Experiment: Synthesis of an Azo dye: 1-(4-hydroxyphenylazo)-2-naphthol

Objectives:
1. Know the properties of the Azo Dye;
2. Know the Synthesis of an Azo Dye, especially 1-(4-hydroxyphenylazo)-2-naphthol.

Principle:
To prepare the azo dye 1-(4-hydroxyphenylazo)-2-naphthol by the diazonium coupling reaction of naphthalen-2-ol with the benzenediazonium ion obtained from 4-aminophenol.

Materials & Apparatus:
Sodium hydroxide; Sodium nitrite(III); 4-Aminophenol Naphthalen-2-ol; Concentrated hydrochloric acid.
150mL Conical flask; Suction flask; 100mL Conical flask(2pcs); 50mL Beaker(2pcs);
Droppers; Buchner funnel; Weighing balance; Glass rods; Watch glass; Filter paper.
Procedure & Phenomena (including the figures of Experiment devices):

Step 1. Prepare 30mL of ~10% sodium hydroxide solution in a 150mL conical flask.

Step 2. Weigh 1.44g of naphthalen-2-ol (0.01mol) and dissolve it into the sodium hydroxide solution. Stir the mixture until completely dissolve. Cool the solution with an ice-water bath.

Step 3. Prepare the benzenediazonium salt solution:

1) Dissolve accurately approximately 0.70g of NaNO₂ (0.01mol) in 5mL of water.

2) Put accurately approximately 1.20g of 4-aminophenol (0.01mol) into 45mL of water in a 100mL conical flask. Add slowly 12mL of concentrated hydrochloric acid and stir the mixture until the 4-aminophenol is dissolved completely.

3) Cool the 4-aminophenol solution in an ice-water bath. Some 4-aminophenol may precipitate out upon cooling. While keeping the solution at 0°C add the sodium nitrate (III) solution slowly with a dropper. The mixture should be well-stirred during addition. When the addition is completed, stir the mixture for another 2~3 minutes. The slightly turbid pale grey solution is the benzenediazonium salt solution.

4) To the alkaline naphthalene-2-ol solution add the benzenediazonium salt solution slowly. The addition takes about 5 minutes. The reaction mixture should be stirred efficiently and cooled in an ice-water bath during the addition.

5) When the addition is completed, stir the mixture at 0°C for 5~10 minutes.

6) Filter the mixture by suction filtration. Wash the product on the Buchner funnel with a small amount of cold water. Dry the product on the Buchner funnel with the suction turning on for a few minutes.

7) Transfer the product to a watch glass. Allow the product to dry for 1~2 days. Weigh the product and determine the percentage yield for the reaction.

8) Determine the melting-point of the product. Compare the melting-point with the literature value of 197~198°C.
Experiment Records & Data Processing:

Theoretical yield:

\[ m = 0.01 \text{ mol} \times 264 \text{ g mol}^{-1} = 2.64 \text{ g} \]

Discussions:

1. Naphthalene-2-ol dissolves well in sodium hydroxide solution but not in pure water and dilute acids, why?

   That’s because when dissolved in sodium hydroxide it becomes a kind of salt. On top of that, naphthalene-2-ol is a slightly acid. So it can’t be dissolved well in water and dilute acids.

2. Why is it advisable to prepare the alkaline naphthalene-2-ol solution before prepare the benzenediazonium salt solution?

   If we convert the order of adding, then we cannot get the T.M. that we want. Instead of the unwanted acid products.