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Thermochromicity in Wool Dyed with 6-Bromoindigo Depends on the Presence and Identity of a Solvent

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Abstract: The thermochromic effect of wool dyed with 6-bromoindigo was found to depend on both heat and a solvent. The dyed fabric must be immersed in a solvent while heating for a color change from purple to blue to occur. Ethanol was the most effective solvent in causing the color change. Water was effective as well. 1-Butanol caused a slight color change, while toluene was completely ineffective. These results are interpreted as interaction of the solvent with both the wool surface and adsorbed dye molecular aggregates, causing changes in the size of large red aggregates to smaller blue ones. The mildest conditions for the color change, immersion in water at 60 °C, are so easily obtained that it is possible that ancient dyers knew of this as a finishing process for their dyeing, or knew to avoid post-dyeing heat treatment.

Keywords: 6-bromoindigo; thermochromic; dyeing; wool; Tyrian purple

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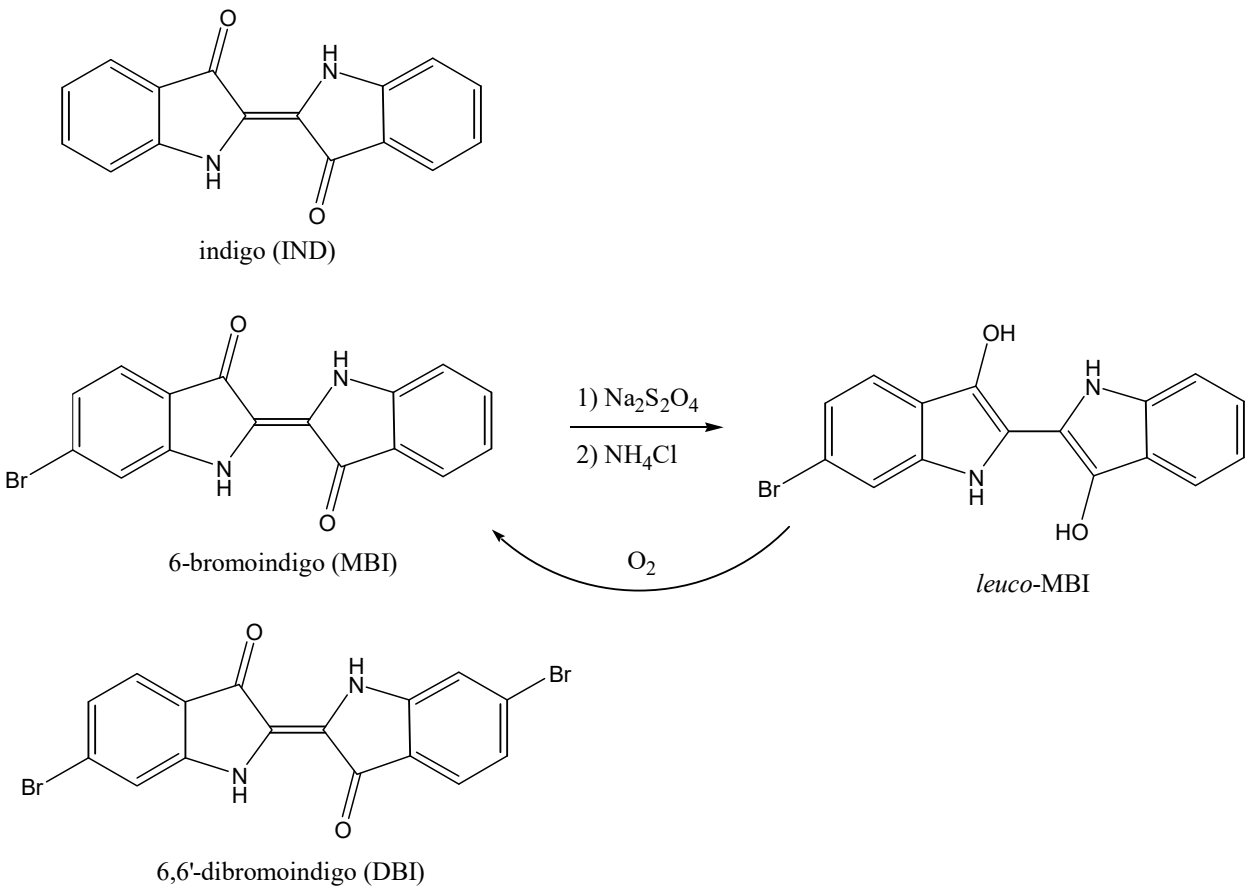
1. Introduction

Shellfish purple (also known as Tyrian purple) is a pigment that is produced from the hypobranchial glands of a variety of shellfish when exposed to sunlight. The precursor in the gland is tyriverdin, which is yellow; as it is converted to the dark-purple 6,6′-dibromoindigo (DBI), the gland fluid undergoes a striking variety of color changes [1]. The color changes were first observed in detail by Mr. William Cole in 1685, when he studied the hypobranchial gland fluid from the dog whelk *Nucella lapillus* when spread onto linen or silk. The initial yellow color changes to light green, then deep green, sea-green, Watchet blue, purplish red and finally deep purple red, "beyond which the sun can do no more" [2]. The similar color changes which take place using the Mediterranean species *Hexaplex trunculus* (*Murex trunculus*) or *Bolinus brandaris* (*Murex brandaris*) were illustrated by A. and G. de Negri in 1876 and reproduced by Cooksey and Sinclair [3]. In contrast to this riot of colors, dilute solutions in dimethyl sulfoxide of the major components of shellfish purple, indigo (IND), 6-bromoindigo (MBI) and DBI (Scheme 1), are all blue [4]. Reflectance spectra of wool dyed with IND, MBI and DBI show a wide diversity. Indigo shows a maximum absorption at 650 nm and 6,6′-dibromoindigo at 527 nm. 6-Bromoindigo in low concentration is similar to indigo, but at higher concentration, moves towards the maximum of 6,6′-dibromoindigo [5]. The study of 6,6′-dibromoindigo was extended to cover the dyeing of six fabrics [3]. The shades of purple obtained are shown in Table 1. The result was illustrated in Plate 14.4 of reference [3].



Scheme 1. Structures of IND, MBI and DBI. Additionally, reduction of the colored oxidized form of MBI by sodium dithionite followed by neutralization by ammonium chloride, giving its reduced colorless *leuco* form, and oxidation of the *leuco* form by aerial oxygen back to the colored oxidized form.

Table 1. Shades of purple obtained from dyeing of fabrics with DBI [3].

Fabric	Color
Cellulose acetate	Strong purple
Cotton	Light purple
Nylon	Moderate violet
Polyester	Pale purple
Acrylic	Light purplish blue
Wool	Moderate reddish purple

More extensive studies were later undertaken using 13 fabrics [6,7]. It was first reported by Ziderman in 2003 that wool dyed with MBI, originally blue–violet in color, turns blue upon heating at 60 °C in water [8]. These conditions are so simple to obtain that ancient dyers may have used this as a post-dyeing treatment, or they may have avoided such treatment, since it would change a rare and costly purple garment into a more commonplace blue one. There are many potential causes for this thermochromic effect, one of which is a chemical change in MBI: MBI could be thermally decomposing through the loss of a bromine atom, resulting in the production of IND. IND is known to dye wool blue. Although the reduced colorless form—the so-called *leuco* form (Scheme 1)—of MBI is known to lose its bromine atom upon exposure to light [9–11], the oxidized colored form which ends up on the fabric is not known to photochemically or thermally decompose. However, it remained to test for thermal decomposition by extracting the dye from heated MBI-dyed fabric, and analyze the MBI for presence of IND. Another possible cause for the thermochromic effect is a physical change in MBI. The color of a substance can depend on

its crystal structure, and heat can cause a change to this crystal morphology. A complicating factor is that dye molecules may interact with a fabric via several modes of interaction, such as hydrogen bonding, dipole–dipole interactions and van der Waals forces. This makes it difficult to model and, thus, predict the final color of a dyeing. For example, MBI is a blue–violet color in bulk form, but may dye fabrics a wide variety of shades of blue and purple [7].Therefore, it is possible that heat could affect bulk MBI differently than MBI adsorbed onto a fabric.

1.1. Effect of Heat on Both Wool-Adsorbed and Crystalline MBI

The theory that MBI adsorbed onto wool loses its bromine atom to become IND, and thus causes the wool to turn blue, was put to rest by an extraction experiment. Wool dyed with MBI was heated in boiling water, and the resulting blue fabric was extracted with a hot solvent to remove the dye from the wool. Analysis with high-performance liquid chromatography (HPLC) showed negligible conversion of MBI to IND [12]. Thus, the color change is not due to a chemical change in the dye molecule.

It has been reported that crystalline MBI undergoes a change in both physical form and color upon heating to the vaporization point, and after deposition of the vapor [8]. We reproduced those experiments, and found that MBI does not change color upon heating to its sublimation point, around 200 °C. Additionally, the vapor-deposition experiment was repeated. The crystals of MBI obtained did appear to the eye to be of a different crystalline form, but X-ray crystallographic analysis showed them to be identical with crystals obtained by recrystallization from a solvent [12,13]. In addition, a crystal obtained from recrystallization [13] did not change in color or in crystallographic properties upon heating to 77 °C [12], a temperature at which MBI-dyed wool rapidly turns blue in water. Thus, it was concluded that MBI, unadsorbed onto wool, does not undergo a heat-induced physical change that would affect its color.

Further experiments and analyses were based on the idea that a physical change to the fabric-adsorbed MBI was occurring. Additionally, IND and DBI were included in the experiments, because they are so closely related in structure to MBI.

1.2. Divergent Behavior of MBI and DBI

Not only did we successfully reproduce the thermochromic effect seen before for MBI-dyed wool, but we also found that many other MBI-dyed fabrics show this same bluing effect upon heating in water [7]. When the thermochromic studies were extended to IND- and DBI-dyed fabrics, our expectation was that they might show this same thermochromic effect, due to similarities in chemical structure between the three indigoids. However, it was found that a wide variety of IND-dyed fabrics showed little, if any, color change upon heating in water, while DBI-dyed fabrics turned distinctly more *red* in hue [7]. Figure 1 shows four wool fabric pieces, each dyed with MBI or DBI, plus the effect of heating the fabrics in water.

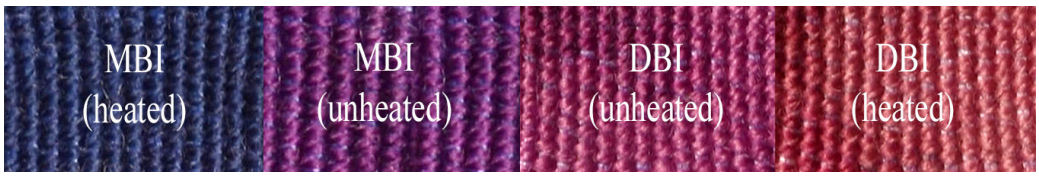


Figure 1. (Left to right) MBI-dyed wool heated in water, MBI-dyed wool with no heat application, DBI-dyed wool with no heat application, DBI-dyed wool heated in water [7].

1.3. Reflectance Spectroscopic Analysis

The color changes were studied qualitatively using reflectance spectroscopy. As has been seen before [5], we found that the reflectance spectra of MBI-dyed wool and DBI-dyed wool are remarkably similar in their spectral features; each has a reflectance minimum around 530 nm (which equates with perceived red color), and a shoulder on this main minimum around 620 nm (which equates with perceived blue color) (Figure 2) [7]. This

means that both types of dyed wool appear to be a mix of blue and red, or similar shades of purple. After boiling in water for 10 min, the reflectance spectra change markedly: MBI-dyed wool shows a loss of the "red" 530 nm minimum, and production of one main "blue" minimum at 620 nm. To the eye, the fabric is now true blue. Conversely, the DBI-dyed wool loses its "blue" shoulder at 620 nm, and is left with only a "red" minimum at 520 nm. To the eye, the fabric is now very red. On the other hand, the spectrum of IND-dyed wool does not change much after heating in water.

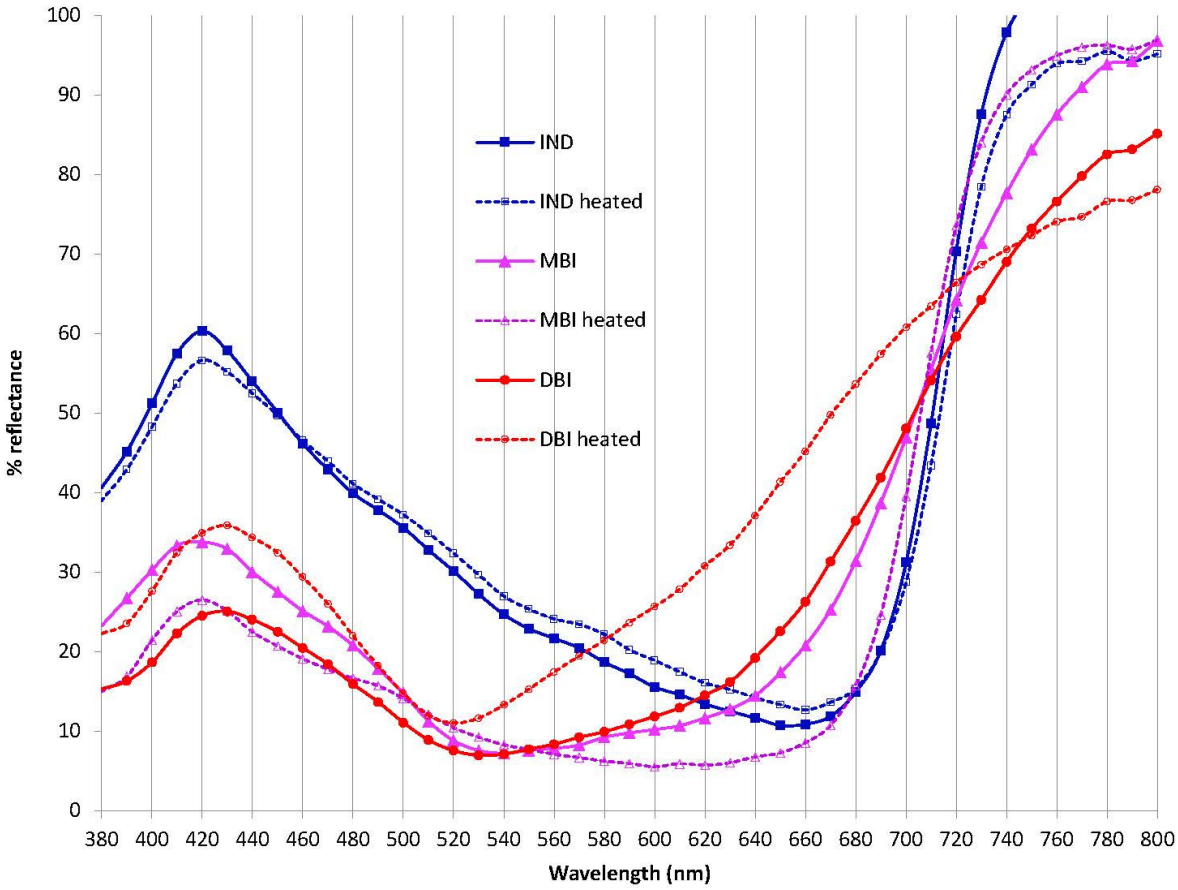


Figure 2. Reflectance spectra of wool dyed with IND, MBI or DBI, showing the effect of heating in water.

1.4. Colorimetric Analysis

The color changes were analyzed a quantitative basis using colorimetric analysis [14]. The shade of MBI- and DBI-dyed wool is determined by the red and blue hue components. For MBI-dyed wool, the blue and red components are of approximately equal magnitude, while for DBI-dyed wool of a similar dye loading, the red component is significantly greater than the blue. The consequence is that MBI-dyed wool can be considered truly purple in color, while DBI-dyed wool is a more reddish purple. Colorimetric analysis of the dyed fabrics after heating in water shows rearrangement of blue and red hue components: for MBI-dyed wool, the magnitude of the red component decreases markedly, and the blue component drops very little, while for DBI-dyed wool, the red hue component rises and the blue component drops [12].

1.5. Generality of the Thermochromic Effect

Another important finding was that the thermochromic effect is not dependent on the type of fabric. Two other natural fabrics (silk and cotton) plus ten synthetic fabrics, when dyed with MBI or DBI, also showed the same type of thermochromicity [7]. Noteworthy is the fact that IND-dyed fabrics showed very little, if any, thermochromic effects. This

mirrors the behavior of IND-dyed wool mentioned earlier. Again, it was seen that strong thermochromic effects on a wide variety of fabrics are only seen with the two brominated indigoids.

1.6. Analysis of Dyed Carbon Nanotubes Using Transmission Electron Microscopy

Taken together, the reflectance spectra and colorimetric analyses suggest that both MBI and DBI, after dispersion on fabrics in their *leuco* forms and aerial oxidation, exist predominantly in two physically distinct types of dye aggregates, one that gives rise to a red color, and the other, a blue color. It was envisioned that they might be viewed using transmission electron microscopy (TEM). However, the dimensions of a fabric fiber are so much greater than that of a possible submicroscopic dye aggregate, it was impossible to analyze a dyed fabric directly. Recourse was made to use carbon nanotubes as a fabric surrogate. Carbon nanotubes are tiny strand-like pieces of tubular graphite, about five nanometers in diameter by about three micrometers in length. Since it had been established above that the thermochromic effect is not substrate-specific, it was hoped that the *leuco* form of MBI could be deposited on carbon nanotubes in the same way as on fabrics, and that whatever happened on the dyed fabrics in hot water would also happen on the dyed nanotubes in hot water. The black nanotubes were vat-dyed with MBI in the usual manner, giving nanotubes which were still black, but which showed a metallic luster [7]. The dyed nanotubes showed dark spots clinging to the surface of the nanotubes, and the spots contained bromine atoms, as determined using energy dispersive X-ray analysis (Figure 3). Therefore, the spots were considered to be dye aggregates, containing dozens or hundreds of individual dye molecules. The aggregates were measured to give a size distribution plot that showed them to be mostly 12 nanometers in diameter, plus a lesser amount with a diameter of 27 nanometers. These dyed nanotubes were heated in water, causing disappearance of the larger aggregates, and appearance of a new set of aggregates only seven nanometers in diameter. Thus far, these results were consonant with the reflectance spectra and colorimetric analyses, which suggested the presence of two dye aggregates, a red type and a blue type. After the TEM analysis, it appeared that the red aggregates were the larger type, while the blue aggregates were the smaller type. If that were the case, then nanotubes dyed with DBI should give the opposite behavior, where smaller aggregates should be converted to larger ones upon heating in water. This turned out to be just the case: DBI-dyed nanotubes before heating showed aggregates of mostly seven nanometers in diameter, while after heating, they became mostly 17 nanometers and larger [12]. The reflectance, colorimetric and TEM analyses summarized above all strongly suggest that size redistribution of dye aggregates is the cause of the thermochromic effects detailed here.

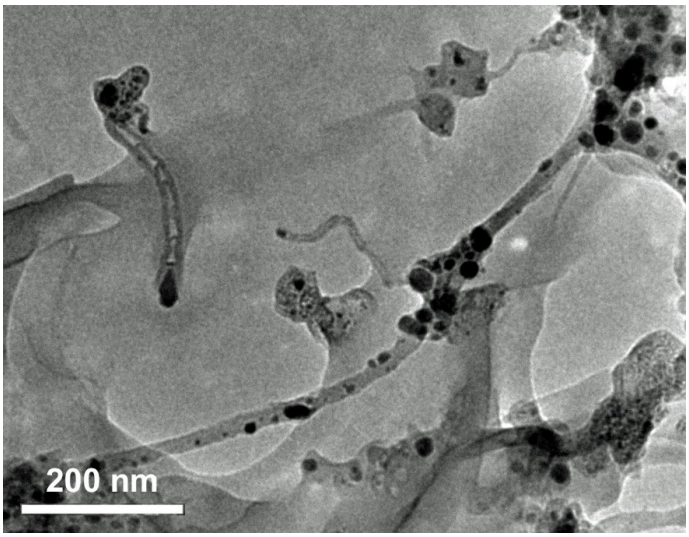


Figure 3. MBI-dyed carbon nanotubes [7].

2. Materials and Methods

2.1. Solvents

Water was distilled. Ethanol (≥99.5%), 1-butanol (≥99.4%) and toluene (≥99.5%) were obtained from Sigma-Aldrich.

2.2. Treatment of the Dyed Fabric with a Solvent

MBI-dyed wool was cut into squares of approximately 1 in. X 1in., and immersed completely in one of the solvents above, which had been pre-heated to 80 °C, for 20 min. The fabric was removed from the solvent, allowed to dry completely, and analyzed using colorimetry.

2.3. Colorimetric Analysis

In the CIELAB color space [14], a color is characterized by three attributes: the lightness, L^*, the hue, which is given by two values, a^* and b^*, and the saturation, which is indicated by the absolute values of a^* and b^*. The L^* value varies from 0 (black) to 100 (white), while the a^* value is positive for redness and negative for greenness, and the b^* value is positive for yellowness and negative for blueness. High absolute values of a^* and b^* signify a highly saturated or vivid color, while low absolute values of these mean a color towards gray. The ΔE^*_{ab} value [14] is a measure of the difference between two colors, and is the Euclidean distance between two points in the three-dimensional color space. The formula for ΔE^*_{ab} is the square root of the sum of the squares of the changes in L^*, a^* and b^* values. CIELAB data were collected with a Konica Minolta Color Reader CR-10 tristimulus colorimeter, with a 10 mm/8 mm aperture/viewing area, 8° illumination angle with CIE standard illuminant D_{65} and CIE 10° viewing angle with diffuse viewing. All samples were backed with an opaque white background. At least six different areas of the front and back of the fabric were analyzed, to give an average reading that had a very small standard deviation.

3. Results and Discussion

We now continue our study to answer several questions about the thermochromic effect: Does the dyed fabric change color over time at room temperature in the absence of water? Does the color-changed fabric revert to its original color over time? Is water a necessary component of the thermochromic effect, or would it happen with just heat? If water is necessary, is it the only solvent that causes a color change? If other solvents are effective at causing the color change, is there a dependence on a fundamental property of the solvent, such as molecular polarity?

Enough time has passed since the production of the dyed fabrics and their heated counterparts to answer the first two questions posed above. Dyed fabrics stored for at least five years under ambient conditions did not change from their original colors, as judged by colorimetric analysis. The same is true for the dyed fabrics which had been heated in water. Thus, heat is a requirement for the color change, or perhaps the combination of water with heat is the requirement.

We proceeded by using wool dyed with MBI under standard conditions [12]. Three different samples of MBI-dyed wool were employed, each dyed under identical conditions. Figure 4 shows a typical sample. The L^* values ranged from 28.1 to 29.1, a^* values from 24.4 to 26.9 and b^* values from −24.2 to −25.6, with standard deviations of 0.5, 1.4 and 0.7, respectively. Small pieces of this dyed fabric were immersed in four solvents, according to the conditions shown in Table 2. The piece was removed from the solvent and allowed to dry at room temperature, and analyzed using colorimetry. The ΔE^*_{ab} value refers to difference in color before and after heating. All solvents except water dissolved some of the dye from the fabric, as evidenced by a blue or violet color change to the solvent during heating.

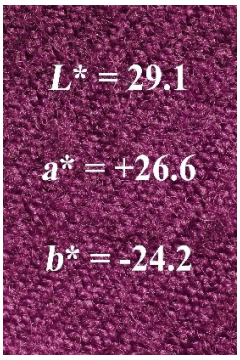


Figure 4. Wool dyed with MBI according to a standardized procedure [12].

Table 2. Effect of four solvents and heat on the color of MBI-dyed wool.

Entry	Solvent	T (°C)	Time (Min)	ΔL^*	Δa^*	Δb^*	ΔE^*_{ab}
1	H_2O	80	20	0.5	−9.8	2.2	10
2	ethanol	80	20	5.2	−19.5	1.5	20
3	1-butanol	80	20	−3.7	−4.9	3.4	7
4	toluene	80	20	0	−0.8	−0.3	0.9
5	toluene	110	100	1.1	−2.3	1.9	3.2
6	(none)	100	20	0.1	−0.3	0.3	0.4
7	(none)	100	60	0.2	−0.7	0.5	0.9
8	H_2O	r.t.	(60 days)	12.4	−4.4	4.5	14

For water (entry 1), 20 min at 80 °C was required for the fabric to exhibit its maximum color change; after 10 min, the ΔE^*_{ab} value was only 5.5, while further heating after 20 min did not change ΔE^*_{ab}. After 20 min at 80 °C, the lightness component L^* had not changed appreciably. However, the hue components a^* and b^* both lessened in magnitude; since the red-green a^* showed greater diminishment, the bluing of the fabric is due to loss of redness rather than gain of blueness (Figure 5). Three other solvents, ethanol, 1-butanol and toluene (entries 2, 3 and 4, respectively), were tested under the same conditions as water. Ethanol had an even greater effect on a^* than water: the a^* value decreased to 7.4 from its original value of 26.9, a drop of 72%. This decrease was the main determinant of the large ΔE^*_{ab} seen. 1-Butanol was less effective in causing a color change: all three color components decreased to a small extent, giving a small ΔE^*_{ab} value and a barely perceptible bluing of the color. The non-polar solvent toluene was completely ineffective at causing a color change after 20 min at 80 °C: the changes in the color components were within the standard deviations of the three values (see above), so, taking this into account, the ΔE^*_{ab} value is actually zero. Further heating in boiling toluene for 100 min (entry 5) was required for a barely perceptible color change.

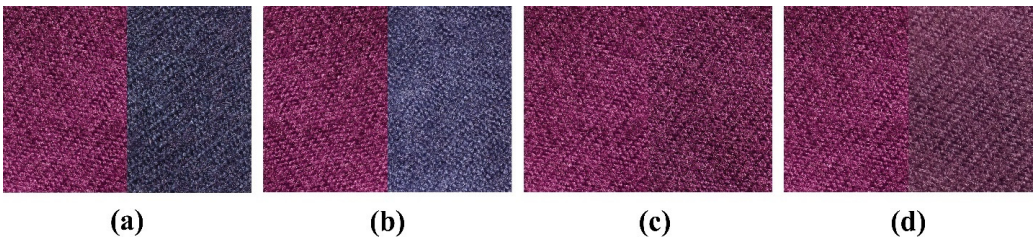


Figure 5. MBI-dyed wool from Table 2 before (left) and after (right) heating in water, ethanol and 1-butanol. (**a**) water, 80 °C; (**b**) ethanol, 80 °C; (**c**) 1-butanol, 80 °C; (**d**) water, r.t.

Table 2 also shows that heat alone is ineffective at causing a color change. Heating the dyed fabric at 100 °C for 20 min (entry 6) or 60 min (entry 7) caused no color change, as the changes in the three color components were within the standard deviation limits.

Treatment with water at room temperature for an extended period of time (entry 8) does cause an appreciable color change, but apparently the change is of a different nature than all the others: the change in the L^* value is the main determinant of ΔE^*_{ab}, and indicates significant lightening of the dyed fabric. Over such a long time period, it is possible that a chemical change to either the dye or fabric had occurred, causing the observed color change.

To summarize, both a solvent and heat are required for a color change, which appears to be irreversible. Water is the most polar of the four solvents, as measured by its dipole moment. However, ethanol was the most effective at causing the color change. Toluene is the least polar, and was ineffective at causing a color change. The more polar solvents would be expected to interact strongly with the polar surface of wool, and also with MBI through hydrogen-bond donation and acceptance. On the other hand, weakly polar solvents such as toluene would be expected to interact with MBI mainly through dispersion forces, but not strongly with the wool the MBI is adsorbed to. The solvent- and heat-induced change in the size of wool-adsorbed dye aggregates appears to involve the interaction of a polar solvent with both the wool and MBI.

4. Conclusions

The data presented here indicate that the size change of wool-adsorbed dye aggregates depends on the interaction of the solvent with both the fabric surface and the aggregates adsorbed to that surface. The sizes and shapes of molecular aggregates deposited when the reduced *leuco* form comes in contact with wool during the vatting process are expected to be different than the sizes and shapes of the oxidized dye aggregates. This is because the *leuco* form of MBI is so different in chemical structure from its oxidized colored form (Scheme 1). Thus, the colored dye aggregates resulting from exposure of the *leuco* form to oxygen in the air may be in a metastable state. The interaction of a solvent with both the dye aggregates and the fabric they are adsorbed to, at an elevated temperature, appears to be essential for the change in size of the adsorbed dye aggregates to their final, more stable sizes. The detailed mechanism of the size change, and why it occurs at all, will be the subject of further investigation.

It is possible that dyers in ancient times knew of these color changes caused by the application of both heat and water. The recipe for purple dyeing was lost and the subject of speculation for over 500 years, until the secret was discovered relatively recently [15,16]. In a study of a Coptic textile dating from the second or third century AD, which is a fragment of a purple medallion and is now in the *Österreichisches Museum für angewandte Kunst* in Vienna, it was found that the major dye, 79%, was 6-bromoindigo [17,18]. Since the color is purple rather than blue, it seems likely that the dyeing was performed without heating of the fabric in water after the final aerial oxidation step.

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