Experiments in Dyes and Dyeing Means to better understand the nature of intermolecular forces

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Abstract

The nature of intermolecular forces is responsible for a vast number of phenomena in our everyday life. It can explain for example, trends in solubility, differences in boiling points, adsorption effects (chromatography) and many other observations.

Our teaching experience shows that it is not easy to explain this issue to students of all levels, but better understanding can be achieved through experimentation. One of the most effective practical experiences we offer our students at BIU or in high schools deals with dyeing fibers with synthetic or natural dyes. We supply our students with pieces of cloth comprised of several different kinds of fibers ("multifiber"). They also receive a series of dyes (in the University some of the dyes are synthesized by the students). We then let them be involved in the process of dyeing. Immediately, one can notice that certain fibers bind some dyes better than others. Discussions and results' sheets follow the experimental work and a better understanding of the nature of the intermolecular forces involved is achieved.

Besides showing the connection of the dyeing results to intermolecular forces, such a workshop on dyes and dyeing, gives also its' participants an opportunity to focus on issues which are not dealt with, in the main curriculum in Chemistry. These include: the history of dyes and dyeing; natural dyes vs. synthetic dyes; chemical nature of dyes; do we synthesize dyes or extract them from natural sources? and differences between dyes for fabrics and other kinds of coloring materials (food dyes, hair colors, paints, etc).

In this article we present four dyeing experiments. For each experiment we specify its context to the curriculum and to which grades it is appropriate. All the experiments use only milligrams of dyes and can be performed personally or in "stations".

INTRODUCTION

Classification of fibers

In general, fibers can be either natural or synthetic. The two natural fibers that are most used and famous are wool and cotton. The most common synthetic fibers used in clothing are: Cellulose esters (cotton derivatives), Polyamides (Nylon 6,6, Nylon 6 etc), Acrylics (Orlon) and Polyesters (Dacron, Terylene etc.). The chemical structures of these six fiber types are shown in Figure 1.

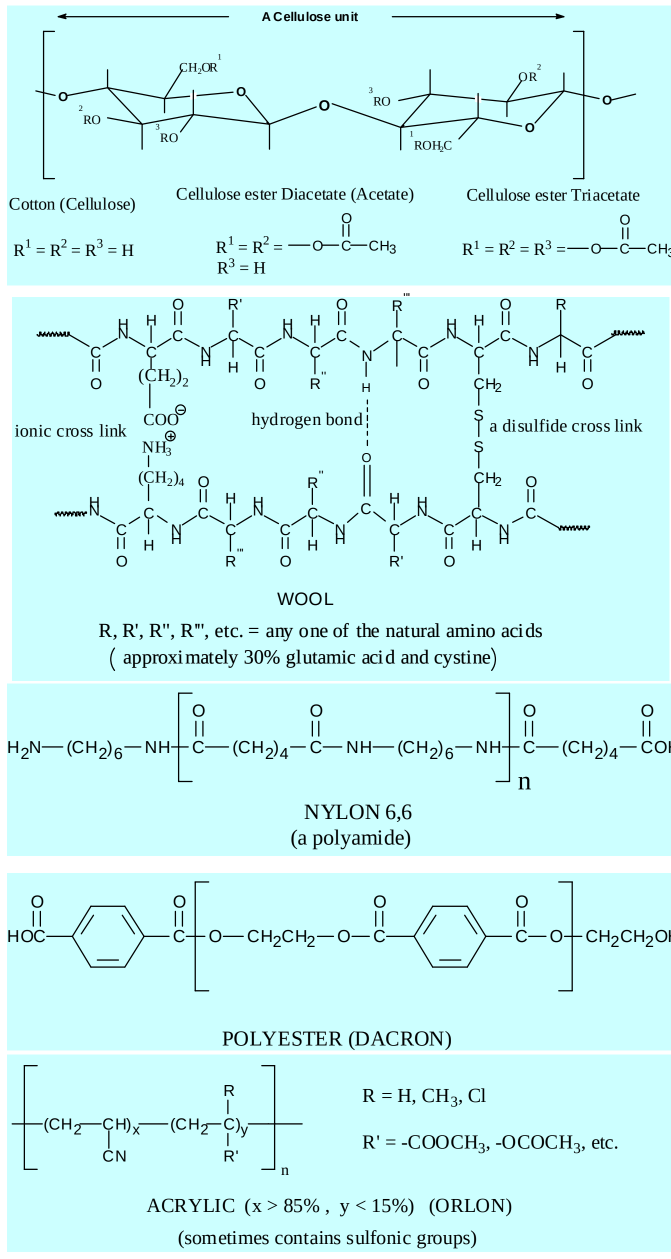

Figure. 1 The six main fibers.

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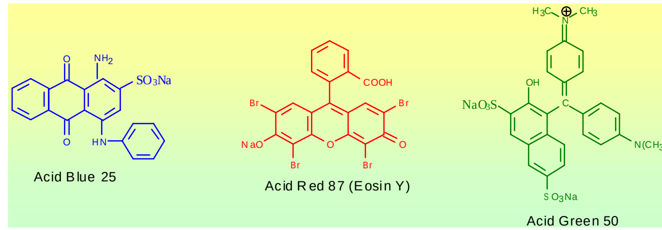
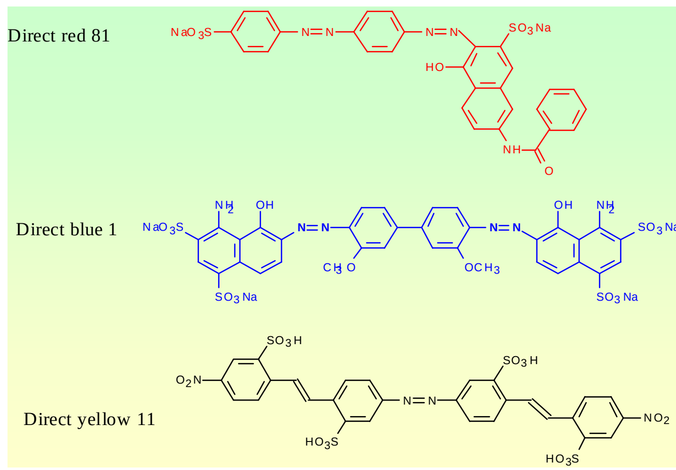
Dyes

As with fibers, dyes can also be either natural or synthetic. Both types though are organic molecules with specific functional groups that act as chromophors. The fiber dyes are characterized by three major criteria:

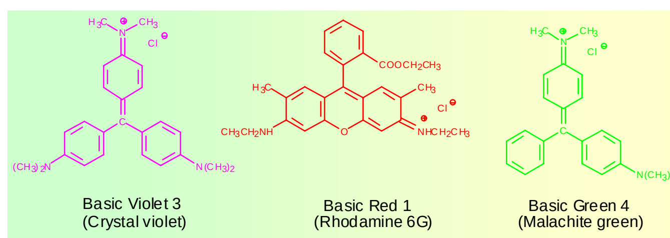
1) *According to their solubility in water.* Many dyes are ionic organic hydrophilic compounds, which dissolve well in water to form clear aqueous solutions. Other dyes are hydrophobic with low water solubility. These dyes tend to form dispersions when introduced into water. Environmental restrictions dictate that in the instructional laboratories we should work only with water based dyes.
2) *According to their chemical nature or the way they are applied to the fiber.* This classification is the most used by industry dyers, and many "commercial" names of dyes are given according to this classification. For example: Acid red 87, Disperse yellow 3 etc. Thus we can find the following common types of dyes:
   1. *Acid dyes* – These are anionic organic compounds that are applied to the fiber from acidic solutions. Acid dyes are mostly used for dyeing natural and synthetic polyamides (wool and nylon). The acid dyes that we use in our experiments are the following ones: Acid blue 25, Acid red 87, Acid green 50 and Acid violet 49. The term "acid" means that the dyeing process is done in an acidic solution.
   2. *Direct dyes* – These are anionic dyes having a good affinity (substantivity) for cellulose fiber. These dyes are normally applied from aqueous dye baths (sometimes containing also an electrolyte). Here are the structures of three direct dyes that are used in our experiments.
   3. *Basic dyes* – Organic ammonium salts. Are applied to the fiber either directly from w ater solutions or from acid solutions. Basic dyes are substantive to silk but used a lot in dyeing acrylic fibers. The three following basic dyes we use in our experiments are:
   4. *Disperse dyes* – These neutral organic compounds which have low water solubility, were developed for dyeing acetate rayon. In the past they had a small market but with the rising of the synthetics afterWorldWar II, they became very important. In our experiments disperse yellow 3 is used.
   5. *Vat dyes* – These are ancient dyes, insoluble in water, that on reduction (with sodium hydrosulfite) form compounds that are soluble in basic solutions. When cotton or other fiber is immersed in such solutions it absorbs the reduced dyestuff, which, on exposure to air, is oxidized; thus forming again the original insoluble compound which is trapped now within the fiber itself. The most known vat dye is INDIGO (see later).
   6. *Azoic dyes* – Organic compounds that contain (as other dyes from other groups), the azo (—N=N—) functional group. The synthesis of the dye can be done directly in the fiber by mixing the two components that form the azo group. Mostly used with cotton.
   7. *Reactive dyes* – These are the most recent developed dyes. Dye molecules react with the functional



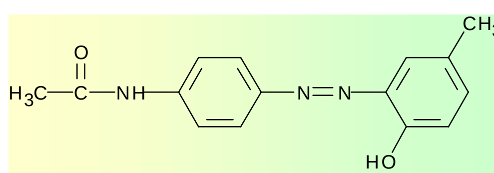
Acid dyes.



Direct dyes.



Basic dyes.



Disperse yellow 3.

groups of the fiber to forming thus a chemical bond (for example, an esteric bond with cotton).
3) *According to the functional group responsible for the color.*

The interactions between the fiber and the dye

In order to get the desired color, the dye molecules should have strong affinity to the fiber (called also *substantivity* to the fiber). This affinity is based mostly on intermolecular forces such as: *ionic bonds, hydrogen bonds van-der-Waals* bonds, and *covalent bonds* (only in the case of reactive dyes).

Experimental

Materials: The fibers we use in most cases are the six major types mentioned before: (wool, cotton, etc). These are squared pieces, ca. 5 × 5 cm, of each individual type, or *multifibers (6, 8 or 12)* in which the six major fibers (or more) are weaved together on one 5 × 5 cm piece (see figure 2). The dyes are organic synthetic compounds, which are readily available from many sources.We purchase both, fibers and dyes, from Testfabrics(*).

The recommended method of the dyeing activity is to use "stations". Each station is dedicated to one type of dyes. Acid dyes are used in Station # 1, direct dyes in station # 2, and so on. In the stations 25-50 mL beakers are used. Alternatively each student (or a couple of students) can get a small vial of each of the dyeing baths (**). It is recommended to prepare the dyeing baths before the actual lab. time and not let the students prepare it. Carefulness should be practiced in order not to let the dyes get in contact with the skin.

General dyeing procedure

The "dyeing bath" is usually a 25 or 50 mL beaker containing approximately 10-15 mg of dye in 25-30 mL of distilled water (tap water is fine too). If microvials are used a mother stock solution with the appropriate quantities should be prepared and its contents distributed to the microvials. The dyeing solution is heated to 50-80°C on a hot plate, and a piece of fiber is immersed into it for 1-3 minutes.Then the piece of fiber is pulled out of the bath, with tweezers, well rinsed with water and dried.

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(**) www.micrecol.de
www.microchem.de/moya1D.html
www.microchem.de/moya2D.html
www.microchem.de/moya3D.html
www.microchem.de/moya3aD.html
www.microchem.de/moya3bD.html
www.microchem.de/moya3cD.html

Figure 2. Multifiber 6 used in the dyeing experiments.

Experiment # 1 – Dyeing with Acid dyes

The purpose of the experiment (and how it can be related to the curriculum)

This experiment can be associated with the subject of ***intermolecular forces***. It emphasizes the trend of ionic materials (dyes) to be attracted to ionic substrates (protonated fibers). The experiment also relates to polymers (fibers) and some characteristics of these can be focused on through it.
The purposes of this experiment are:

1) To understand how an acid dye is adsorbed to the fiber.
2) To show that the interaction between the dye and the fiber is based on intermolecular forces.
3) To be familiar with the kind of compounds (polymers) that comprise the most used fibers in clothing.
4) To show examples of ionic organic compounds (dyes).
5) To understand on what principles we choose the appropriate dye for a typical fiber

The experiment is most suitable to the higher grades of high-school (ages 15-18), and of course to undergraduates.

Experimental

Prepare a dyeing baths for each acid dye you want to use (see above) by adding 10-15 mg of the solid dye to a 50 mL beaker (For stations. If "personal" baths are preferred, use micro vials to which few milliliters from the stock solution are added). Add to the beaker few drops of concentrated acetic acid and heat to 50-80°C. With the aid of a tweezers insert a piece of multifiber 6 to each of the baths and let it stay there for 1-2 minutes. After that take the fiber piece out of the bath

Figure 3. Pieces of multifiber 6, dyed with acid red 81, acid blue 25, acid green 50, direct red 81 and direct blue 1 (2 cotton, 3 nylon, 6 wool).

with the pincette, (hold a paper towel underneath the fiber in order to prevent spillage of dye droplets on the bench or floor). Rinse the dyed fiber well with tap water and let it dry in the air.

Results

Some of the dyeing results (for Acid blue 25 and Acid red 81) are shown in Figure 3. It is clearly seen that the acid dyes are only substantive to wool and nylon. Other fibers give light shades at the most. The results are explained as follows: In acid solutions (in which the dyeing is performed), the amino groups of wool and nylon are protonated to form ammonium salts. These positively charged ions form *ionic* (*intermolecular*) bonds with the anionic dye groups and thus only these fibers are dyed.

Experiment # 2 – Dyeing with Direct dyes

The purpose of the experiment (and how it can be related to the curriculum)

As in experiment # 1 this experiment too is associated with the subject of *intermolecular forces* and fits undergraduates and 15-18 years old students. But this time not only the ionic-ionic bonds interaction are important but hydrogen and van der waals too.

Experimental

Similar to experiment 1, but *without adding the acetic acid into the dyeing baths.*

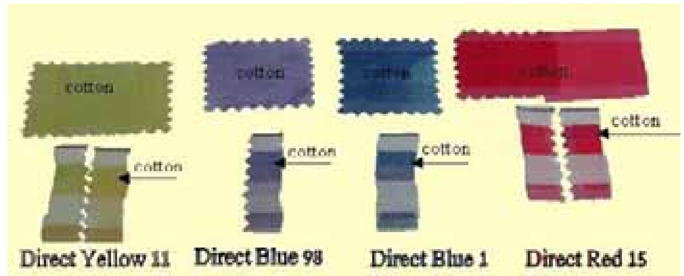


Figure 4. Pieces of cotton dyed with 4 Direct Dyes (compare Figure 3).

Results

Some results are shown in Figure 4 and show that direct dyes are dyeing well wool nylon and cotton. Since the dyes are anionic in nature it is understood why they "inter molecu - lary" bond well to wool and nylon. However they are substantive to cotton for which acid dyes are not effective. The bonding to cotton is through *hydrogen and v.d.w. bonds.* Ionic bonds are impossible since cotton is non-ionic. It is important to note though that the structure of the dyes is playing here also some role. All four dyes used are "long" molecules and they "fit" with the cotton long sugar chains.

Experiment # 3 – Dyeing with Basic and disperse dyes

The purpose of the experiment (and how it can be related to the curriculum)

Similar to experiment # 1. Here the dyes are attached to the fiber by dipole-dipole interactions (Basic dyes) or van der Waals interactions (Disperse dye). This experiment when combined with the former two dyeing experiments gives a broad picture of all the possible intermolecular interactions between dyes and fibers. This experiment is best suitable for students aged 15-18 that take chemistry as a major subject in their studies. It is noteworthy to indicate that this experiment (and experiments 1 and 2) can be offered to the students as enquiry experiments or mini projects.

Figure 5. Three pieces of Orlon dyed with three dye types under the same conditions.

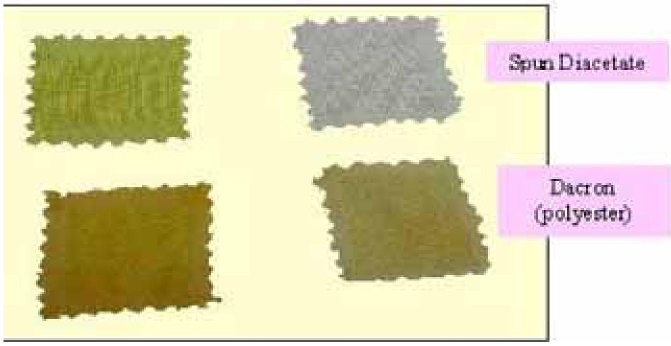


Figure 6. Spun acetate and Dacron, dyed with the two yellow dyes: disperse 3 and direct 11.

Experimental note

See experiments 1 and 2. Here especially squared individual fiber pieces can be used for comparison. Note that the disperse yellow dye is not soluble in water.

Results

Basic dyes

Basic dyes are almost the only dyes which are substantive to acrylics (orlon). Nevertheless it is not so obvious when a piece of multifiber 6 is used in the dyeing process. The reason for that stems from the fact that wool and nylon are well dyed with basic dyes and the orlon looks fainter relative to that. Therefore another experiment is done in which orlon pieces are seperately dyed (with three diferent red dyes). These results which are presented in Figure 5, show that orlon is well dyed by basic red but not with either acid red or direct red. The substantivity of basic dyes to acrylic fibers can be explained by ionic bonds between the positive nitrogen groups with sulfonate end groups on the fibers (which are being introduced occasionally into the orlon in the process of its preparation). Another intermolecular interaction possible, is between the positively charged nitrogens on the dye molecules and the negative dipole on the nitrile groups that are part of the fiber.

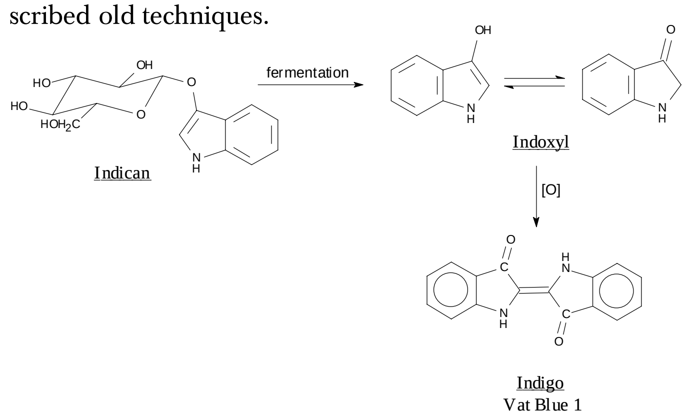
Disperse dye

Besides wool and nylon that have affinity even to the disperse dye, a nice yellow color is obtained with dacron (polyester) and cellulose acetate (which is also a kind of polyester). This is shown in figure 6. The hydrophobic polyesters can be dyed only by the hydrophobic (disperse) dyes. The intermolecular forces in these cases are v.d.w. forces and the rule "like dissolves like" is demonstrated.

Experiment # 4 – Vat dye – Indigo

Short background

Indigo has been the most famous and important of all dyes. The dyers of antiquity knew it and it is still in great demand providing for the very popular, always fashionable blue jeans. In the past, indigo came from the leaves of the *Indigofera* plants that were cultivated in India and other places. Indigo was present in the leaves as a glycoside called indican. The leaves were put in vats containing water and were let to ferment. As a result a soluble indoxyl was liberated from the glucose part and its solution was transferred to large open vats in which it was oxidized by air to indigo. The insoluble indigo was then precipitated, filtered off, and dried. Between the years 1890-1900 several syntheses of indigo were accomplished and since then, it is no more supplied by the described old techniques.



Dyeing with Indigo is described in figure 7 and the result follows (figure 8).

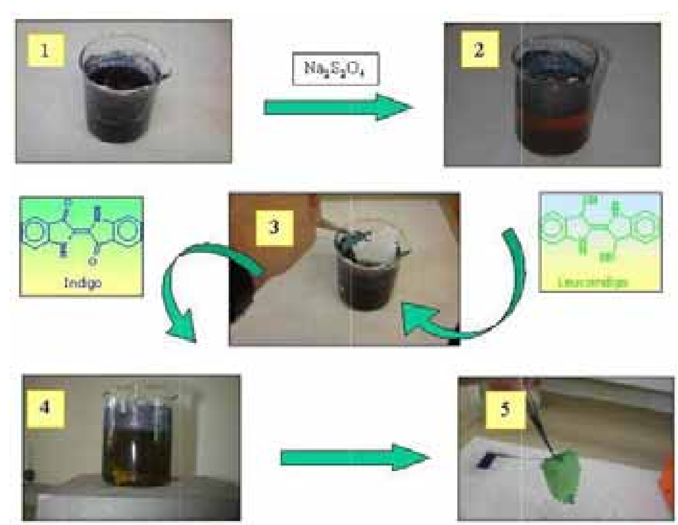
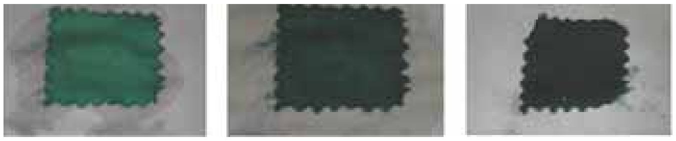


Figure 7. Dyeing a piece of cotton with Indigo. (1). A solution of Indigo in water (insoluble) is prepared. (2). $Na_2S_2O_4$ is added and reduction to leucoindigo occurs. (3). A piece of cotton is immersed into the warm solution. (4). The fiber is left in the bath for 1-2 minutes. (5). The cotton piece is taken out, rinsed and put on a white paper. At this stage the coton has no blue colour since leucoindigo is colourless.



After 1 minute After 2 minutes After 3 minutes

Figure 8. The result of dyeing a piece of cotton with Indigo. After standing for a short time in the air, a permanent deep blue colour is obtained. This is caused by back oxidation of leucoindigo to the blue indigo (figure 7).

The purpose of the experiment (and how it can be related to the curriculum)

The purposes of this experiment are:

1) To demonstrate how the "Blue-Jeans" get their blue color.
2) To show how the dyeing mechanism involves Oxidation and Reduction processes.
3) To show the dependence of the solubility on structure (Intermolecular forces). While the Indigo is insoluble in water, its' reduced form, leucoindigo (which has two hydroxyl groups), is soluble.

The experiment with all the mechanism and explanations is most suitable to the higher grades of high-school (ages 15-18). But it will also be enjoyable and attractive to younger students.

Experimental

1. Into a 50 mL beaker introduce: 0.1 g of indigo, 0.5 g of Sodium hydrosulfite and 0.1 g of NaOH. Mix the contents and heat on a hot plate to 80-100°C (with stirring).
2. Add to the bath a piece of cotton (and a piece of gabardine wool) and let it dye for 1-2 minutes.
3. Take the piece(s) of fiber out of the bath (with tweezers), rinse well with water and put it on a white towel paper. Watch what happens.

Remarks

1. Quantities can be modified according to the beaker size. (Reduced by five for example when a 10 mL beaker is used).
2. Sodium hydrosulfite ($Na_2S_2O_4$) contains sometimes small amounts of decomposed by products, which spread an unpleasant smell. The hydrosulfite should therefore be kept tight close. It is preferred to use a fresh material for the reduction.
3. Several dips of the fiber will give it a darker shade. The shade of the color can be manipulated by the number of dips and immersion time.

After standing for a short time in the air, a permanent deep blue colour is obtained. This is caused by back oxidation of leucoindigo to the blue indigo (Figure 7). ◩

References

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