

Mechanism Involved in the Dyeing of Wool with an Oil-in-Water Microemulsion System

Roshan Paul, Conxita Solans, Pilar Erra

Departamento de Tecnología de Tensioactivos, Instituto de Investigaciones Químicas y Ambientales de Barcelona, Consejo Superior de Investigaciones Científicas, Jordi Girona 18-26-08034, Barcelona, Spain

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ABSTRACT: This article investigates the influence of oil-in-water (o/w) microemulsions, used as media for both dye solubilization and dye baths, on the dye uptake on fiber surfaces. An acetic acid solution/Synperonic L7/benzyl alcohol microemulsion system was used to solubilize a water-insoluble antimicrobial natural dye (C.I. Natural Orange 2) and to dye wool fabric at an acidic pH. The results clearly show that the dye exhaustion on the fabric took place mainly when the temperature of the dye bath promoted a change in the molecular organization of the microemulsions with the liberation of the dye solubilized in the oil droplets of the microemulsions. Although uniformly and evenly dyed fabrics were obtained, they showed very

low wash fastness. To confirm the mechanism involved and to achieve dyed fabrics with good wash-fastness properties, two different dyeing methods were also studied. The first method was dyeing at a constant low temperature, at which the o/w microemulsion remained a monophasic system; the second one was dyeing at a high temperature, at which it was transformed into a multiphase system. Both the dye exhaustion and wash fastness improved considerably for the fabrics dyed at a high temperature. Moreover, uniform and even dyeing was achieved. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 156–162, 2008

Key words: colloids; dyes/pigments; fibers; phase behavior

INTRODUCTION

Dye uptake and fixation on textiles depend on several factors such as the surface and bulk properties of the fiber, the molecular structure of the dyes, and the dye-bath media in which the dye molecules are dispersed or dissolved.¹ The water-insoluble dyes may result in nonuniform and uneven dyeing if dyeing is performed with aqueous media by the exhaustion method. In this study, the mechanism involved in dye uptake on fiber surfaces and its diffusion into the bulk was examined for textile substrates such as wool dyed with a water-insoluble dye by the exhaustion method with oil-in-water (o/w) microemulsions as the dye-solubilizing and dye-bath media.

A water-insoluble natural dye, C. I. Natural Orange 2, which can result in antimicrobial textiles² after dyeing, was used in this study. The phase

behavior of a water/Synperonic L7/benzyl alcohol system at 25°C has been previously studied (Fig. 1).³ Several authors have proposed benzyl alcohol as a carrier or as a solvent in solvent-assisted dyeing.^{4–11} However, its use as a component of an o/w microemulsion system for dye solubilization and textile dyeing has not been studied yet. Because an o/w microemulsion has been proposed to be made of three pseudophases—the oil core of the droplet, the surfactant-rich interfacial region coating the droplet, and the surrounding water continuum¹²—we have concluded that the insoluble dye is preferentially solubilized in the oil core of the droplet.

Wool fabric was used as the textile substrate in this study. The mechanism of wool dyeing has been deeply studied, and it has been proposed that the dye enters the wool fiber between the cuticle cells and later diffuses throughout the nonkeratinous regions of the cell membrane complex, the endocuticle and the intermacrofibrillar material. As the dyeing cycle advances, the dye progressively transfers from nonkeratinous regions to sulfur-rich proteins of the matrix.¹³ Wool contains both acidic and basic groups and consequently behaves as an ampholyte. At neutrality, both groups are fully ionized ($^+\text{NH}_3\text{—W—COO}^-$, where W is wool), and the net electrical charge carried by the fiber is zero. Under acidic conditions, protonation of the carboxyl group occurs, and the fiber exists as $^+\text{NH}_3\text{—W—COOH}$. When the fabric is dyed with anionic dyes at an acidic pH, the

Correspondence to: P. Erra (pesqst@iiqab.csic.es).

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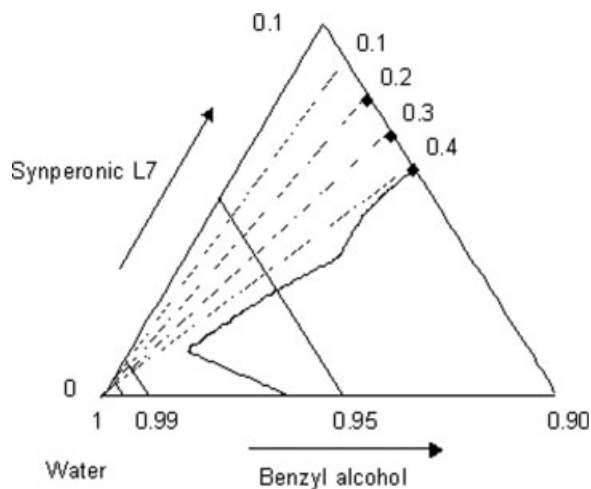


Figure 1 Enlarged water-rich region containing more than 90% water of the phase diagram of the water/Synperonic L7/benzyl alcohol system. Diamonds indicate microemulsions selected for dye solubilization with R values of 0.2, 0.3, and 0.4.

dye anions attach to the positively charged basic groups of the fiber.^{14,15}

In our previous work,³ dye uptake on wool fiber was studied with o/w microemulsions of a constant pH (5), and the water component of the o/w microemulsions was replaced by an acetate buffer. With the aim of enhancing the substantivity of the dye for wool, the dyeing process was carried out at pH 3.2 in this work. Furthermore, to confirm the mechanism involved and to produce dyed fabrics with good wash-fastness properties, two different dyeing methods were also studied. In the constant low-temperature dyeing method, the o/w microemulsion remained a monophasic system, and in the high-temperature (HT) method, it was transformed into a multiphase system.

EXPERIMENTAL

Materials

A water-insoluble natural dye, C. I. Natural Orange 2, with inherent antimicrobial properties² was purchased from Alps Industries, Ltd. (Ghaziabad, India). The main phenolic component in this dye, obtained from *Mallotus philippinensis*, is Rottlerin ($C_{30}H_{28}O_8$), and its phenolic structure³ limits the solubility in water. It was purified before use as reported earlier.³ Synperonic L7 ($C_{12-14}E_7$) was supplied by Uniqema. It is a technical-grade nonionic surfactant with a hydrocarbon chain length of 12–14 and with an average of 7 mol of ethylene oxide per surfactant molecule. Benzyl alcohol (purity > 99%) was purchased from Fluka (Seelze, Germany). Water was deionized by Milli-Q filtration. Woven worsted

Merino wool suiting fabric, supplied by Artextil S.A. (Sabadell, Spain), was cleaned by Soxhlet extraction with dichloromethane and was further rinsed with ethanol and water.

Methods

Dye-bath preparation

To carry out dyeing at an acidic pH, 0.1% (w/w) purified dye was solubilized in selected microemulsions containing a 90% acetic acid solution (10% oil and surfactant and 90% water acidified with acetic acid) at pH 3.2 with oil weight fractions [$R = \text{oil}/(\text{oil} + \text{surfactant})$] of 0.2, 0.3, and 0.4. Wool fabrics were dyed directly with these three different microemulsion compositions. Fabric samples were also dyed with microemulsions containing 99.0, 99.5, 99.6, or 99.7% acetic acid solutions containing 0.1% (w/w) dye. To prepare these microemulsions, 1% purified dye was first solubilized in microemulsions containing 90% acetic acid solutions and then diluted by the addition of an acetic acid solution.

For comparison, dyeing was also carried out in aqueous media, and this is termed the conventional method (CM). The dye was first solubilized in alkaline media, and then acetic acid was added, so the final pH of the dye bath was 3.2. After the addition of acetic acid, the dye precipitated, becoming a dispersion.

Dyeing

The wool samples were dyed with 2% shade on weight of fabric with microemulsions containing 90 or 99% acetic acid solutions and by CM. All the dyeing was carried out in a Mathis Labomat laboratory dyeing machine at a liquor ratio of 20 : 1 and pH 3.2. The fabric was wetted for 5 min in the dye bath at 30°C before dye was added and dyeing commenced. Only in the case of the microemulsions containing a 90% acetic acid solution was the fabric added directly to the dye bath, in which the dye had been previously solubilized. The temperature was then raised from 30 to 85°C over 25 min and maintained for another 60 min. During dyeing, no auxiliary chemicals or mordants were added to the dye bath. The dyed samples were divided into two sets for comparison. One set was kept unwashed, and the other was washed with water and 0.5 g/L Synperonic 91/6, a fatty alcohol ethoxylate based nonionic detergent, at a liquor ratio of 50 : 1 at 60°C for 20 min.

Constant-temperature dyeing. The wool fabric samples were dyed with a microemulsion with $R = 0.4$ containing a 99% acetic acid solution at various constant temperatures of 30, 40, 60, 70, and 85°C for 60 min of dyeing time.

HT dyeing. In the HT method, dyeing was carried out at 120°C with a microemulsion with $R = 0.4$ containing a 99.0, 99.5, 99.6, or 99.7% acetic acid solution. All other dyeing conditions were the same as before, and no wool protecting agents^{16,17} were added to the dye bath. Dyeing was also carried out by CM at a high temperature for comparison.

Dye uptake. Dye uptake was determined by the measurement of the absorbance of the diluted dye bath at the wavelength of maximum absorption (λ_{\max}) of the dye (279 nm) with a Varian Cary 300 Bio ultraviolet-visible spectrophotometer. This wavelength was chosen because it corresponded to the highest and sharpest peak. The spectrophotometer was calibrated every time for the absorbance because of the various amounts of oil in the microemulsions. The dye uptake percentage (U) was then calculated with the following equation:

$$U = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 and A_t represent the absorbances of the dye solution before the dyeing process and after time t , respectively.

K/S values

The K/S values indicate the depth of shade reflected from the dyed fabric surface. The measurements were carried out at $\lambda_{\max} = 380$ nm with a Macbeth Color-Eye 3000 spectrophotometer under illuminant D₆₅ with a 10° observer and were calculated with the Kubelka–Munk equation.

Wash fastness

The wash-fastness values of the selected samples were determined according to IWS Test Method 193, which is based on ISO 105-C06:1978 (color fastness to washing).

RESULTS AND DISCUSSION

The dye uptake as a function of time on fabrics dyed with o/w microemulsions with R values of 0.2, 0.3, and 0.4 containing 90 or 99% acetic acid solutions is shown in Figure 2(A,B). The dye uptake obtained by CM, in which the dye-bath medium was water at pH 3.2, is also included.

The dye uptake on wool from the microemulsions with R values of 0.2 and 0.3 containing 90% acetic acid solutions was very poor in the first 15 min [30–52°C; Fig. 2(A)], but it increased to around 49 and 88%, respectively, in a dyeing time of 30 min (85°C) and to 73 and 100%, respectively, at the end of dye-

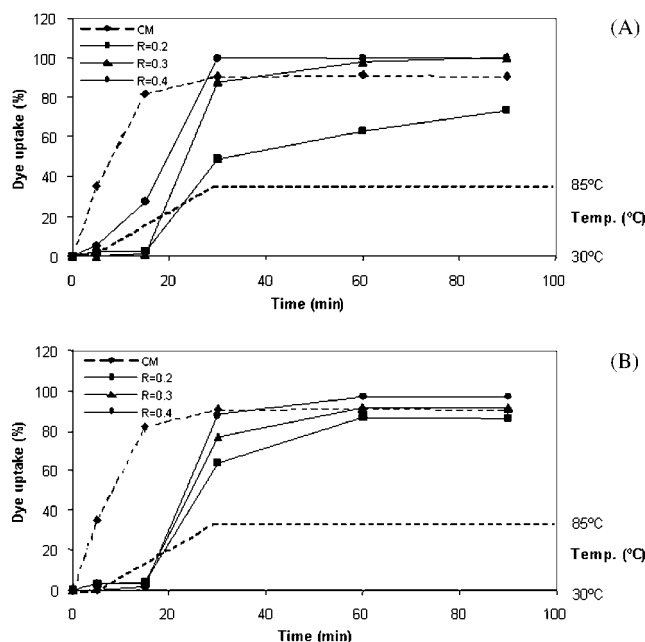


Figure 2 Dye uptake on wool as a function of the dyeing time: (A) dyeing with microemulsions containing a 90% acetic acid solution with different R values and CM and (B) dyeing with microemulsions containing a 99% acetic acid solution with different R values and CM. The temperature scale is indicated on the right ordinate axis.

ing. However, the dye uptake increased steadily to reach a maximum of 100% in 30 min in the case of the microemulsion with $R = 0.4$.

The dye uptake was also very poor in the first 15 min (30–52°C) for all the microemulsions containing a 99% acetic acid solution [Fig. 2(B)]. At a dyeing time of 30 min (85°C), the dye uptake increased to around 63, 77, and 88%, and at the end of dyeing, it was 86, 92, and 97% for R values of 0.2, 0.3, and 0.4, respectively. For CM, the dye uptake increased steadily from the start of dyeing and reached a maximum of around 91% in 30 min.

To understand the mechanism involved in the dyeing process, the phase behavior of the dye-bath microemulsions containing 90 or 99% acetic acid solutions with 0.1% (w/w) solubilized dye was studied [Fig. 3(A,B)] as a function of temperature (from 8 to 85°C).

Figure 3(A) shows that at 25°C, only the microemulsions with R values of 0.2 and 0.3 were in one liquid-phase region, whereas the one with $R = 0.4$ fell in the multiphase region. All three microemulsions showed multiphase behavior far below 85°C. The dye-uptake process could be related to the phase transition from a one-phase microemulsion to a multiphase system. When the dye bath was formed from a one-phase microemulsion ($R = 0.2$ and 0.3), in the first 15 min of dyeing, the dye might have preferentially remained in the oil core of the microemulsion droplet, resulting in a low dye uptake.

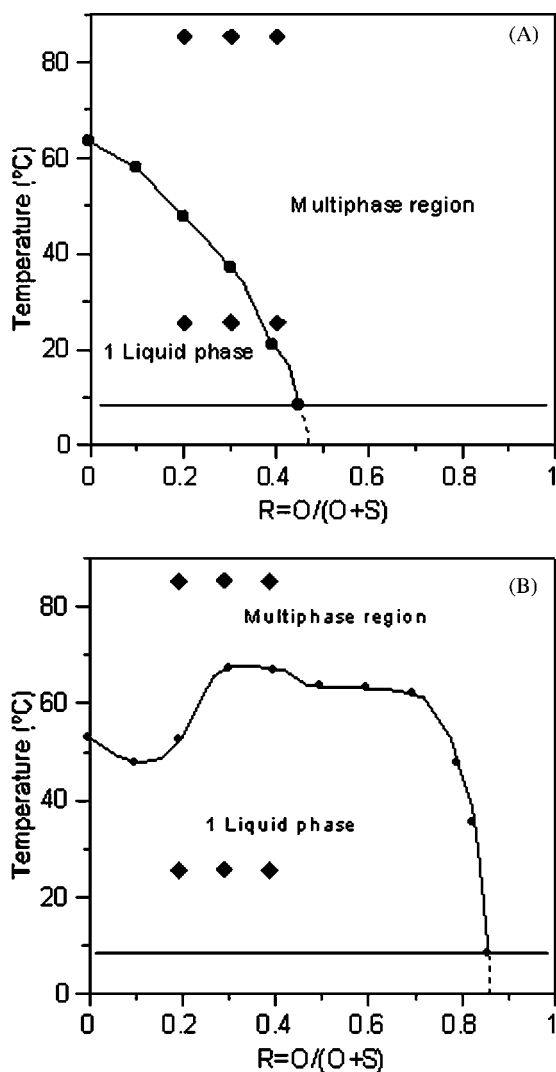


Figure 3 Phase behavior as a function of temperature and R values: acetic acid solution/Synperonic L7/benzyl alcohol systems containing 0.1% solubilized dye and (A) a 90% acetic acid solution or (B) a 99% acetic acid solution. Diamonds indicate microemulsions selected for dye solubilization with R values of 0.2, 0.3, and 0.4 at 25 and 85°C (O = oil; S = surfactant).

However, with the temperature increased to 85°C, there was a phase transition from one phase to a multiphase system with a new molecular organization, which allowed the dye to migrate to the fiber surface, thus resulting in high dye uptake. When R was 0.4, the dye-bath formulation consisted of a multiphase system, even at the start of dyeing, and so the dye uptake increased steadily [Fig. 2(A)].

Figure 3(B) shows the phase behavior of the dye-bath microemulsions containing a 99% acetic acid solution and 0.1% (w/w) solubilized dye. All the dye baths ($R = 0.2, 0.3,$ and 0.4) were in one liquid-phase region at 25°C. However, a phase transition from a one-phase microemulsion to a multiphase system took place at 50–70°C. The dye exhaustion

was very poor in the first 15 min (30–52°C), as at this temperature all dye-bath formulations consisted of one-liquid-phase microemulsions. However, the dye uptake increased considerably when the temperature was increased to 85°C because of the phase transition.

The obtained dye uptake results were very similar to those obtained previously³ with microemulsions containing a buffer solution of pH 5 instead of an acetic acid solution of pH 3.2. Therefore, it is confirmed that the molecular organization of the dye bath provided by microemulsions plays an important role in the dye uptake on a textile substrate when the dye has low substantivity for the substrate and when it is insoluble in water. Furthermore, the pH value of the dye bath has a minimum influence on the exhaustion of this dye on wool.

To determine whether the solubilized dye in the microemulsion is transferred directly from the microemulsion droplets to the substrate or a breakdown of the droplets is needed, dyeing was carried out at different constant temperatures for a period of 60 min, and the dye and benzyl alcohol exhaustion was determined (Fig. 4).

Benzyl alcohol was also adsorbed on the fabric along with the dye, and at 85°C, 100% uptake of both took place. These results are in accordance with those proposed by Beal and Corbishley,⁶ suggesting the formation of a solvent-rich layer on the surface of the fiber when benzyl alcohol is used as a solvent in solvent-assisted dyeing. The dye concentrates in this layer, thus ensuring that there is an adequate supply of the dye for the fiber surface as long as there is dye in the dye bath. The particle size of the dye is very small in this solvent layer, and thus the dye is able to diffuse more quickly into the fiber.

Moreover, it was found that the dye and benzyl alcohol uptake increased as a function of temperature, and it increased significantly only from 70°C

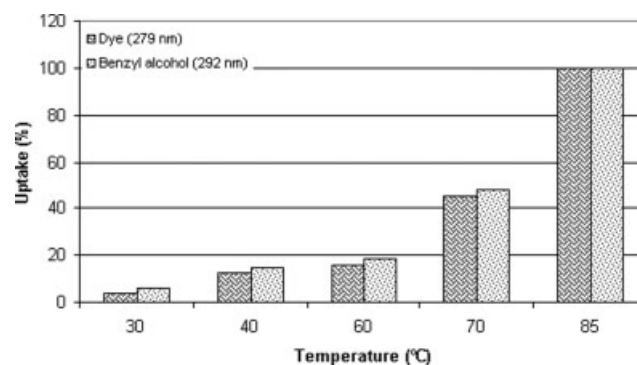


Figure 4 Maximum dye uptake ($\lambda = 279$ nm) and benzyl alcohol uptake ($\lambda = 292$ nm) for a period of 60 min in constant-temperature dyeing with a microemulsion with $R = 0.4$ containing a 99% acetic acid solution at different constant temperatures.

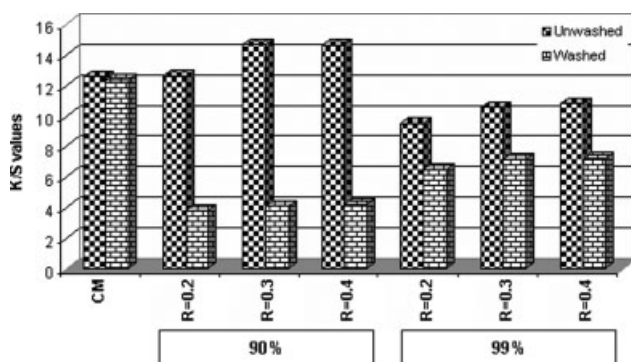


Figure 5 K/S values of unwashed and washed wool samples dyed at 85°C by microemulsions with different R values containing 90 and 99% acetic acid solutions and by CM.

onwards, as there was a phase transition from a one-phase microemulsion to a multiphase system. Therefore, it is further concluded that this phase transition and the subsequent breakdown of the microemulsion droplets promote the dye uptake.

However, high dye stripping was observed from all samples dyed at 85°C during washing (Fig. 5). This revealed that the dye diffusion into the bulk of the fibers was very low. With the aim of enhancing this diffusion and thus improving the washing fastness, dyeing was carried out by the HT method with a microemulsion with $R = 0.4$ containing a 99.0, 99.5, 99.6, or 99.7% acetic acid solution (Fig. 6). For nonreactive dyes, the thermodynamic equilibrium with wool is not established until the process of dye transfer into the keratinous regions is complete. This stage is usually not achieved for some time after the dye-bath exhaustion, and for this reason, a prolonged time at an elevated temperature is required to produce satisfactorily dyed wool.¹³

Figure 6 shows that CM produced a dye uptake of 94% in 30 min when the dyeing temperature was 120°C , and all the microemulsion dye baths showed

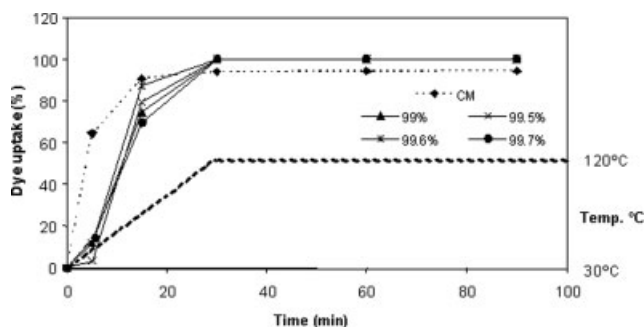


Figure 6 Dye uptake on wool dyed by the HT method with a microemulsion with $R = 0.4$ at various dilutions and by CM as a function of the dyeing time. The temperature scale is indicated on the right ordinate axis.

a similar trend with 100% dye uptake in 30 min. It is remarkable that the fabrics dyed with the microemulsion dye baths were evenly dyed. Moreover, as the pH of the dye bath was acidic, the wool damage could be minimal at this temperature. Additionally, wool can be protected from degradation at a high temperature by the addition of suitable protecting agents such as Irgasol HTW NEW (Ciba) and maleic acid derivatives.^{16,17}

Figure 5 shows the K/S values of the washed fabrics with respect to the unwashed ones dyed at 85°C with microemulsions containing 90% acetic acid solutions. As observed in the previous work,³ the surface of the fabrics showed a sticky and oily appearance even after drying. This was attributed to the formation of an aggregate on the fabric surface consisting of an oil, surfactant, and dye. After washing, a sharp decline in the color values was observed, and this indicated that the dye preferably remained on the fabric surface and that the dye diffusion into the fiber core was very poor. Therefore, microemulsions containing 90% acetic acid solutions are not recommended as dyeing media.

The decrease in the K/S values after washing was lower for the fabrics dyed with the microemulsions containing 99% acetic acid solutions (Fig. 5). After drying, these fabrics showed evenly dyed surfaces, without any sticky or oily appearance. This indicated that the dye diffusion into the fiber was much better. The unwashed and washed fabrics dyed by CM showed K/S values of 12.59 and 12.37, respectively. However, these samples showed commercially unacceptable uneven surfaces.

Figure 7 shows the K/S values of the unwashed and washed wool samples dyed at various constant temperatures. The K/S values increased as a function of the dyeing temperature in accordance with the previous results for the dye uptake. The samples dyed at 70 and 85°C showed an important decrease in the K/S values after washing, and this indicated

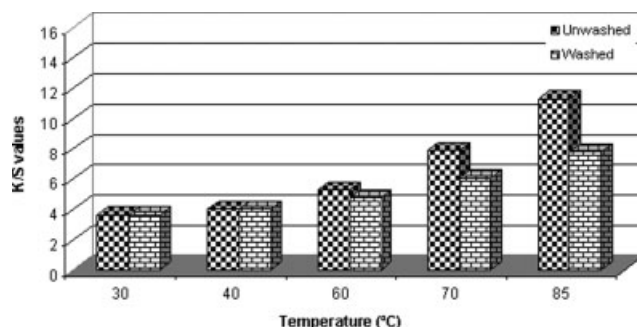


Figure 7 K/S values of unwashed and washed wool samples dyed at different constant temperatures with a microemulsion with $R = 0.4$ containing a 99% acetic acid solution.

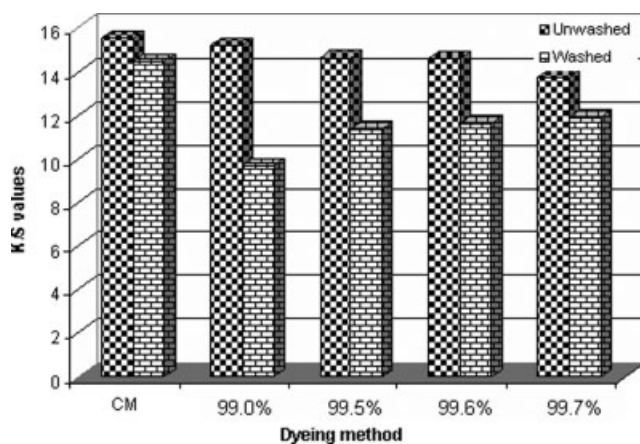


Figure 8 *K/S* values of unwashed and washed wool samples dyed by the HT method.

that the dye diffusion into the fiber occurred only partially. To confirm this, the wash liquors from the samples dyed at 70 and 85°C were analyzed spectrophotometrically, and this showed intense peaks of both the dye and benzyl alcohol. Therefore, benzyl alcohol was also stripped out of the fabric along with the dye.

The *K/S* values of unwashed and washed wool fabrics dyed by the HT method (Fig. 8) increased remarkably in all cases in comparison with dyeing at 85°C. As expected, the fabric dyed by CM showed an unevenly dyed surface after washing. It was found that dye stripping during the washing of the fabrics dyed with the microemulsion dye baths decreased as a function of the reduction of the oil content in the dye bath. This confirms that to reduce the dye stripping, the oil content in the dye bath should be minimized. The samples dyed with the microemulsion dye baths containing 99.5, 99.6, or 99.7% acetic acid solutions showed evenly dyed surfaces, and the color values after washing were on par with those of the sample dyed with CM at 85°C. Thus, the HT dyeing method can be used to develop evenly dyed fabrics of high color values in the case of water-insoluble dyes.

The wash fastness of all the samples dyed by the HT method was measured after washing. On the scale used for the change in the color of the specimens, the samples dyed with microemulsions showed a better rating of 4–5 in comparison with the sample dyed with CM, which had a rating of 4. On the scale for the staining of the undyed fabric, both cotton and wool showed a rating of 5 in all cases.

CONCLUSIONS

Wool fabrics were dyed with a water-insoluble natural dye, C.I. Natural Orange 2, after its solubilization

in microemulsions of an acetic acid solution/Synperonic L7/benzyl alcohol system containing a 90 or 99% aqueous phase. These microemulsions underwent a phase transition from one liquid phase to a multiphase system during the dyeing process at temperatures above 70°C. For this reason, the dye uptake on the fabric was lower than 20% below this temperature. However, at higher temperatures, the dye uptake increased to values higher than 80% because of a change in the molecular organization of the dye bath leading to the deposition of dye/surfactant/benzyl alcohol aggregates on the fabric surface. These aggregates were easily stripped by washing, and this indicated that the diffusion into the fiber was very poor, especially for the microemulsions with a 90% aqueous phase. Even though the microemulsions containing a 90% aqueous phase are not useful as dye-bath media, they are proposed as standard dye formulations that can be used for dyeing after proper dilution.

However, the microemulsions containing a 99% aqueous phase provided an evenly dyed fabric surface without any sticky appearance, and after being washed, the fabric maintained higher *K/S* values than fabric dyed with the microemulsions containing a 90% aqueous phase. This was due to improved dye diffusion into the fiber and the reduction in dye/surfactant/benzyl alcohol aggregate formation on the fabric surface.

For wool fabrics dyed at constant low temperatures (<60°C), at which the o/w microemulsion remained as one liquid phase, the *K/S* values were unchanged by washing, but the dye exhaustion was very poor. HT dyeing using 99.5, 99.6, or 99.7% acetic acid solutions resulted in very high dye exhaustion and fixation, providing fabrics with evenly dyed surfaces.

This article is basically a scientific contribution on the mechanism involved in dyeing processes carried out with an o/w microemulsion system. However, it also suggests new methods for textile dyeing with water-insoluble dyes through the use of adequate surfactants and oils, giving uniformly and evenly dyed wool fabrics. Furthermore, by optimization of the microemulsion dilution (>99%) and temperature (<120°C), an industrial process with high dye diffusion and fixation can be developed.

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