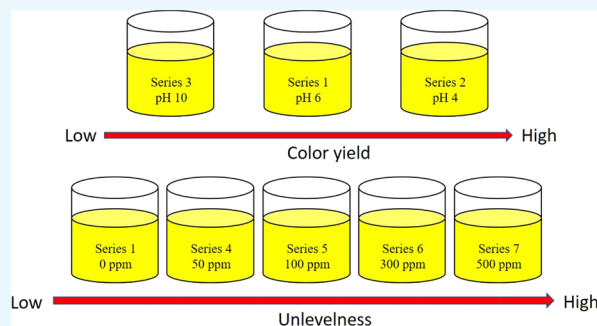


Reverse Micellar Dyeing of Cotton Fiber with Reactive Dyes: A Study of the Effect of Water pH and Hardness

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ABSTRACT: Effects of hardness and the pH value of water in a water pool on PEG-based nonionic surfactant dyeing of cotton fiber with reactive dyes in a heptane reverse micelle system were investigated in terms of the color yield, reflectance, CIE $L^*a^*b^*$ value, and unlevelness. Results reveal that the effect of the water-pool pH value on the color yield and reflectance are more significant than the effect of hardness in the water pool. The dyed fabrics under an alkaline water-pool condition obtain a lower color yield and higher reflectance percentage than those under acidic and nearly neutral conditions. The increase of hardness in a water pool has higher influence on unlevelness of dyed samples than the increase or decrease of the pH value in a water pool. The changes in hardness and the pH value in a water pool did not result in a significant change in CIE $L^*a^*b^*$ values of dyed specimens, and no chromatic change was found in dyed fabrics. Excellent washing fastness results of the dyed fabrics, guaranteeing adequate removal of unfixed dyes, assure accuracy of the results in a spectrophotometric measurement.



Excellent washing fastness results of the dyed fabrics, guaranteeing adequate removal of unfixed dyes, assure accuracy of the results in a spectrophotometric measurement.

1. INTRODUCTION

In a conventional aqueous textile dyeing process, water plays the most essential role as the medium for dyeing of natural and synthetic textile fibers. The dyeing quality and final shade of textile products are highly influenced by the quality of water used throughout the dyeing process. However, water supplied from nearly all sources contains impurities to some extent. The most common impurities are hardness, heavy metals, alkalinity, etc.^{1,2}

Water hardness can be regarded as the amount of calcium and magnesium salts presented in water, and it is expressed as of the calcium carbonate (CaCO_3) equivalent.³ The unit of measurement is parts per million (ppm). If the amount of hardness in water is less than 60 ppm, it is regarded as soft water. If the amount of hardness is more than 180 ppm, it is termed as hard water.⁴ Hard water is generally undesirable in the dyeing process since it may cause dye precipitation, promoting dye aggregation, which results in certain dyeing defects such as uneven dyeing,⁵ color specks, and loss of depth.^{2,3,6,7} In addition, hard water may interfere with solubility of the dye,⁸ alter the color of the dye, and adversely affect color appearance of textile products.⁹

Alkalinity is also one of the influential factors for conventional reactive dyeing of cotton fabrics. Reactive dyes are different from other dye classes. They rely on elevated pH (alkaline condition) to have a reaction with the hydroxyl group of cellulose, mostly by nucleophilic substitution or addition, to form covalent bonds. However, the competing reaction of the dye with hydroxide ions in the dye bath is prominent, which may produce a hydrolyzed, nonreactive form of the dye, leading to serious environmental problems due to the

production of colored effluent discharge after soaping and washing-off processes.¹⁰ To eliminate the environmental impact, works have been done on dyeing cotton at a neutral pH condition^{11–13} or by low add-on technology controlling the wet-pick up.¹⁴ Novel methods, such as chemical grafting of the disperse dye onto polyacrylonitrile,¹⁵ dyeing of nylon 6 with extracted natural dyes from waste leaves,¹⁶ computational and experimental assessment on corona discharge surface ionization of poly(ethylene terephthalate) (PET),¹⁷ and dyeing of PET with various nanosilica particles,¹⁸ have also been investigated.

In our previous papers, we have studied feasibility of applying computerized color matching (CCM) on reverse micellar dyed cotton¹⁹ and analyzing the influence of the hydrophilic–lipophilic balance value and dye agglomeration on a reverse micellar dyeing system.^{20,21} However, influences of hardness and the pH value in water for forming a water pool in the reverse micellar nonaqueous reactive dyeing of cotton are still unknown and have not yet been reported in the literature. Therefore, this study focuses on examining the influences of water hardness and the pH value on reverse micellar dyeing of cotton for the following purposes: (i) to dye cotton fabrics with the use of reactive dyes in a reverse micellar heptane-assisted dyeing system under different water hardness and pH (acidity and alkalinity) in a water pool, (ii) to assess the color strength and unlevelness of the fabrics colored with a water pool containing deionized water and the fabric dyed with a

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water pool comprising different water hardness and pH values, (iii) to compare and assess the difference between fabrics dyed with a water pool containing deionized water and the fabric dyed with a water pool comprising different water hardness and pH values based on reflectance (R , %), color strength (K/S_{sum} value), and unlevelness (relative unlevelness index), and (iv) to evaluate the washing fastness property of dyed fabrics.

2. RESULTS AND DISCUSSION

2.1. Reflectance. **2.1.1. Reflectance at Different pH Values.** Figure 1 illustrates reflectance curves of red, blue, and yellow dyed fabrics: series 1 (pH 6 of deionized water without any pH manipulation), series 2 (pH 4, which is in an acidic condition), and series 3 (pH 10, which is in an alkaline condition). Reflectance curves of series 1 and 2 in each color were found to exhibit nearly the same reflectance percentage

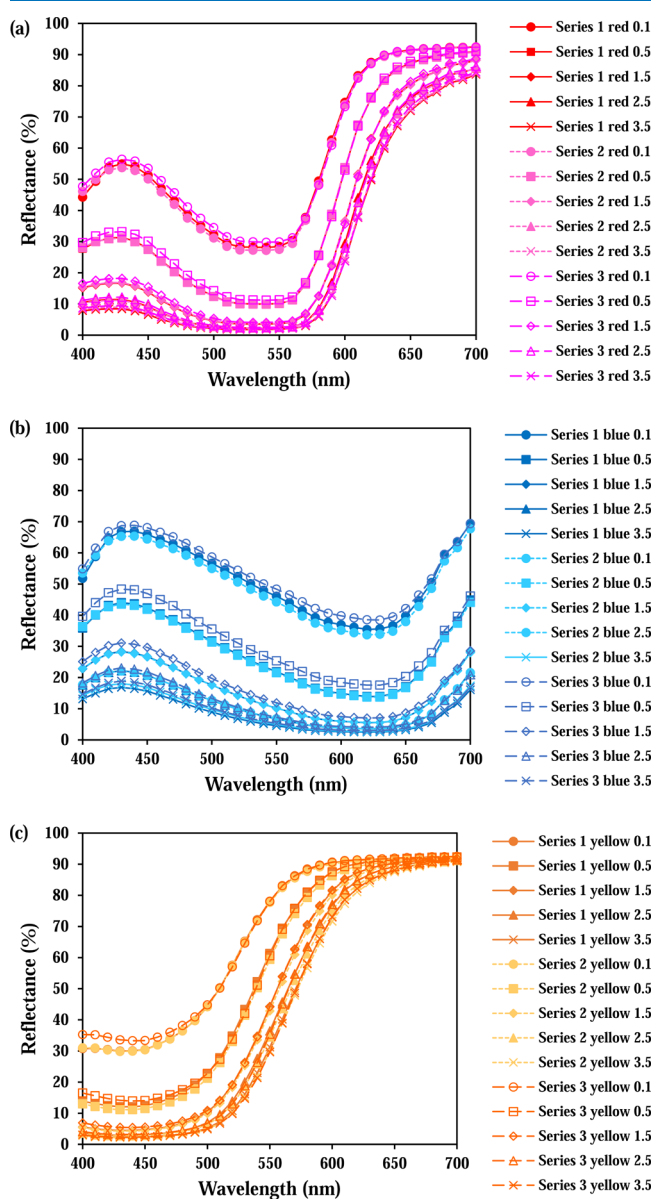


Figure 1. Curves showing the reflectance of colored cotton substrates under different pH conditions: (a) red, (b) blue, and (c) yellow colors (0.1, 0.5, 1.5, 2.5, and 3.5 represent 0.1%, 0.5%, 1.5%, 2.5%, and 3.5% o.w.f., respectively).

without noticeable differences, leading to similar final shades of the fabrics as when dyed in a PEG-based nonionic reverse micelle system. However, when the fabrics were dyed in an alkaline condition (series 3 in pH 10), the reflectance percentages of red, blue, and yellow colors are slightly higher than fabrics dyed in nearly neutral and acidic conditions (series 1 and 2). As a higher reflectance percentage means lower dye absorption, this indicates that the dyeing in alkaline conditions results in a lighter shade when compared with that in nearly neutral and acidic conditions. The possible reason is alkaline hydrolysis of the dye in the core of the reverse micelle (water pool). Although the volume of the water pool is small in the core of the reverse micelle that can largely minimize the impact of dye hydrolysis, a certain degree of dye hydrolysis is inevitable when under an alkaline condition.²⁴ In addition, reflectance curves (Figure 1) are identical in shape and have their own pattern corresponding to the color. No shifting of the peak along the range of 400 to 700 nm was observed, indicating there is no chromatic change under different pH conditions.

2.1.2. Reflectance at Different Water Hardness. Figure 2 presents reflectance curves of fabrics dyed with different water hardness (ppm): series 1 (deionized water), series 4 (50 ppm), series 5 (100 ppm), series 6 (300 ppm), and series 7 (500 ppm). The results reveal that the fabric samples dyed with or without hardness in a PEG-based nonionic reverse micelle system exhibit similar reflectance curves, without noticeable variation in the reflectance percentage within 400 to 700 nm. This indicates that hardness, caused by the presence of calcium ions in the water pool, has minimal impact on the dye molecules since the volume of the water pool in the reverse micellar core is very little (0.5 mL). In addition, it was also found that the increase of hardness does not have a catastrophic effect on peak shifting of the curves and the chromatic change in the dyed fabric samples.

2.2. Color Yield. The color yield, based on K/S_{sum} values, of the colored cotton substrates is shown in Table 1. Regarding the influence of water-pool pH values (series 1 to 3) on a PEG-based reverse micellar dyeing system, the experiment results reveal that fabrics dyed under an alkaline condition (series 3) obtain a significantly lower color yield than fabrics dyed in deionized water without a pH adjustment (series 1), while fabrics dyed under an acidic condition (series 2) achieve a color yield comparable to series 1, except that the high concentration (3.5%) of red and blue reactive dyes is used. This indicates that the use of an alkaline water pool is unfavorable to a nonionic reverse micellar system since alkaline hydrolysis of the dye may cause lower dye reactivity, resulting in the lower dye uptake, lower color yield, and lighter shade of the fabrics. Concerning the influence of hardness in a water pool, the color yield of the dyed fabrics increases or decreases only slightly when the hardness in the water pool increases from 50 to 500 ppm (series 4 to 7). The effect of hardness on the water pool is not significant since only a small volume of the water pool is required for reverse micellar coloration of cotton so that the impact of hardness can be greatly minimized.

2.3. CIE $L^*a^*b^*$ Values. L^* values in the CIE system are defined as lightness.²¹ In a two-dimensional chart, the value of a^*b^* can be used to locate the color of the dyed substrates into one of the four regions: (a) red-yellow region, (b) yellow-green region, (c) green-blue region, and (d) blue-red region. Table 2 illustrates $L^*a^*b^*$ values in the CIE system of the

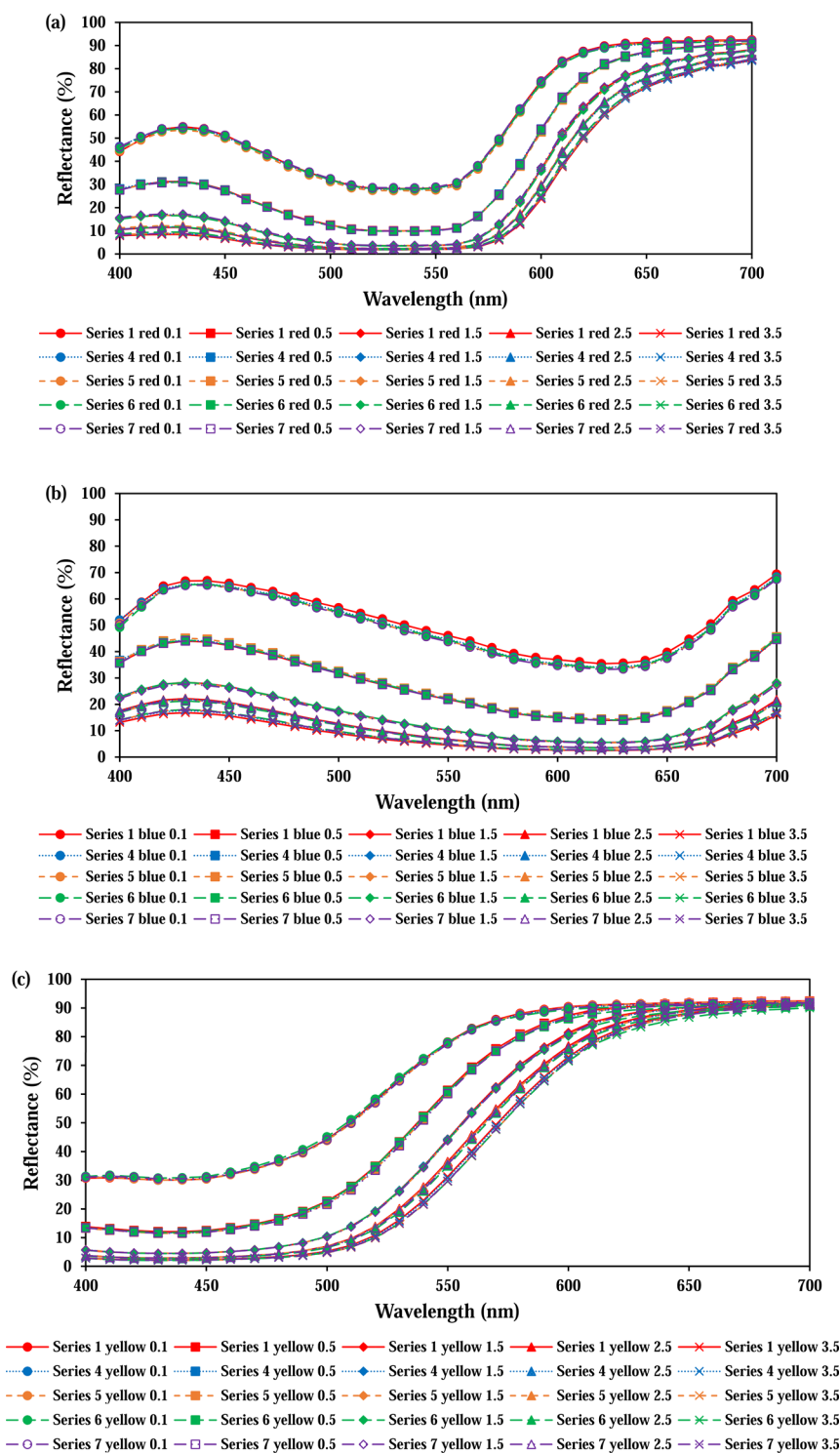


Figure 2. Curves showing the reflectance of colored cotton substrates under different hardness conditions: (a) red, (b) blue, and (c) yellow colors (0.1, 0.5, 1.5, 2.5, and 3.5 represent 0.1, 0.5, 1.5, 2.5, and 3.5% o.w.f., respectively).

colored substrates in the PEG-based reverse micellar dyeing system under different pH and hardness conditions. Generally speaking, $L^*a^*b^*$ values in the CIE system of the reverse micellar colored substrates under different pH and hardness conditions are nearly the same. This indicates that the changes of water hardness and the pH value in the reverse micellar system for dyeing of cotton fiber are not significant and influential since only a small volume of the water pool is used in the system.

2.4. Relative Unlevelness Indices (RUI). The relative unlevelness indices of the dyed fabrics are listed in Table 3. Fabrics dyed in different pH (series 1 to 3) values and different water hardness (series 4 to 7) achieved good (unlevelness under close examination) to excellent levelness (undetectable unlevelness) with RUI values below 0.50 except three samples (series 4 red 3.5 and series 6 red 1.5 and 3.5) in which poor levelness ranged from 0.51 to 0.63. This indicates that the

Table 1. K/S_{sum} Values of Dyed Fabrics

| dye conc. (%) | K/S_{sum} values of colored cotton substrates | | | | | | |
|---------------|--|----------|----------|----------|----------|----------|----------|
| | series 1 | series 2 | series 3 | series 4 | series 5 | series 6 | series 7 |
| red 0.1 | 10.17 | 10.75 | 9.20 | 10.33 | 10.78 | 10.28 | 9.95 |
| red 0.5 | 42.95 | 43.01 | 37.42 | 43.24 | 43.27 | 43.79 | 43.62 |
| red 1.5 | 133.38 | 130.55 | 115.36 | 130.76 | 132.54 | 136.35 | 127.42 |
| red 2.5 | 218.55 | 221.67 | 201.49 | 216.50 | 202.56 | 216.86 | 214.86 |
| red 3.5 | 293.71 | 276.86 | 262.84 | 289.01 | 282.94 | 270.21 | 288.47 |
| blue 0.1 | 8.55 | 9.44 | 7.37 | 9.25 | 9.62 | 9.46 | 9.75 |
| blue 0.5 | 37.66 | 38.46 | 28.97 | 37.25 | 35.98 | 37.21 | 37.67 |
| blue 1.5 | 108.83 | 107.94 | 87.44 | 107.79 | 111.42 | 108.08 | 113.58 |
| blue 2.5 | 174.90 | 173.00 | 158.35 | 175.88 | 182.55 | 182.97 | 178.58 |
| blue 3.5 | 264.36 | 240.40 | 221.75 | 251.36 | 243.35 | 240.32 | 244.32 |
| yellow 0.1 | 8.17 | 8.21 | 6.94 | 8.15 | 8.21 | 7.81 | 8.05 |
| yellow 0.5 | 31.00 | 34.25 | 26.89 | 32.34 | 33.02 | 31.99 | 32.95 |
| yellow 1.5 | 95.68 | 100.97 | 80.45 | 94.71 | 94.57 | 96.21 | 96.11 |
| yellow 2.5 | 152.31 | 163.38 | 144.06 | 152.57 | 150.69 | 163.99 | 156.63 |
| yellow 3.5 | 202.85 | 214.01 | 200.22 | 205.99 | 220.92 | 221.79 | 218.33 |

Table 2. Values of CIE $L^*a^*b^*$ of Dyed Sample Series

| dye conc. (%) | CIE $L^*a^*b^*$ values | | | | | | | | | | | |
|---------------|------------------------|-------|-------|----------|-------|-------|----------|-------|-------|----------|-------|-------|
| | series 1 | | | series 2 | | | series 3 | | | series 4 | | |
| | L^* | a^* | b^* | L^* | a^* | b^* | L^* | a^* | b^* | L^* | a^* | b^* |
| red 0.1 | 72.1 | 39.2 | -5.0 | 71.5 | 39.9 | -4.9 | 72.6 | 37.4 | -6.4 | 71.9 | 39.2 | -5.0 |
| red 0.5 | 56.9 | 55.2 | -1.2 | 56.9 | 55.2 | -0.9 | 57.8 | 53.5 | -3.2 | 56.9 | 55.4 | -1.0 |
| red 1.5 | 45.9 | 61.7 | 6.6 | 46.0 | 61.4 | 6.3 | 46.4 | 60.6 | 3.6 | 45.9 | 61.3 | 6.2 |
| red 2.5 | 41.5 | 61.8 | 12.0 | 41.0 | 61.3 | 11.7 | 41.4 | 61.2 | 9.3 | 41.4 | 61.6 | 11.4 |
| red 3.5 | 39.2 | 60.8 | 14.5 | 38.8 | 60.4 | 14.4 | 38.8 | 60.4 | 12.7 | 38.5 | 60.5 | 14.7 |
| blue 0.1 | 73.9 | -5.0 | -17.5 | 72.8 | -5.0 | -18.2 | 75.5 | -4.3 | -16.7 | 73.0 | -5.1 | -18.0 |
| blue 0.5 | 55.0 | -4.2 | -25.9 | 54.7 | -4.1 | -25.9 | 58.6 | -3.5 | -24.9 | 55.1 | -4.1 | -26.1 |
| blue 1.5 | 40.1 | -1.9 | -29.9 | 40.1 | -2.0 | -29.7 | 42.9 | -1.7 | -29.4 | 40.1 | -1.8 | -29.8 |
| blue 2.5 | 33.6 | 0.1 | -30.5 | 33.7 | -0.1 | -30.3 | 34.7 | 0.3 | -30.4 | 33.4 | 0.1 | -30.4 |
| blue 3.5 | 27.9 | 1.9 | -29.6 | 29.3 | 1.4 | -30.0 | 30.1 | 1.7 | -30.2 | 28.7 | 1.8 | -30.0 |
| yellow 0.1 | 88.0 | 8.0 | 41.9 | 87.9 | 8.0 | 41.8 | 88.1 | 8.9 | 38.3 | 87.9 | 7.9 | 41.7 |
| yellow 0.5 | 80.9 | 19.9 | 63.4 | 80.0 | 20.8 | 64.5 | 80.7 | 20.9 | 59.4 | 80.5 | 20.1 | 63.9 |
| yellow 1.5 | 73.6 | 31.5 | 78.5 | 72.9 | 32.0 | 78.5 | 73.7 | 31.7 | 74.9 | 73.5 | 31.2 | 78.2 |
| yellow 2.5 | 69.9 | 36.4 | 82.0 | 68.8 | 37.4 | 81.7 | 69.6 | 37.5 | 80.6 | 69.6 | 36.5 | 81.6 |
| yellow 3.5 | 67.2 | 39.6 | 82.9 | 66.4 | 40.2 | 82.7 | 66.7 | 41.0 | 81.9 | 66.9 | 40.0 | 82.8 |
| dye conc. (%) | series 5 | | | series 6 | | | series 7 | | | | | |
| | L^* | a^* | b^* | L^* | a^* | b^* | L^* | a^* | b^* | | | |
| red 0.1 | 71.5 | 39.7 | -4.9 | 71.9 | 38.9 | -4.9 | 72.3 | 38.7 | -4.9 | | | |
| red 0.5 | 56.7 | 55.0 | -1.1 | 56.7 | 55.5 | -1.0 | 56.8 | 55.5 | -0.7 | | | |
| red 1.5 | 45.7 | 61.3 | 6.2 | 45.6 | 61.5 | 6.4 | 46.4 | 61.6 | 6.1 | | | |
| red 2.5 | 42.0 | 61.6 | 10.7 | 41.4 | 61.8 | 11.3 | 41.6 | 61.8 | 11.7 | | | |
| red 3.5 | 38.7 | 60.7 | 14.6 | 39.2 | 60.8 | 13.8 | 38.7 | 60.9 | 14.9 | | | |
| blue 0.1 | 72.6 | -5.0 | -18.3 | 72.8 | -5.0 | -18.1 | 72.5 | -5.0 | -18.4 | | | |
| blue 0.5 | 55.6 | -4.2 | -26.0 | 55.2 | -4.3 | -25.9 | 55.0 | -4.1 | -26.0 | | | |
| blue 1.5 | 39.7 | -1.6 | -30.2 | 40.1 | -1.9 | -29.8 | 39.5 | -1.7 | -30.0 | | | |
| blue 2.5 | 33.0 | 0.3 | -30.5 | 32.9 | 0.1 | -30.1 | 33.2 | 0.1 | -30.2 | | | |
| blue 3.5 | 29.1 | 1.7 | -30.1 | 29.2 | 1.4 | -29.9 | 29.0 | 1.6 | -29.9 | | | |
| yellow 0.1 | 87.8 | 8.3 | 41.7 | 88.0 | 7.3 | 40.7 | 87.8 | 8.2 | 41.0 | | | |
| yellow 0.5 | 80.5 | 20.4 | 64.4 | 80.5 | 19.5 | 63.6 | 80.3 | 20.6 | 64.1 | | | |
| yellow 1.5 | 73.3 | 31.6 | 77.8 | 73.3 | 31.0 | 78.1 | 73.3 | 31.6 | 78.2 | | | |
| yellow 2.5 | 69.6 | 36.5 | 81.4 | 69.1 | 37.1 | 82.2 | 69.4 | 36.9 | 81.8 | | | |
| yellow 3.5 | 66.3 | 40.8 | 83.1 | 66.2 | 40.3 | 83.1 | 66.4 | 40.6 | 83.0 | | | |

influence of hardness on levelness of the samples is higher than the influence of the pH value to a certain extent.

2.5. Color Fastness to Laundering. Table 4 shows the results of the color change of the colored fabric series and color

staining of the multifiber fabrics under the AATCC standard laundering fastness test. Nearly all samples have an excellent color change and staining rating of 5 against accelerated laundering except the high concentration of red and blue

Table 3. Relative Unlevelness Indices of Dyed Fabric Series^a

| dye conc. (%) | RUI | | | | | | |
|---------------|----------|----------|----------|----------|----------|----------|----------|
| | series 1 | series 2 | series 3 | series 4 | series 5 | series 6 | series 7 |
| red 0.1 | 0.13 | 0.27 | 0.16 | 0.14 | 0.28 | 0.07 | 0.17 |
| red 0.5 | 0.44 | 0.26 | 0.15 | 0.32 | 0.32 | 0.34 | 0.07 |
| red 1.5 | 0.11 | 0.24 | 0.21 | 0.21 | 0.21 | 0.51 | 0.48 |
| red 2.5 | 0.08 | 0.16 | 0.27 | 0.40 | 0.34 | 0.42 | 0.36 |
| red 3.5 | 0.07 | 0.15 | 0.33 | 0.58 | 0.09 | 0.63 | 0.30 |
| blue 0.1 | 0.10 | 0.05 | 0.14 | 0.13 | 0.28 | 0.10 | 0.17 |
| blue 0.5 | 0.33 | 0.32 | 0.21 | 0.14 | 0.10 | 0.41 | 0.06 |
| blue 1.5 | 0.07 | 0.19 | 0.27 | 0.08 | 0.10 | 0.13 | 0.29 |
| blue 2.5 | 0.21 | 0.26 | 0.17 | 0.29 | 0.38 | 0.42 | 0.12 |
| blue 3.5 | 0.28 | 0.18 | 0.15 | 0.18 | 0.20 | 0.09 | 0.07 |
| yellow 0.1 | 0.03 | 0.04 | 0.01 | 0.03 | 0.04 | 0.04 | 0.05 |
| yellow 0.5 | 0.07 | 0.10 | 0.03 | 0.04 | 0.11 | 0.09 | 0.08 |
| yellow 1.5 | 0.19 | 0.24 | 0.09 | 0.14 | 0.14 | 0.14 | 0.11 |
| yellow 2.5 | 0.16 | 0.19 | 0.07 | 0.21 | 0.08 | 0.06 | 0.25 |
| yellow 3.5 | 0.28 | 0.06 | 0.17 | 0.05 | 0.15 | 0.22 | 0.20 |

^aSuggested interpretation of the RUI values: <0.2 = excellent levelness; 0.2–0.49 = good levelness; 0.5–1.0 = poor levelness; >1.0 = bad levelness.²³

Table 4. Laundering Fastness of the Dyed Cotton Samples^a

| dye conc. (%) | color fastness | | |
|---------------|--------------------------|-------------------------|-------------------------|
| | A | C | W |
| red 0.1 | 5/5/5/5/5/5 ^b | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| red 0.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| red 1.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| red 2.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| red 3.5 | 4–5/4–5/4–5/4–5/4–5/4–5 | 4–5/4–5/4–5/4–5/4–5/4–5 | 4–5/4–5/4–5/4–5/4–5/4–5 |
| blue 0.1 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| blue 0.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| blue 1.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| blue 2.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| blue 3.5 | 4–5/4–5/4–5/4–5/4–5/4–5 | 4–5/4–5/4–5/4–5/4–5/4–5 | 4–5/4–5/4–5/4–5/4–5/4–5 |
| yellow 0.1 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| yellow 0.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| yellow 1.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| yellow 2.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |
| yellow 3.5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 | 5/5/5/5/5/5 |

^aA: change in color; C: staining on cotton multifiber strip; W: staining on wool multifiber strip. 5 means the least change and staining of the color, while 1 means the highest change and staining of the color. ^bThe rating indicates series 1/series 2/series 3/series 4/series 5/series 6/series 7.

colors (3.5%), which have scored ratings of 4–5 with a very small and nearly unnoticeable change of color and staining. This result indicates that after thorough rinsing following the dyeing process, unfixed and hydrolyzed dyes were sufficiently removed from the colored fabric samples.

3. CONCLUSIONS

The effects of water hardness and the pH value on PEG-based nonionic surfactant dyeing of cotton fiber with reactive dyes in a heptane reverse micelle system were investigated in terms of the color yield, reflectance, CIE $L^*a^*b^*$ value, and unlevelness. Results reveal that the effect of water-pool pH on the color yield and reflectance is more significant than that of water-pool hardness. Generally speaking, water hardness did not have a significant effect in the reverse micellar dyeing system. The dyed fabrics under an alkaline water-pool condition (pH 10) obtained a lower color yield and higher reflectance than those under acidic (pH 4) and nearly neutral (pH 6) conditions due to alkaline hydrolysis of dyes. The increase of hardness in the

water pool has higher influence on unlevelness of the dyed samples than the increase or decrease of the pH value in the water pool. The changes of water-pool hardness and the pH value do not cause a tremendous change on CIE $L^*a^*b^*$ values of dyed fabrics due to a small volume of the water pool required for nonionic reverse micellar dyeing of cotton. Excellent washing fastness results of the dyed fabrics, guaranteeing adequate removal of unfixed dyes, are obtained, which assure accuracy of the results in a spectrophotometric measurement.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. Reagent grade nonionic poly(ethylene glycol) (12) tridecyl ether (PEG-12), 1-octanol, and *n*-heptane were used as surfactant, cosurfactant, and solvent, respectively. These were purchased from Sigma-Aldrich and Acros Organics. Sodium carbonate (NaCO_3) was used for fixation in reactive dyeing. Reactive dyes were supplied by Dystar from Shanghai and were directly used

without further purification (Levafix CA Red, Levafix CA Blue, and Levafix CA Yellow). Two grams of pure cotton interlock bleached fabric was used for dyeing. The fabric count was 40 × 40 and expressed as wales and courses per inch, respectively. It was first cleaned with detergent (2 g/L) at 49 °C for 45 min, tumble-dried, and conditioned at 65 ± 2% RH and 20 ± 2 °C for 24 h.

4.2. Preparation of Water with Different Degrees of Hardness and pH Values. Hard water was prepared by adding calcium chloride (CaCl₂) to deionized water and titrated with EDTA solution (0.01 M). Total water hardness is expressed as parts per million (ppm).²² Water with a pH value of 4 was prepared by adding sodium acetate (NaAc) and acetic acid (HAc) (reagent grade) to deionized water to lower the pH value, whereas water with a pH value of 10 was prepared by adding ammonium chloride (NH₄Cl) and ammonia solution (NH₃·H₂O) (reagent grade) to deionized water to increase the pH value. The pH values of the liquors were monitored and measured by a portable pH meter (Thermo Scientific, Singapore).

4.3. Dye-Encapsulated Heptane Reverse Micellar Solution. A PEG-12 surfactant (nonionic in nature) was initially mixed with a cosurfactant (1-Octanol) to form a surfactant/cosurfactant mixture. Heptane (min 99% pure) was then added into the mixture, forming a reverse micelle solution. Aqueous dye solutions were added to the reverse micelle solution dropwise. The dye/reverse micelle solution mixture was then stirred until it was well dispersed with the dye encapsulated in the reverse micelle without phase separation. The ratio and volume required for the formation of the dye-encapsulated reverse micelle solution are listed in Table 5.

Table 5. Ratio and Volume for Dye-Encapsulated Reverse Micelle Solution

| parameter | dye-encapsulated reverse micelle solution |
|---|---|
| surfactant–water mole ratio | 1:25 |
| surfactant–cosurfactant mole ratio | 1:8 |
| solvent–cotton weight ratio (g/g) | 10:1 |
| dye concentrations of reactive dye aqueous solution (w/v) | 0.2%, 1%, 3%, 5%, 7% |
| dye volume in water pool (mL) | 0.5 |

4.4. Heptane-Based Nonaqueous Coloration of Cotton. Five dye concentrations (%), which were 0.1, 0.5, 1.5, 2.5, and 3.5, were used for coloration of cotton, and they are expressed in on weight-of-fiber (o.w.f.). Cotton fabrics were first immersed in a series of dye-encapsulated reverse micelle solutions. Series 1, used as the control, was dyed with the water pool made of deionized water without a pH adjustment and hardness manipulation. Other series were prepared with different water-pool hardness and pH values according to Table 6. The workflow of heptane-assisted dyeing of cotton fabrics (without salt) is shown in Figure 3. The dye liquors were put into a water bath and agitated for 10 min at 30 °C. The dyeing temperature was increased to 70 °C under control (2 °C/min.). Dyeing of cotton was conducted at 70 °C for 40 min, followed by the addition of 0.3 mL of soda ash of different concentrations (Table 7) to allow fixation of the dye on cotton for 60 min. The dyed fabrics were then soaped twice

Table 6. Water Hardness and pH Value of Dye Liquors

| series | water hardness (ppm) | pH value |
|----------|----------------------|----------|
| series 1 | 0 | 6 |
| series 2 | 0 | 4 |
| series 3 | 0 | 10 |
| series 4 | 50 | 6 |
| series 5 | 100 | 6 |
| series 6 | 300 | 6 |
| series 7 | 500 | 6 |

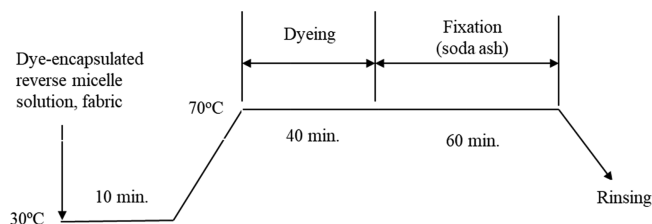


Figure 3. Workflow of heptane-based cotton dyeing in reverse micelle.

Table 7. Sodium Carbonate of Various Dye Concentrations

| dye concentration (% o.w.f.) | fixation agent-to-cotton weight ratio (g/g) |
|------------------------------|---|
| 0.1 | 0.04 |
| 0.5 | 0.04 |
| 1.5 | 0.05 |
| 2.5 | 0.06 |
| 3.5 | 0.07 |

(2 g/L soap) at 50 °C for 20 min, water rinsed, air-dried, and conditioned for 24 h before the subsequent experiment.

4.5. Color Property Measurement. Color strength of colored substrates was measured by an SF650 spectrophotometer manufactured by DataColor International in U.S. under the illuminant D₆₅ and 10° standard observer with a large aperture (30 mm). *K/S* values in the range of 400–700 nm were measured based on eq 1.³ A higher *K/S* value represents better color strength of the dyed substrates. *K/S*_{sum} values were obtained by the sum of *K/S* values obtained over a wavelength of 400–700 nm. The average *K/S*_{sum} value of four measurements was taken for each sample

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (1)$$

where *K* is the absorption coefficient, based on the colorant concentration, *S* is the coefficient of scattering of the colored specimen, and *R* is the reflectance of the colored substrate.

The CIE *L*a*b** values of the colored cotton substrates were obtained by using similar apparatus and conditions as stated for the color strength measurement. Four repeated measurements were conducted. The averages of CIE *L** values, *a** values, and *b** values of the four measurements for each dyed substrate were taken.

4.6. Unevenness Evaluation. The unevenness of the dyed cotton fabrics was measured by relative unevenness indices (RUI).²³ Reflectance (*R*, %) at four random spots of the colored substrates was measured with the use of similar apparatus and conditions as stated in Section 4.5. Four repeated measurements were conducted, and RUI values were calculated according to eq 2

$$RUI = \sum_{\lambda=400}^{700} (s_{\lambda}/\bar{R})V_{\lambda} \quad (2)$$

where S_{λ} is the standard deviation of reflectance at a specified wavelength, \bar{R} is the reflectance at a specific wavelength, and V_{λ} is the photopic relative luminous efficiency function.

4.7. Laundering Colorfastness Testing. The color fastness to accelerated laundering of colored cotton substrates was tested by the Test Method 61, No. 2A (2013) from AATCC. The ratings of the change in color of colored cotton substrates and their staining ratings on multifiber fabrics were reported.

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Notes

The authors declare no competing financial interest.

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