in solution or it may separate as a fine suspension.

B. Coupling with 2-Naphthol and Ingrain Dyeing

Caution: 2-Naphthol and Orange II are irritating. Sodium hydroxide (NaOH) is toxic and corrosive.

Obtain eight strips of cotton cloth from your laboratory instructor.

Add 20 mL of 10% NaOH to a 50-mL beaker. Dissolve 0.35 g of 2-naphthol in the 10% NaOH. If necessary, warm the beaker on a hot plate to dissolve the 2-naphthol.

Once the solid has dissolved, cool the solution in the ice-water bath.

For ingrain dyeing, dip three strips of cotton cloth in the 2-naphthol solution. Allow excess solution to drip off the cloth. Then dip each strip in the diazotized sulfanilic acid solution from Part A. [NOTE 3]

NOTE 3: Some Orange II color will remain in the diazotized sulfanilic acid solution.

Again, allow excess solution to drip off the cloth. Briefly rinse the strips with running water. Hang the strips over the glass rod to dry.

Place the beaker of 2-naphthol solution on a magnetic stirrer. Add a stir bar. Stir the solution at low speed.

Use a glass stirring rod to stir the diazotized sulfanilic acid solution from Part A. Pour the diazotized sulfanilic acid solution *slowly* into the 2-naphthol solution.

Stir the mixture for 5 min. Then cool the solution in the ice-water bath.

Using a Pasteur pipet, slowly add 20–25 drops of concentrated HCl to the solution, with stirring, to precipitate the red dye.

Using a Büchner funnel, collect the product by vacuum filtration.

Prepare a saturated NaCl solution by adding 3.6 g of NaCl to 10 mL of water. Pour the NaCl solution into the Büchner funnel to rinse the dye.

C. Direct Dyeing with Orange II

Caution: Acetic acid is corrosive. Sodium sulfate (Na_2SO_4) is irritating.

Label three 100-mL beakers 1–3, respectively. Add 50 mL of water to beakers 1 and 2. Add 25 mL of water and 25 mL of 10% NaOH to beaker 3.

Using the demonstration amount of Malachite Green as a guide, add approximately 100 mg of Orange II to each beaker.

Prepare a buffer solution by adding 1 mL of acetic acid and approximately 200 mg of Na_2SO_4 to beaker 2.

Use a hot plate to heat the three solutions to boiling. Add a cotton strip to each beaker. Heat for 2 min.

Remove the beakers from the hot plate.

Label another 100-mL beaker as beaker 4. Add 50 mL of water to beaker 4. Move the beaker to a ***fume hood***. Then carefully add 6 mL of concentrated HCl to beaker 4.

Remove the strip from beaker 3. Put the cloth strip dyed in beaker 3 into the acid solution to fix the dye. Let it sit for 2 min.

Rinse the strips from all three beakers in running water. Note the color retention of the cloth. Lay the wet strips over a horizontal glass rod to dry.

Compare the three strips. Dye two additional strips in the best dye solution. Rinse the strips and hang them up to dry.

3. Oxidation and Reduction of Dyes on Fabric

A. Hypochlorite Oxidation

Caution: Sodium hypochlorite (NaOCl) is corrosive and an oxidizer.

Place 45 mL of water into a 100-mL beaker. Heat the water to 50–60 °C. Add 5 mL of bleach (5% NaOCl).

Place one strip each of cloth dyed with Malachite Green, Congo Red, ingrain Orange II, and direct-dyed Orange II into the beaker. Allow them to soak for 10 min.

Remove the strips and rinse them thoroughly with running water. Hang them up to dry.

B. Hydrosulfite Reduction

Caution: Sodium hydrosulfite ($Na_2S_2O_4$) is flammable. Keep away from flames or other heat sources.

Place 50 mL of water into a 100-mL beaker. Heat the water to 50–60 °C. Dissolve 0.5 g of $Na_2S_2O_4$ in the hot water.

Place one strip each of cloth dyed with Malachite Green, Congo Red, ingrain Orange II, and direct-dyed Orange II into the beaker. Allow them to soak for 10 min.

Remove the strips and rinse them thoroughly with running water. Hang them up to dry.

4. Dyeing with Indigo

Caution: Indigo and iron(II) sulfate ($FeSO_4$) are irritating. Concentrated ammonium hydroxide (NH_4OH) is corrosive.

Obtain two strips of cotton cloth from your laboratory instructor.

Prepare a hot-water bath by placing 100 mL of water into a 150-mL beaker. Heat the water to boiling.

Place 0.5 g of iron(II) sulfate and 100 mg of blue indigo into a large test tube. Add 5 mL of water and 5 mL of concentrated NH_4OH.

Swirl and heat the test tube in the hot-water bath for 1–3 min to convert the indigo into its soluble form. Allow the solution to settle 10–15 s. Decant the liquid into a 100-mL beaker.

Add two strips of cotton cloth to the beaker. Stir the strips a few seconds to saturate them. Then hang them up to air-oxidize. Note the time.

Rinse one strip with water after 1 min of oxidation. Hang it back up to dry. Rinse the other strip after 30 min. Hang it back up to dry. At the end of the laboratory period, wash both strips to determine whether the dye is fast.

5. Cleaning Up

Use the labeled collection containers provided by your laboratory instructor. Use dilute HCl to remove any residue or stain left in the indigo procedure. Clean your glassware with soap or detergent.

Caution: Wash your hands with soap or detergent before leaving the laboratory.

Post-Laboratory Questions

1. Which direct dyeing procedure worked best for Orange II? Briefly explain.
2. Compare ingrain dyeing and direct dyeing with Orange II. Which worked better? Propose a reason for this result.
3. What effect did sodium hypochlorite have on each of the dyed cotton strips?
4. What effect did sodium hydrosulfite have on each of the dyed cotton strips?
5. Compare and describe the differences in indigo oxidation when the cotton strips were rinsed after 1 min and after 30 min.

NAME SECTION DATE

SYNT 730/Dyes and Dyeing

Pre-Laboratory Assignment

Use your text or other sources to supplement the Background Information.

1. This experiment uses cotton fabric as the medium for testing dyes. Draw a small segment of the molecular structure of cellulose, the principal constituent of cotton.

2. Propose the kinds of attractive forces that might bind Congo Red to cotton fabric.

3. Which of the dyes used in this experiment are azo dyes? Why does this name apply?

4. Predict the products that result when Orange II is subjected to an oxidizing agent such as bleach. Similarly, predict the products from reduction of Orange II with sodium hydrosulfite.

5. Why is the anion of 2-naphthol used in the synthesis of Orange II?

6. Polypropylene fabrics are not easily dyed. How would you produce a brightly colored polypropylene fabric?

7. Show how Congo Red might be synthesized using azo coupling.

8. Looking at the structures of blue indigo and white indigo, how can you tell that white indigo has been reduced?

9. Why is white indigo soluble in a basic solution?

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