

One-Bath Union Dyeing of Wool/Acrylic Blend Fabric with Cationic Reactive Dyes Based on Azobenzene

Hang Xiao¹ and Tao Zhao^{1,2*}

¹College of Chemistry, Chemical Engineering and Bio-technology, Donghua University, Shainghai 201620, China

²The Key Lab of Textile Science & Technology, Ministry of Education, Donghua University, Shainghai 201620, China

(Received April 1, 2017; Revised August 2, 2017; Accepted August 21, 2017)

Abstract: Three unreported cationic reactive dyes based on azobenzene were synthesized using a novel synthetic route. Synthesized dyestuffs containing three primary color dyes were characterized by FTIR, H-NMR, LC-MS, Element Analysis and UV-vis spectroscopic techniques. The absorption spectra of dyes were measured in three solvents with different polarities. The dyeing and color fastness properties of three cationic reactive dyes on wool, acrylic and wool/acrylic blend fabrics were determined. The optimum pH for wool and acrylic fabrics were 6 and 5, respectively. Effect of temperature, time on dyeing properties and color fastness properties on wool fabric showed the same tendency with acrylic fabric. The *K/S* value of wool fabric dyed with three dyes was similar to that of acrylic fabric when both fabrics were dyed simultaneously in the same dyebath using low dye concentration. Wool/acrylic blend fabric dyed with three cationic reactive dyes using one-bath one-step method achieved good union dyeing property and excellent color fastness.

Keywords: Cationic reactive dyes, Synthesize, Blend fabric, One-bath one-step method, Union dyeing

Introduction

Achieving versatile applications in household textiles and industrial textiles, blend fabrics possessing outstanding characters of each single component meet different requirement of customers and also can be capable of reducing the production cost. Comparing the wool/acrylic blend fabrics with acrylic or wool fabrics, the wool/acrylic blend fabrics show unparalleled properties in crease recovery, abrasion resistance and dimensional stability. Additionally, the price of the wool/acrylic blend fabrics is not prohibitively expensive [1,2]. However, in the case of the distinctive dyeability of the acrylic and wool fiber, cationic dyes and acid dyes are applied for acrylic fabrics and wool fabrics, respectively. Conventional dyeing of the wool/acrylic blend fabrics is always conducted in two baths or one bath with two steps. Moreover, conventional dyeing processes may cause severe damage to environment, including water pollution and the discharge of various chemical auxiliaries. Reduction of water consumption and simplification of dyeing process are key to sustainable development in the textile dyeing industry.

Taking the time, cost-saving and effluent into consideration, one-bath one-step dyeing with one dye is an alternative selection for textile industries [3]. In order to obtain desired union dyeing, together with energy saving, some researchers utilized one kind of dyes (acid dye or cationic dye) to dye the wool/acrylic blend fabrics modified with some eco-friendly chemicals. This mode of application is reliant upon the same dyeing characteristic being present in the blend fabrics to react with one kind of dye and thereby furnish union dyeing with sacrificing mechanical properties of two fibers [4,5]. A

better approach to eliminating the disadvantages of traditional dyeing method for blend fabrics is to synthesize one kind of dyes that show similar affinity for, and high fastness properties on, both fibers of blend fabrics. Nishida *et al.* [6] had prepared a series of conjugated type of cationic reactive dyes and dyed the blend fabrics with resulting dyes. In this case, the light properties of dyed fabrics were undesirable and there remains much scope for improvement. A number of reactive cationic dyes containing various numbers of the cationic group were investigated by Soleimani-Gorgani and Taylor [7]. However, much less has been reported on the application properties of reactive cationic dyes on blend fabrics. Subsequently, research into the chemistry and the application of reactive cationic dyes focused overwhelmingly on multifunctional dyes which possess dyeing and antibacterial properties [1].

Cationic reactive dyes possessing characteristics of cationic dye and reactive dye show affinity for acrylic fiber and protein fiber. As a multifunctional dye, cationic reactive dye has been found to be a promising alternative dye in conventional dyeing of blend fabric, which can reduce the consumption of water and energy in dyeing process. This result is very interesting in the cleaner production of textile industry.

In continuation of our interest in the direction of one-bath one-step dyeing for blend fabrics, the present work describes the synthesis of three primary color cationic reactive dyes achieved through a novel synthetic method, which the condensation process was prior to diazo-coupling reaction [8]. The feasibility of one-bath one-step dyeing of blend fabrics using cationic reactive dyes were discussed. Then we applied three cationic reactive dyes for dyeing of wool, acrylic and wool/acrylic blend fabrics. Different factors affecting dyeability of cationic reactive dyes and fastness

*Corresponding author: tzhao@dhu.edu.cn

properties were thoroughly investigated.

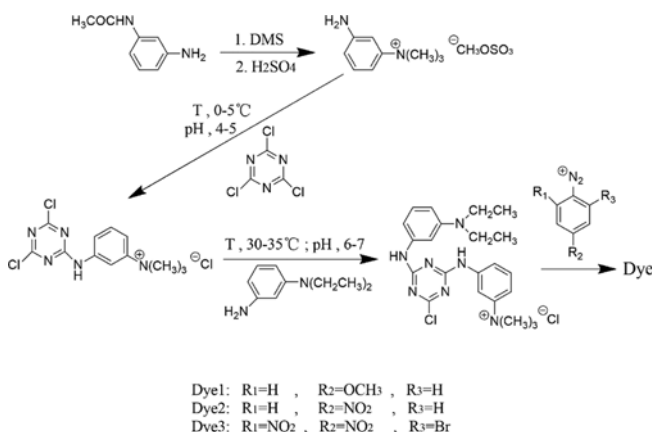
Experimental

Materials and Chemicals

Cyanuric chloride was provided by Sigma-Aldrich Corporation and was reagent grade. Dimethylsulfate was obtained from Shanghai Chemical Reagent Plant, Shanghai, China. 3-(N,N-diethylamino) acetanilide was kindly provided by Longsheng Chemical Engineering Company, Shaoxing, China. Other chemicals were commercially available and used without further purification. Acrylic, wool and acrylic/wool (50/50) blend fabrics were kindly provided by Test fabrics Inc, Shanghai, China.

Equipments

Melting points of dyes were recorded with a Mel-Temp capillary melting point apparatus (made in Shanghai, China) at a heating rate of 1 °C/min. FTIR spectrum was determined by an OMNI 98 Sampler of the Nexus-670 FTIR-Raman Spectrometer (Nicolet Analytical Instruments, America). ¹H NMR spectrum was measured in DMSO-d₆, using TMS as the internal standard, on a Bruker Avance 400 (Bruker Co., Faellanden, Switzerland). Element analysis for C, H, N were recorded on a Vario EL III (Elementar Co., Germany). The mass spectra were obtained on Varian LC-MS (Varian Co., America) using methanol: water as eluent. The UV-Vis experiments were performed on Lambda 35 spectrophotometer (PekinElmer. Co., America). High performance liquid chromatography (HPLC) was performed using a Techcomp LC 2000 with a 10 cm, Sharpsil AQ RP-18 (5 μm) packing. The mobile phases used were deionied water as solvent A and acetonitrile (HPLC grade) as solvent B. These solvents were passed through the column, maintained at 30 °C, in a fixed ratio A:B (80:20) at the standard gradient rate 1 ml/min, and the samples were analyzed spectroscopically using a LC 2030 UV detector at a wavelength range from 250 to 650 nm.



Scheme 1. Synthesis of Dye1, Dye2 and Dye3.

Synthesis of Cationic Reactive Dyes

m-Aminophenyltrimethylammounium Salt

The synthetic routes were depicted in Scheme 1. To a three-necked bottom flask equipped with a condenser pipe, 3-aminoacetanilide (0.1 mol, 15 g), distilled water (150 ml), sodium bicarbonate (0.4 mol, 33.6 g) were added, dimethylsulphate (DMS) (0.4 mol, 42 ml) was slowly added dropwise over 1 h at 25 °C. The mixture was continued for 12 h at 65 °C and then allowed to cool at room temperature. The reaction was monitored by HPLC (starting material: t_R=2.94 min; product: t_R=1.92 min) and TLC (starting material: R_F=0.29; product: R_F=0) using acetone: n-hexane (2:3) as eluent. After the concentrated sulphuric acid (8 ml) was gradually added to the solution of 3-(acetylaminophenyl) trimethylammounium methosulphate, the solution was stirred at 95 °C for 1 h, and the reaction was controlled by HPLC (starting material: t_R=1.92 min; product: t_R=2.08 min). Then the product of *m*-aminophenyltrimethylammounium methosulphate (the purity was 95 %) was obtained and used for next reaction without isolation.

3-((4-chloro-6-((3-(diethylamino)phenyl)amino)-1,3,5-triazin-2-yl)amino)-N,N,N-trimethylbenzenaminium Chloride

Cyanuric chloride (2.21 g, 0.012 mol) was stirred in a mixture of acetone (50 ml) and crushed ice (10 g) to form a uniform suspension. A neutral solution of *m*-aminophenyltrimethylammounium methosulphate (25 ml, 0.01 mol) was added in such a way that the temperature did not exceed 5 °C. The mixture was stirred for 3 h at 0-5 °C, the pH was maintained at 4 by adding 2 M sodium carbonate solution. The reaction was monitored by TLC, using methanol: dichloromethane (1:3) as eluent. The reaction was completed until the dot of cyanuric chloride on silica plate disappeared. N,N-diethylbenzene-1,3-diamine (1.64 g, 0.01 mol) prepared according to the literature [9] was dissolved in dilute hydrochloric acid solution (30 ml) and was slowly added dropwise to the obtained solution of 3-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-N,N,N-trimethylbenzenaminium chloride. The mixture was then stirred for 5 h at pH 6-6.5 and at 30-35 °C, with control by TLC using acetone: n-hexane (2:3) as eluent. The disappearance of the dot of N,N-diethylbenzene-1,3-diamine on silica plate indicated that the reaction proceeded completely. The resulting solution of 3-((4-chloro-6-((3-(diethylamino)phenyl)amino)-1,3,5-triazin-2-yl)amino)-N,N,N-trimethylbenzenaminium chloride was cooled to 0-5 °C and used as coupling components.

Diazotization Reaction

4-Methoxyaniline (1.23 g, 0.01 mol) was dissolved in a mixture of water (20 ml) and concentrated hydrochloric acid (3 ml). The solution of sodium nitrite (0.83 g, 0.012 mol dissolved in water, 5 ml) was slowly added to the above solution at 0-5 °C, the reaction proceeded for 30 min, then a moderate quantity of sulfamic acid was added to destroy the excess nitrous acid.

4-Nitroaniline (1.38 g, 0.01 mol) was stirred in hot water at 65 °C (50 ml) and concentrated hydrochloric acid (3 ml) to form a fine suspension. The solution of sodium nitrite (0.83 g, 0.012 mol dissolved in water, 5 ml) was rapidly poured into the above solution at 0-5 °C and the diazotization was continued for 1 h. After the reaction proceeded completely, some sulfamic acid was added to destroy the excess nitrous acid and then filtered to get clear solution [10].

2-Bromine-4,6-dinitro-aniline (2.62 g, 0.01 mol) was dissolved in concentrated sulphuric acid (5 ml) at room temperature until a clear solution was obtained. Nitrosylsulfuric acid (40% in sulfuric acid, 3.5 ml) was added in small amounts for 10 min to the above solution at 30-35 °C and the diazotization was continued for 3-4 h. A small amount of the reactant solution was withdrawn at intervals to monitor the reaction and the reaction was carried out until the reactant became water soluble.

Coupling Reaction

Different freshly prepared diazonium salt solution (0.01 mol) was added dropwise to well-stirred solution of 3-((4-chloro-6-((3-(diethylamino)phenyl)amino)-1,3,5-triazin-2-yl)amino)-N,N,N-trimethylbenzenaminium chloride (0.01 mol). The pH was adjusted to 5-6 by adding 2 M sodium carbonate solution and coupling reaction was continued for 4 h at 0-5 °C. After the coupling reaction was done, the solid products were filtered, washed and dried in vacuum freeze drier. The obtained cationic reactive dyes (Dye1, Dye2, and Dye3) were purified by column chromatography with methanol/dichloromethane (1:6) as eluent.

3-((4-chloro-6-((5-(diethylamino)-2-((4-methoxyphenyl)diazenyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)-N,N,N-trimethylbenzenaminium Chloride (Dye1)

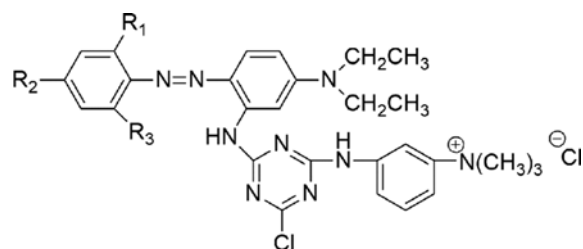
Yellow solid, yield 45 %, m.p. 170-172 °C; IR (KBr): ν (cm⁻¹) 3272 (NH), 3067 (Ar-H), 2968 (aliph-H), 1598 (N=N), 796 (C-Cl); ¹H NMR [DMSO-d₆]: δ 9.76-6.29 (m, 11H, Ar-H), 3.99 (s, 2H, NH), 3.84 (s, 3H, O-CH₃), 3.63 (q, 4H, CH₂), 1.19 (t, 6H, CH₂-CH₃), 1.07 (s, 9H, N⁺-CH₃). Anal. Calcd for C₂₉H₃₅C₁₂N₉O (596.55): C, 58.38; H, 5.91; N, 21.13. Found: C, 57.79; H, 5.53; N, 21.41; MS: m/z 561 (M-Cl)

3-((4-chloro-6-((5-(diethylamino)-2-((4-nitrophenyl)diazenyl)phenyl)amino)-1,3,5-triazin-2-yl)amino)-N,N,N-trimethylbenzenaminium Chloride (Dye2)

Red solid, yield 74 %, m.p. 194-196 °C; IR (KBr): ν (cm⁻¹) 3253 (NH), 3096 (Ar-H), 2971 (aliph-H), 1585 (N=N), 1328 (NO₂), 796 (C-Cl); ¹H NMR [DMSO-d₆]: δ 8.38-6.65 (m, 11H, Ar-H), 4.00 (s, 2H, NH), 3.55 (q, 4H, CH₂), 1.10 (t, 6H, C-CH₃), 0.86 (s, 9H, N⁺-CH₃). Anal. Calcd for C₂₈H₃₂Cl₂N₁₀O₂ (611.53): C, 54.99; H, 5.27; N, 22.90. Found: C, 55.28; H, 5.46; N, 21.13; MS: m/z 576 (M-Cl)

3-((4-((2-((2-bromo-4,6-dinitrophenyl)diazenyl)-5-(diethylamino)phenyl)amino)-6-chloro-1,3,5-triazin-2-yl)amino)-N,N,N-trimethylbenzenaminium Chloride (Dye3)

Blue solid, yield 78 %, m.p. 171-173 °C; IR (KBr): ν (cm⁻¹)



Dye1:	R ₁ =H,	R ₂ =OCH ₃ ,	R ₃ =H
Dye2:	R ₁ =H,	R ₂ =NO ₂ ,	R ₃ =H
Dye3:	R ₁ =NO ₂ ,	R ₂ =NO ₂ ,	R ₃ =Br

Scheme 2. Chemical structures of Dye1, Dye2 and Dye3.

3355 (NH), 3083 (Ar-H), 2975 (aliph-H), 1578 (N=N), 1325 (NO₂), 793 (C-Cl); ¹H NMR [DMSO-d₆]: δ 9.47-6.46 (m, 9H, Ar-H), 4.00 (s, 2H, NH), 3.55 (q, 4H, CH₂), 1.23 (t, 6H, CH₂-CH₃), 1.02 (s, 9H, N⁺-CH₃). Anal. Calcd for C₂₈H₃₀BrCl₂N₁₁O₄ (735.42): C, 45.73; H, 4.11; N, 20.95. Found: C, 45.38; H, 4.75; N, 21.03; MS: m/z 700.9 (M-Cl). The chemical structures of the synthesized dyes are showed in Scheme 2.

Dyeing Process

The acrylic, wool and acrylic/wool blend fabrics were dyed with yellow, red and blue reactive cationic dyes, using IR dyeing machine (PYROTEC-2001, England). Dyeing procedures of wool, acrylic and wool/acrylic blend fabrics are shown in Figure 1. 1 g piece of fabric was dyed at a liquor ration of 40:1. Fabrics were introduced in the dyebath at 40 °C and the temperature was increased to 95 °C at a rate of 1 °C/min. Dyeing process was conducted under different condition (dyeing time, dyeing temperature, and pH), afterward, the fabrics were removed and subsequently washed with a

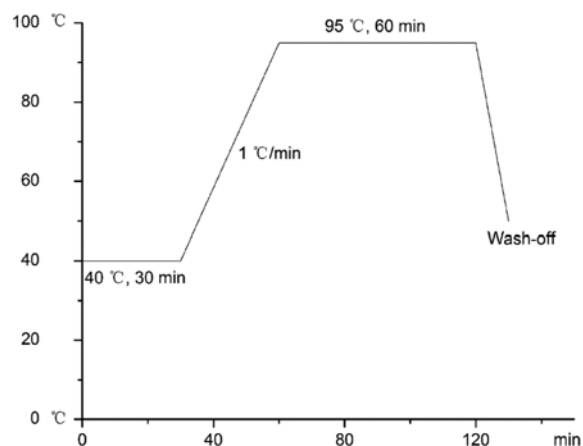


Figure 1. Dyeing profile of acrylic, wool, and wool/acrylic fabrics using cationic reactive dyes.

soaping agent, 2 g/l, at 95 °C for 10 min, and rinsed thoroughly with tap water and dried at 60 °C.

Measurement

Dye Exhaustion

A UV/vis spectrophotometer was employed to determine dye exhaustion by measuring the absorbance of each dyebath solution before and after the dyeing process at the λ_{\max} of each dye. The dyebath exhaustion (%E) was calculated using equation (1),

$$\%E = (A_0 - A_1)/A_0 \times 100\% \quad (1)$$

where A_0 and A_1 are the absorbance of the dyebath before and after dyeing, respectively.

Color Strength (K/S) on Fabric

The color strength (K/S) of the dyed fabrics were measured by Datacolor 650 spectrophotometer (Datacolor, Switzerland). The color parameters (L , a , b and c) of the dyed fabrics were determined under D65 lamp using the 10° standard observer. The reflectance at the maximum wavelength absorption (λ_{\max}) was used to calculate the colour strength of the dyed fabrics by the Kubelka-Munk equation [11] equation (2)

$$K/S = (1 - R)_2/2R \quad (2)$$

where K is the absorption coefficient of the substrate, S is the scattering coefficient of the substrate and R is the reflectance of the dyed fabric at λ_{\max} .

Union Dyeing Properties

The union dyeing balance value K was calculated according to equation (3):

$$K = (K/S)_{\text{acrylic}}/(K/S)_{\text{wool}} \quad (3)$$

where $(K/S)_{\text{acrylic}}$ and $(K/S)_{\text{wool}}$ are K/S of acrylic and wool fabrics dyed in a same dyebath with various dye concentration, respectively.

Levelling Properties

The color differences on five points can indicate levelling properties of cationic reactive dyes on dyed fabrics. The color differences are calculated using the measured values of CIELAB (equation (3)) [12].

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (4)$$

ΔL , Δa and Δb are the difference in the color parameters of the dyed fabrics.

Fastness Properties

The color fastness to washing, dry and wet rubbing, perspiration and light were assessed according to ISO 105-C10(2006), ISO 105-X12(2001), ISO 105-E04(1994), ISO 105-B02(1994), respectively.

Visible Absorption Spectra of Dyes

The solutions of three dyes were prepared in the concentration ranged from 0.01 to 0.05 g/l by dissolving dyes in various solvent. The absorbance of each solution was measured at the λ_{\max} of the dyes and the molar extinction coefficients (ϵ_{\max}) of the dyes were calculated.

Results and Discussion

UV-visible Spectra of Reactive Cationic Dyes

Electronic spectral data of synthesized dyes dissolved in different solvents are listed in Table 1. As shown in the Table 1, the bathochromic effect can be observed by comparing the maximum absorptions (λ_{\max}) and the molar extinction coefficients (ϵ) of Dye2 with those of Dye1. The bathochromic effect is attributed to the introduction of electron withdrawing group of nitro at the p-position of the diazonium component [13]. A remarkable bathochromic shift is obtained by increasing the number of electron withdrawing group in the diazonium component of Dye3, this give considerable shift of 43 nm relative to Dye2. The maximum absorbance of the three dyes shift in the order: DMSO>Acetonitrile>Methanol. With increasing the polarity of the solvent, all of the dyes show significant bathochromic shift, which is interpreted by the interactions between dyes and solvents. This is consistent with the known behavior of interaction of this type in which the hydrogen bond and dipolar forces could benefit the stabilization of the π^* orbital as compared to the π orbital in the polar solvent [14,15].

Dyeing Properties

Wool Dyeing

The dyebath pH is a very important factor in wool dyeing. Dyeing is performed at 95 °C varying pH from 3 to 9 with three dyes and the effect of pH on the dye exhaustion are shown in Figure 2. It can be seen that exhaustion of the three cationic reactive dyes increased with the increase of pH and reaches the maximum at pH 6. The reason of high exhaustion at pH 6 and 7 might be that the anions on wool fiber quickly attract the dye cations by electrostatic interaction. In

Table 1. UV-visible spectra data of the reactive cationic dyes in three solvents

Dye	λ_{\max} (nm)			ϵ ($l \text{ mol}^{-1} \text{ cm}^{-1}$)		
	DMF	Acetonitrile	Methanol	DMF	Acetonitrile	Methanol
Dye1	466	463	460	15356	15444	13781
Dye2	525	514	512	36921	20598	31829
Dye3	567	559	550	38839	34182	39660

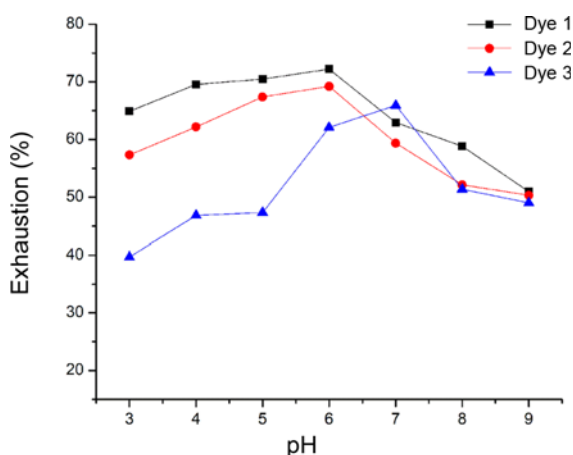


Figure 2. Effect of pH on the exhaustion of Dye1, Dye2 and Dye3 on wool fabrics; dyeing conditions: shade 2 % omf, liquor 40:1, 95 °C for 60 min.

addition, when the dyebath pH is approaching neutral, wool fiber does not carry positive charge and the nucleophilicity of the amino group in wool fiber becomes high. The nucleophilic substitution reaction between amino groups on wool fiber and monochlorotriazine groups on the dye takes place.

In order to determine the influence of the dyebath temperature and dyeing time on dyeing properties, the dyebath temperature was increased from 40 °C to 95 °C at a rate of 1 °C/min and maintained at 95 °C for 80 min. From the results shown in Figure 3, the K/S value of wool fabric increases with the increase of temperature. This can be explained by the fact that the high temperature enhances the solubility of cationic reactive dyes and the swell of wool fiber, which facilitate the dye diffusion in fiber [16,17]. With prolonging dyeing time at such high temperature (95 °C), a little decline in color strength took place, this result reflected that the equilibrium of sorption and desorption was shifted to desorption by increasing dyeing time.

Grades of fastness to washing, light, perspiration and rubbing of dyed wool fabrics with three cationic reactive dyes are shown in Table 2. Washing fastness, rubbing fastness and perspiration fastness are good to excellent with grade 4-5, while the light fastness is moderate. Figure 4 shows that satisfactory coloration behaviors of all the cationic reactive dyes were achieved on wool fabrics.

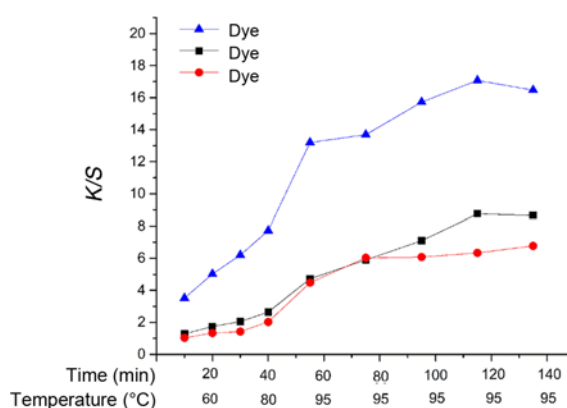


Figure 3. Effect of time on the color strength of Dye1, Dye2 and Dye3 on wool fabrics; dyeing conditions: shade 2 % omf, liquor 40:1, pH 6.

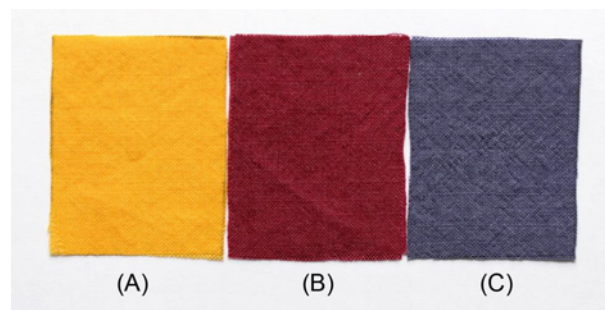


Figure 4. The coloration sample of the obtained cationic reactive dye 1 (A), 2 (B), 3 (C) on wool fabrics.

Acrylic Dyeing

Effect of pH on exhaustion of acrylic dyed with three cationic reactive dyes at various pH is shown in Figure 5. The exhaustion of acrylic fabrics dyed at pH 5 are about 75-80 %, those value are somewhat higher than the exhaustion of wool dyed with three dyes. This can be attributed to the fact that the hydrolyzed cationic reactive dyes still show high affinity toward acrylic fiber by electrostatic attraction between anionic groups in acrylic fiber and the cationic groups present in the dye molecules.

Color strength of acrylic fabrics dyed with three cationic reactive dyes at different temperature and different time are shown in Figure 6. It can be see that a dramatic increase in color strength of acrylic fabrics dyed with Dye1 and Dye2

Table 2. Fastness properties results of Dye1, Dye2 and Dye3 on wool fabrics

Dye	Light	Rubbing		Washing		Perspiration	
		Dry	Wet	SC	SW	SC	SW
Dye1	4	4	4	4	4-5	4	4-5
Dye2	3-4	4-5	4	4	4-5	4-5	4-5
Dye3	4	4	4-5	4	4	5	4

SC, staining on cotton; SW, staining on wool.

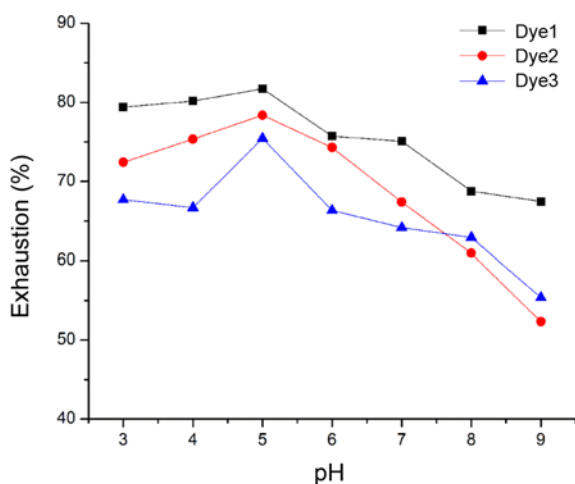


Figure 5. Effect of pH on the exhaustion of Dye1, Dye2 and Dye3 on acrylic fabrics; dyeing conditions: shade 2 % omf, liquor 40:1, 95 °C for 60 min.

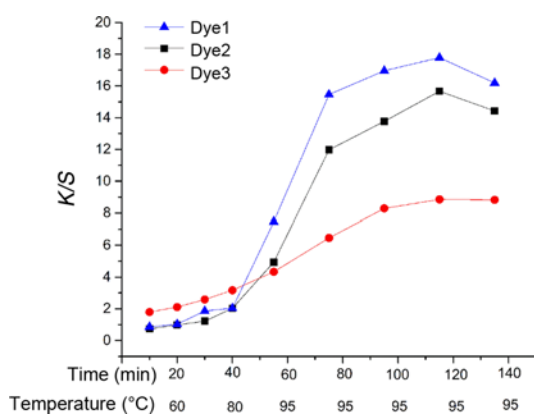


Figure 6. Effect of time on the color strength of Dye1, Dye2 and Dye3 on acrylic fabrics; dyeing conditions: shade 2 % omf, liquor 40:1, pH 5.

was observed, as the dyeing time approaches 50 min (dyeing temperature was near 90 °C). This may suggest that in the case of the expansion of amorphous regions, when the dyebath temperature exceeded glass transition temperature (T_g) of acrylic fabrics, hence it facilitated the diffusion of reactive cationic dyes in acrylic fiber [18].

The fastness properties of acrylic fabric dyed with the three cationic reactive dyes are summarized in Table 3.

Table 3. Fastness properties results of Dye1, Dye2 and Dye3 on acrylic fabrics

Dye	Light	Rubbing		Washing		Perspiration	
		Dry	Wet	SC	SW	SC	SW
Dye1	4	4	4	4	4-5	4-5	4-5
Dye2	3-4	3	3	3-4	4	4-5	4
Dye3	3-4	4	4-5	4	4	4-5	4

SC, staining on cotton; SW, staining on wool.

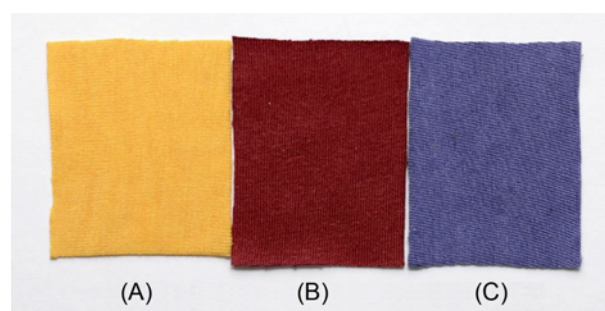


Figure 7. The coloration sample of the obtained cationic reactive dye 1 (A), 2 (B), 3 (C) on acrylic fabrics.

Washing fastness, rubbing fastness and light fastness of dyed samples with Dye1 are slightly better than those of Dye2 and Dye3. Perspiration fastness of Dye2, Dye3 is the same as Dye1. The good coloration behaviors on acrylic fabrics dyed with three cationic reactive dyes are depicted in Figure 7.

Wool/acrylic Blend Fabric Dyeing

Wool/acrylic blend fabric is usually dyed by two-bath method: dyeing acrylic by cationic dye at 90-95 °C and pH 4-5, followed by dyeing of wool with acid dyes at 95-100 °C in acidic condition. If one-bath one-step dyeing method using a cationic reactive dye is applied, it will be difficult to analyze the dyeing characteristics of each component fiber in wool/acrylic blend fabric. Therefore, the simultaneous dyeing of wool and acrylic fabrics with three cationic reactive dyes was performed at 95 °C varying dye concentration from 1 % to 5 % [19]. Wool and acrylic fabrics are prepared as the weight ratio of wool and acrylic fibers in wool/acrylic blend fabric (wool/acrylic=50/50, w/w) and dyed in the same bath. The color strength of dyed acrylic fabrics is measured and presented by K/S values in Figure 8. Higher K/S values are obtained with three dyes as the dye concentration increases. Dye1 shows higher dye uptake than both Dye2 and Dye3 since it has lower molecular weight than Dye2 and Dye3, which enhance the diffusion of Dye1 in fiber.

Color strength of wool fabrics dyed with the cationic reactive dyes at five different dye concentrations are shown in Figure 9. Three dyes exhibit similar build-up properties on both wool and acrylic fabrics. Comparing the results of the simultaneous dyeing to those of homogeneous dyeing, wool does not show much difference in its color strength, whereas K/S values of wool are smaller than that of acrylic at

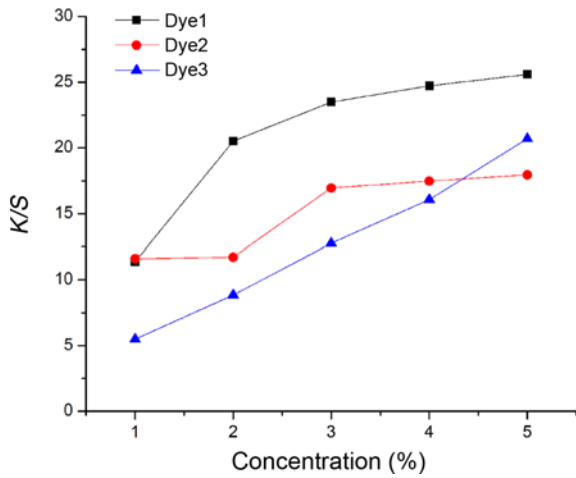


Figure 8. Effect of dye concentration on color strength of Dye1, Dye2 and Dye3 on acrylic fabrics in the simultaneous dyeing; dyeing conditions: pH 5, liquor 40:1, 95 °C for 60 min.

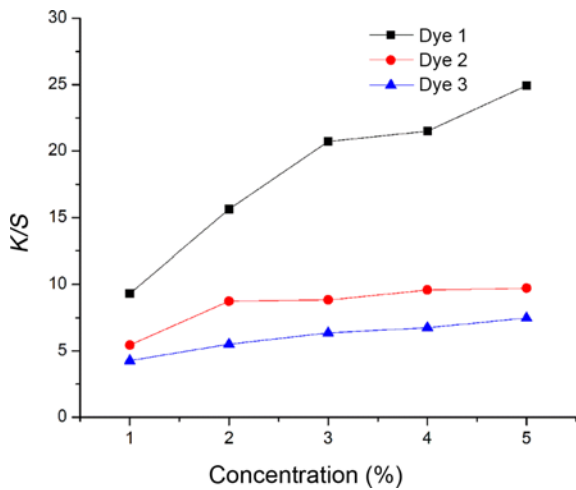


Figure 9. Effect of dye concentration on color strength of Dye1, Dye2 and Dye3 on wool fabrics in the simultaneous dyeing; dyeing conditions: pH 6, liquor 40:1, 95 °C for 60 min.

high dye concentration.

In order to understand the color differences between wool and acrylic fabrics dyed with same dyebath, the union color index, K, is applied. It is well known that the union dyeing results are better when the value of the union dyeing balance, K, is close to 1 [20]. As shown in Figure 10, with increasing dye concentration, there was a rapid increase of K value of Dye2 and Dye 3, resulting in low color uniformity on acrylic and wool fabrics. Whereas, the union dyeing property of Dye 1 was far superior to the other two dyes, indicating that the molecular size of dyes may be more important in determining union dyeing properties on acrylic/wool blend fabrics. Comparing the chemical structure of Dye1, Dye2 and Dye3, the better union dyeing was

generally believed to be attributable to the small molecular size of Dye1, which may help further dye diffusion.

Wool/acrylic fabric is dyed with three cationic reactive dyes by one-bath one-step method at pH 6 and 95 °C. The

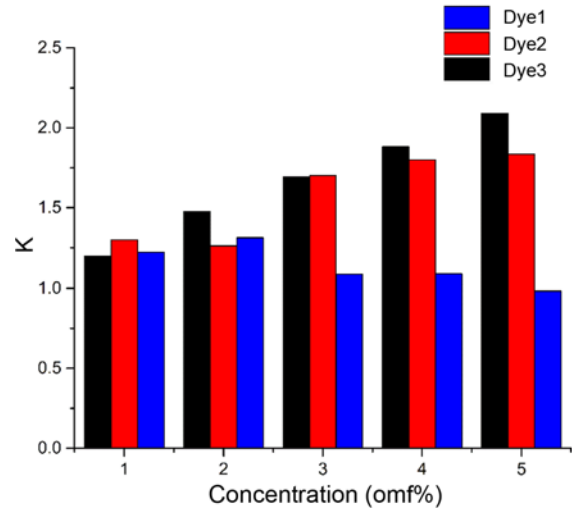


Figure 10. Effect of reactive cationic dye concentration on the union dyeing on acrylic and wool fabrics; dyeing conditions: liquor ratio 40:1, pH 5, at 95 °C for 60 min.

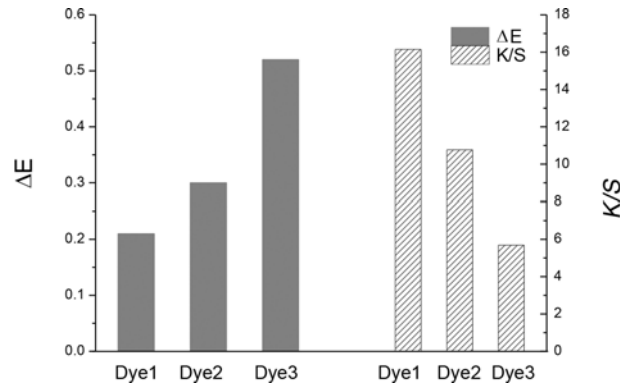


Figure 11. Comparative color difference and color strength of three dyes on wool/acrylic fabrics; dyeing conditions: shade 1 % omf, liquor ratio 40:1, pH 6, at 95 °C for 60 min.



Figure 12. The coloration sample of the obtained cationic reactive dye 1 (A), 2 (B), 3 (C) on wool/acrylic blend fabrics.

Table 4. Fastness properties results of Dye1, Dye2 and Dye3 on acrylic/wool blend fabrics

Dye	Light	Rubbing		Washing		Perspiration	
		Dry	Wet	SC	SW	SC	SW
Dye1	4	4-5	4	4	4-5	5	4-5
Dye2	4	4	3	4	3-4	4-5	4-5
Dye3	3-4	4	4-5	4	4	4-5	4

SC, staining on cotton; SW, staining on wool.

levelling properties of wool/acrylic blend fabrics dyed with the three dyes using 1 % omf shades are showed in Figure 11. It is clear that the average color difference (ΔE) of the dyed fabrics shows good levelling properties in all cases ($\Delta E < 1$). As shown in Figure 11, the levelling properties of yellow dyes are better than those of both red and blue dyes. This result is attributed to structural difference as mentioned before. Furthermore, Figure 12 also reveals that satisfactory levelling properties were achieved for the three cationic reactive dyes (Dye1, Dye2, Dye3) on wool/acrylic blend fabrics. Compared the wool/acrylic blend fabrics with 100 % wool fabric and 100 % acrylic fabric, K/S values of dyed wool/acrylic blend fabric seem to be higher than each component fiber. This result may be in good agreement with the cooperation between the two fibers in the dyebath. Because the presence of carboxylate or sulphonate groups in the acrylic component that would facilitate dye uptake by the wool component as a result of electrostatic attraction between these groups and the cationic groups present in the dye molecules. Then the nucleophilic substitution reaction between amino groups on the wool fiber and monochlorotriazine group on the dyes takes place.

Color fastness to washing, light, perspiration and rubbing of the dyed wool/acrylic blend fabric, listed in Table 4, show similar tendency to those of wool and acrylic.

Conclusion

Three cationic reactive dyes (yellow, red and blue) were successfully prepared in good yield using a novel synthetic route. The dyeing and color fastness properties of the cationic reactive dyes on wool, acrylic, wool/acrylic blend fabrics have been investigated. The optimum pH for wool and acrylic fabrics were 6 and 5, respectively. Effect of temperature, time on dyeing properties and color fastness properties on wool fabric showed the same tendency with acrylic fabric. The K/S value of wool fabric dyed with three dyes was similar to that of acrylic fabric when both fabrics were dyed simultaneously in the same dyebath using low dye concentration. The wool/acrylic blend fabric dyed with three cationic reactive dyes using one-bath one-step dyeing method showed good union dyeing property and the build-up property was better than 100 % wool and acrylic fabrics. Washing, rubbing and perspiration fastness for wool/acrylic

blend fabric were excellent and the light fastness was moderate. For the dyes investigated, the effect of dye structure on dyeability of the fabrics revealed that the smaller size of the dye molecule, the better union dyeing was obtained. The success for one-bath union dyeing of acrylic/wool blend fabrics with reactive cationic dyes would suggest the potential application in cleaner textile production.

Acknowledgements

This work was financially supported by the Fundamental Research Funds for the Central Universities (NO.16D310510).

References

1. R. Farouk, Y. Youssef, A. Mousa, and H. Ibrahim, *World Appl. Sci. J.*, **26**, 1280 (2013).
2. K. Xie and A. Hou, *J. Disper. Sci. Technol.*, **29**, 436 (2008).
3. Y. C. Chao and S. M. Lin, *Dyes Pigment.*, **37**, 357 (1998).
4. Y. Dong, W. S. Lyoo, and J. Jang, *Fiber. Polym.*, **11**, 213 (2010).
5. R. M. El-Shishtawy, M. M. El-Zawahry, and N. S. Ahmed, *Color. Technol.*, **127**, 28 (2011).
6. K. Nishida, T. Tamura, K. Takayama, Y. Ando, T. Morimoto, H. Iwamoto, and H. Toda, *Rev. Prog. Color.*, **95**, 9 (1979).
7. A. Soleimani-Gorgani and J. A. Taylor, *Dyes Pigment.*, **76**, 610 (2008).
8. M. S. Javadi, J. Mokhtari, M. Nouri, and M. J. Mehdipour, *Fiber. Polym.*, **14**, 195 (2013).
9. Y. Sun, D. Zhao, and H. S. Freeman, *Dyes Pigment.*, **74**, 608 (2007).
10. L. Min, Z. Kai, and K. Xie, *Carbohydr. Polym.*, **113**, 77 (2014).
11. M. V. D. Kraan, M. V. F. Cid, G. F. Woerlee, W. J. T. Veugelers, and G. J. Witkamp, *J. Supercrit. Fluids.*, **40**, 470 (2007).
12. K. Xie, A. Gao, M. Li, and X. Wang, *Carbohydr. Polym.*, **101**, 666 (2014).
13. A. Airinei, M. Homocianu, and D. O. Dorohoi, *J. Mol. Liq.*, **157**, 13 (2010).
14. H. Hamidian, N. Zahedian, D. Ghazanfari, and S. Fozooni, *J. Spectrosc.*, **2013**, Article ID 276413 (2013).
15. A. Mohammadi, M. R. Yazdanbakhsh, and L. Farahnak,

- Spectrochim. Acta. A.*, **89**, 238 (2012).
16. R. M. El-Shishtawy, Y. A. Youssef, N. S. E. Ahmed, and A. A. Mousa, *Dyes Pigment.*, **72**, 57 (2007).
17. F. A. Nagia and R. S. R. El-Mohamedy, *Dyes Pigment.*, **75**, 550 (2007).
18. J. H. Jun, K. Sawada, T. Takagi, G. B. Kim, C. H. Park, and M. Ueda, *Rev. Prog. Color.*, **121**, 25 (2005).
19. S. D. Kim, Y. J. Choi, H. Y. Lee, and J. L. Lee, *Fiber Polym.*, **13**, 199 (2012).
20. J. Zheng, X. Liu, and P. Rex Brady, *Color. Technol.*, **124**, 204 (2008).