Article

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Synthesis and Evaluation of Technical Properties of Novel Cationic Mono-*s*-chloro Triazinyl (MCT) Reactive Dyes on Cotton

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Two novel cationic mono-*s*-chloro triazinyl (MCT) reactive dyes together with their analogues were synthesized via reacting an N,N-dimethyl dodecylamine with p-nitrobenzyl bromide. The resultant was reduced using stannous chloride and hydrochloric acid to produce the primary amine. The quaternary ammonium salt containing primary amine was then diazotized and coupled to H-acid/J-acid reacted with cyanuric chloride and sulfanilic acid. The analogue dyes were prepared via the same route without quaternary ammonium salt making stage. The dyes were characterized using FTIR, ^{1}H NMR, UV-Vis spectroscopy and elemental analysis. The substantivity, exhaustion and fixation of the dyes were investigated on cotton fabric. It was found that these functional dyes could be effectively introduced to cotton for achieving simultaneous coloration and functional finishing effects. All the dyed fabrics exhibited softening efficacy. The washing and light fastness of the dyed samples were further studied.

Keywords: Cationic reactive dye; Dyeing; Quaternary ammonium group.

INTRODUCTION

In recent years, the most prominent developments in dye chemistry and application have been announced in the field of functional dyes.[1-6] They are important class of the synthesis colouring materials and have attracted much attention due to their potential functions for specialty and high-technology applications.

Reactive dyes are attached to suitable fibres via covalent bond. They are known for their bright colours and very good to excellent light and wash fastnesses; however, their resistance to chlorine bleach is poor.[7] Several broad classes of reactive dyes are available. Most of them are intended for cellulosic fibres. There are two classes of chromophores for reactive dyes, namely anthraquinone and azo. Azo dyes and pigments constitute by far the most important chemical class of commercial organic colorant. They account for around 60-70% of the dyes used in traditional textile applications.[8]

Quaternary ammonium salt (QAS) is one of the major components of cationic surfactant. These compounds are widely used as disinfectants due to having a positively charged quaternary nitrogen. They inflict on microbes via a variety of detrimental effects, including damage to cell membranes, denaturation of proteins and disruption of the cell structure.[6] During inactivation of bacterial cells, the quaternary ammonium group remains intact and retains its antibacterial ability as long as the compound is attached to textiles.[9] Although high solubility enables dyes to more readily form positive ions in aqueous solution, thereby inhibiting bacterial growth by adsorbing onto bacterial surfaces.[4]

Several disperse dyes possessing quaternary ammonium salts have been synthesized.[4,6] However, less work has been done in the field of soluble dyes such as reactive dyes. In this paper, the main goal is to design a reactive dye combined with a quaternary ammonium to benefit the desired properties of both reactive dye and quaternary ammonium moiety. For this purpose, two novel reactive dyes containing quaternary ammonium moiety (Scheme I) are synthesized. The dyes are characterized using FTIR, ^{1}H NMR, melting point and UV/visible spectrophotometer. The technical properties of the dyes are also studied via examining mechanical properties (Tear Strength, Abrasion Resistance, Flexibility, and Crease recovery angle tests) of the dyed substrates.

EXPERIMENTAL

Instrumental and analysis methods

The UV/Vis absorption spectra of dyes (in water) were recorded using a Cintra 10 UV/visible spectrophotometer (GBC Co., Australia).

Thin layer chromatography (TLC) was used for monitoring reactions. This technique was performed using aluminium plates coated with silica gel 60 F254 (Merck) as

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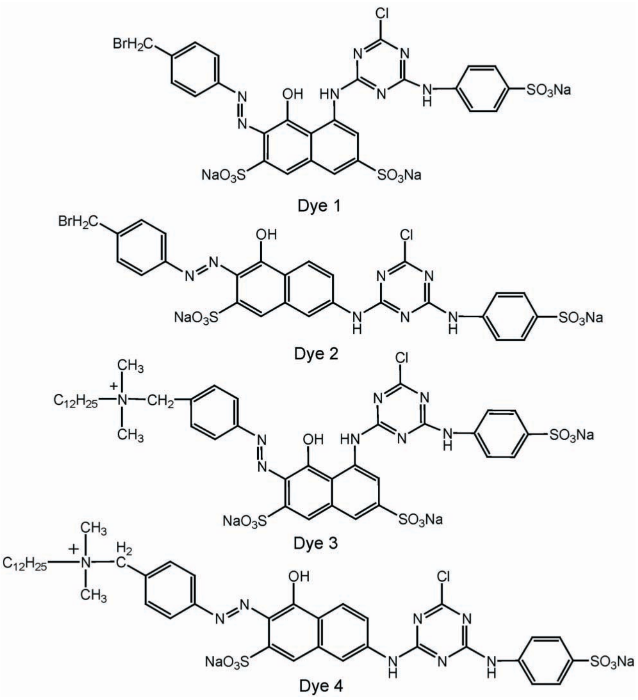
Scheme I Structures of dyes



stationary phase and a mobile phase consisting of n-butanol: acetone: water (2:2:1). The developed plates were visualized under both short and long wavelength ultraviolet light (254 nm, 365 nm).

The FTIR spectra of dyes were determined on a Nicolet magna-ir 560 infrared spectrometer (USA) using KBr pellets.

The ^{1}H NMR spectra of dyes were recorded on a Bruker AVANCE-500 MHZ (USA) spectrometer.

The melting points of the products were determined via capillary method using a Barnstead electrothermal 9200 (UK).

Elemental analyses for carbon, hydrogen and nitrogen were carried out at the Department of Chemistry, Guilan University, on a Carlo Erba 1108 elemental analyser.

Synthesis of intermediates and dyes

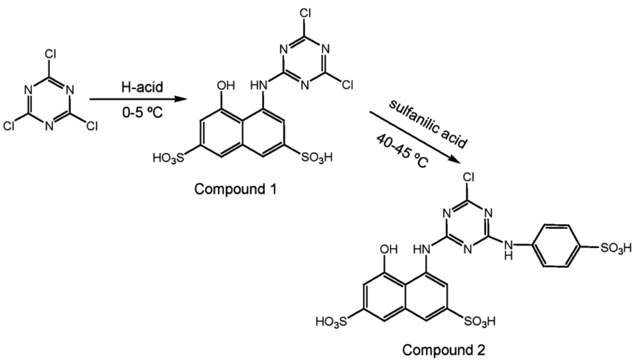
Materials

P-nitrobenzyl bromide, N,N-dimethyl dodecylamine, cyanuric chloride, H-acid (92%), J-acid (90%), sulfanilic acid, sodium nitrite,stannous chloride and hydrochloric acid (36%) were all obtained from Aldrich Co. and used as received.

Synthesis of compound 1

Compound **1** was synthesized according to ref[10]. 2,4,6-trichloro-s-triazine (2.43 g, 0.013 mol) was dissolved in acetone (15 mL). The solution was then added dropwise to a mixture of crushed ice (40 g) and water (40 mL) to prepare a fresh suspension of 2,4,6-trichloro-s-triazine. To the resulting suspension, an aqueous solution of H-acid (0.01 mol in 40 mL water) was added very slowly at below 5 °C, pH 3-4. The reaction was continued for 2 h with stirring and completion of the reaction was determined with the aid of Ehrlich's reagent and TLC. The synthesis route is shown in Scheme II.

Scheme II Synthesis route for compounds **1** and **2**



Synthesis of compound 2

Sulfanilic acid (0.011 mol) was dissolved in water (30 mL) at pH 7. The solution was then added very slowly to the reaction mixture prepared in previous section at 40-45 °C and pH 5-6. The mixture was stirred for 2 h and completion of the reaction was determined with the aid of Ehrlich's reagent and TLC. The synthesis route is shown in Scheme II (Yield 94%, black in colour).

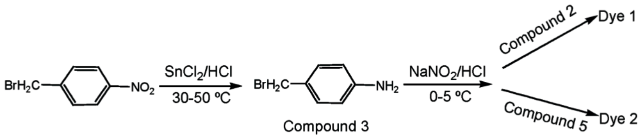
Synthesis of compound 3

Compound **3** was synthesized according to ref[4]. 4-nitro benzyl bromide (0.0092 mol) was dissolved in acetone (20 mL) in a two-neck flask. A mixture of $SnCl_2/2H_2O$ (0.0324 mol) and concentrated hydrochloric acid (36%, 0.14 mol) was added dropwise to the flask at room temperature. The whole mixture was allowed to react at 45-50 °C for 12 h. The pH was adjusted to 8-10 with sodium hydroxide aqueous solution (10%). The mixture was filtered to remove impurities. The filtrate was then evaporated under vacuum to obtain product. The synthesis route is shown in Scheme III (Yield 92%, yellow in colour).

Synthesis of dye 1

Compound **3** (0.0085 mol) was dissolved in concentrated hydrochloric acid (36%, 0.1238 mol) and water (15 mL) at 0-5 °C. An aqueous solution of sodium nitrite (30%,

Scheme III Synthesis route for dyes **1** and **2**



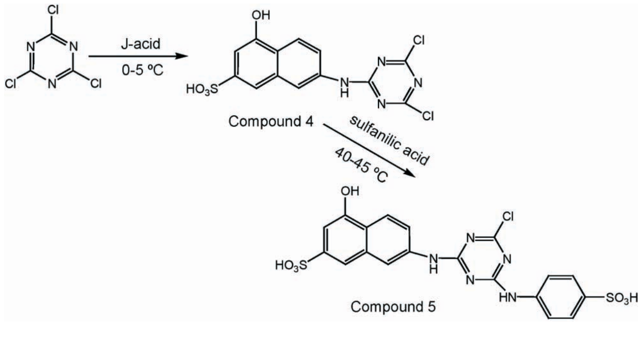
0.009 mol) was added to the solution dropwise to prepare diazonium salt. The reaction was continued for 2 h to completion, which was controlled by TLC.

Compound **2** (0.0094 mol) was dissolved in water (100 mL) with stirring at 5-10 °C and pH 7-8. To the solution, the prepared diazonium salt was then added dropwise to produce the dye. The pH of the reaction mixture was adjusted to 7-8 by dropwise addition of aqueous sodium hydroxide solution (10%) and the reaction was continued at the same temperature for 3-5 h to completion, which was controlled by TLC and reacting the mixture with β-naphthol. The product was salted out with sodium chloride, filtrated and dried. The residue was dissolved in acetone and indiscerptible salt was filtrated off. Finally, the filtrate was evaporated under vacuum to obtain the product. The synthesis route is shown in Scheme III (Yield 70%, violet in colour).

Synthesis of dye 2

By following the procedures for dye **1**, dye **2** was prepared using J-acid instead of H-acid (Scheme IV). J-acid was reacted with cyanuric chloride and then followed reacting with sulfanilic acid according to ref [11]. The synthesis route is shown in Scheme IV (Yield 73%, red in colour).

Scheme VI Synthesis route for compounds **4** and **5**



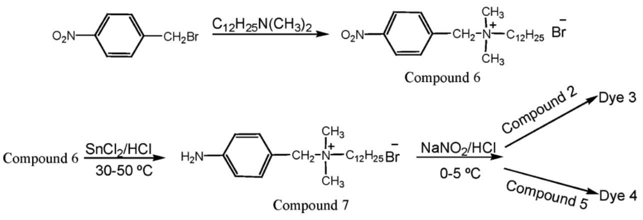
Synthesis of compound 6

Compound **6** was synthesized according to ref [4]. The synthesis route is shown in Scheme V.

Synthesis of compound 7

Compound **7** was synthesized according to ref [4]. The synthesis route is shown in Scheme V. (Yield 84%, yellow in colour).

Scheme V Synthesis route for compounds **6**, **7** and dyes 3, 4



Synthesis of dye 3

Sodium nitrite (0.018 mol) was dissolved in concentrated sulfuric acid (0.225 mol) at 5-15 °C. Compound **7** (0.0075 mol) was added dropwise to the solution with stirring. The pH was adjusted to 4 by dropwise addition of acetic acid (0.122 mol). The diazotisation was completed over 2 h. Compound **2** (0.0094 mol) as coupling component was dissolved in water (100 mL) with stirring. The prepared diazonium salt solution was then added dropwise to the coupling component solution. The pH was adjusted to 7-8 by dropwise addition of aqueous sodium hydroxide solution and the reaction was continued at 5-10 °C for 3-5 h. The product was salted out with sodium chloride, filtrated off and dried. The obtained residue was dissolved in acetone; the indiscreptible salt was filtrated off. Finally, the filtrate was evaporated under vacuum to obtain the product. The synthesis route is shown in Scheme V (Yield 71%, maroon in colour).

Synthesis of dye 4

Dye 4 was prepared in the same procedures of dye 3 using J-acid instead of H-acid. The synthesis route is shown in Scheme V (Yield 73%, orange in colour).

Characterisation of compounds and dyes

In order to characterise the compound and the dyes, they were submitted to UV-Vis spectroscopy, melting point determination, FT IR and ^{1}H NMR spectroscopy and elemental analysis.

By UV-Vis spectroscopy, wavelength of maximum absorption (λ_{max}) and molar absorptivity coefficients (ε_{max}) of the dyes were determined using beer-lambert law eq. (1).

$$A = \varepsilon l C \qquad (1)$$

where A is absorbance, ε is molar absorptivity coefficient and C is concentarion in mol/l, l is pass length of cell (1 cm).

Solutions of the four novel dyes, achieved in distilled water, were prepared in the concentration range 0.01-0.03 g/l and the absorbance of each solution was measured at the λ_{max} of the dye using 1 cm cells and a Cintra 10 spectrophotometer. The molar absorptivity coefficients (ε_{max}) of the dyes were determined and are shown in Table 1.

The synthesised compound s and dyes were subjected to melting point determination. The results are shown in Table 1.

FT IR and ^{1}H NMR data and elemental analysis reults for compounds **2**, **3** and **7** and dyes 1-4 are shown in Tables 2 and 3, respectively.

Dyeing

Plain woven cotton fabric (138.8 g/m^2) was purchased from domestic producer. The fabric were scoured in a 1% nonionic detergent for 30 min at 50 °C with a liquor to fabric ratio of 40:1, then rinsed thoroughly in tap water and dried in the open air. Dyeing were carried out using a Roaches dyeing machine (Mathis Labomat BFA 12): 5 g pieces of fabric were dyed at a liquor ratio of 20:1, using stainless steel dye pots, each of 200 cm^3 capacity. The dyeing method used is depicted in Fig. 1. At the end of dyeing, the dyed fabric was removed and rinsed in cold water. Washing the dyed fabric was performed at liquor ratio of 30:1 with 3 g/l detergent and 2 g/l sodium carbonate at 100 °C for 15 min. An initial series of dyeing was carried out at four different alkali values using of 5, 10, 15 and 20 g/l by adding sodium carbonate. No additional electrolyte, leveling agent or alkali was used. Having determined the optimum alkali, further experiments were carried out to determine the optimum salt of dyeing. For this purpose, a series of dyeing were set off at four different salt values of 10, 20, 30 and 40 g/l by sodium chloride. Subsequent dyeing was carried out on 1 g pieces of fabric, at four depths of shade (1, 2, 4 and 6% o.m.f.).

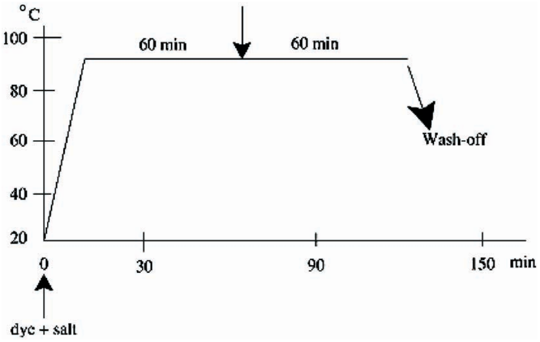


Fig. 1. Dyeing profile for reactive dyes.

Colour strength (K/S) of dyes on fabric

Reflectance measurements on the dry dyed fabrics were carried out using a Data colour Spectra Texflash specrophotometer using D65 illumination; the dyed fiber was folded twice so as to provide four layers and the average of three reflectance measurements, taken at different positions, was used.

Measurement of the SER$_5$F profiles of dyes

The SER$_5$F (S, substantivity; E, exhaustion; R$_5$, reactivity after 5 min; and F, fixation) profiles of the dyes were determined according to refs [11-13]. The SER$_5$F profiles of the dyes were compared at the same depth of shade (1% o.m.f). Most of researchers[14] suggested that the use of urea can make dyeing faster. Therefore, the effect of urea on the dye adsorption was evaluated in this test.

Determination of the migration indices of dyes

Migration refers to the movement of a dye molecule from one site to another on the textile substrate via a desorption process into the dyebath. By this mean, a uniform dyeing over the whole of the textile substrate can be achieved. Because a reactive dye forms a covalent bond with cellulose under alkaline conditions, migration must take place primarily during the neutral salting phase in order to achieve a uniform dyeing. This is particularly the case with high substantivity (S) dyes. Opportunity for migration after the addition of alkali will be limited. The migration properties of reactive dyes can be readily estimated using a simple test, which seeks to define a migration index (MI) for an individual dye when applied under a given set of conditions.[11,13,15] In order to determine the migration index, a typical method is described. 4 pieces of plain cotton and two baths (dye and blank bath) were used. Dye bath contain dye, salt and water and 2 pieces of fabrics D_1 and D_2. Blank bath contain salt and water and 2 pieces of fabrics B_1 and B_2. The two baths were set at 80 °C and exhaustion allowed to proceed for 30 min, thereafter sample D_2 from the dye bath was swapped with sample B_2 from the blank bath, excess liquor being squeezed off when carrying out the transfer. Sample B2 was rolled inside sample D1 before being returned to the dyebath. In a similar manner, sample B1 was rolled inside sample D2 before being returned to the blank bath.

The process was continued for 30 min at the same temperature (to allow migration to occur in the blank bath) before the alkali was then added. The dyeing was continued according to the dyeing profile of dyes. The patterns were then removed, washed and dried. The migration index of a dye can be calculated using eq. (2).

$$MI = (K/S) \text{ of fabric } B_1 * 100 / (K/S) \text{ of fabric } D_2 \quad (2)$$

Fastness testing

Colour fastness was determined according to the respective international standards: The wash fastness properties of dyes were assessed using the ISO105-C01:1993(E) and ISO105-C04:1993(E) wash fastness test. The change in shade and the degree of cross staining were assessed visually using grey scales. Light fastness properties of dyes were assessed using the ISO105-B02:1994(E) light fastness test. The change in shade was assessed visually using blue scales.

Softening properties

The softening properties of the functional group incorporated in the cationic reactive dyes were evaluated via examining mechanical properties (Tear Strength, Abrasion Resistance, Flexibility, and Crease recovery angle tests) of the dyed substrates using the following method:

The samples were divided into two sections: 1. The samples which only dyed with novel dyes in different concentration; 2) The samples were dyed with dyes 1 and 2 then finishing with cationic softener (Celloube CM). For finishing, the dyed fabric was padded in softener solution (10 g/l) with pick up 70% and dried at 100 °C. Then, softener properties were evaluated by means of Tear Strength, Abrasion Resistance, Flexibility, and Crease recovery angle tests.

Tear Strength

The control and dyed fabrics were tested for tear strength in the warp direction using a MICRO 250 (Shirley, UK) tensile tester according to ASTM D 2261. A gauge length of 3 in. and a crosshead speed of 2 in/min were used for testing. Five samples were tested for each condition, and the average of the readings was calculated.

Abrasion Resistance

Abrasion resistance was measured in terms of the number of abrasion cycles required for failure with a 1 lb load on a MARTINDALE 2000 Abrasion tester according to ASTM D 3886. Five specimens were tested, and the average reduction of fabric mass of the sample is reported.

Flexibility

Bending lengths of the samples were measured using SDL003 Shirley stiffness tester. Fabric flexibility was measured in terms of flexural rigidity according to ASTM D 1388 using eq. (3). The higher the flexural rigidity of a fabric, the lower is the flexibility, and vice versa. Therefore, the inverse of flexural rigidity gives an indication of fabric flexibility.

$$G = WC^3 \quad (3)$$

where G represents flexural rigidity, mg/cm; W represents fabric mass per unit area, mg/cm^2; and C represents bending length, cm.

Crease Recovery Angle

Crease angle measurements were made by AATCC Standard Test Method 66 using a M003A Shirley Crease Recovery Tester.

RESULTS AND DISCUSSION

Structure characterization

UV-Vis spectra of the dyes were determined in the aqueous solution. The corresponding λ_{max} and molar absorptivity coefficient (ε_{max}) were summarized in Table 1. Data in Table 1 show that the presence of H-acid in dyes 1 and 3 related to J-acid in dyes 2 and 4 caused a bathochromic effect (36-40 nm) in dyes 1 and 3. This could be due to an extra sulphonic acid present on the dayes containg H-acid.[16]

It was found that alkyl chain did significantly affect the λ_{max} in all of the dyes. Quaternary ammonium group present on the dye structures is more powerfully electron-withdrawing and attracted electron as chromophore and led to hypsochromic shift in dyes 3 and 4 in compared with dyes 1 and 2, respectively. Absorption of dyes 3 and 4 was decreased due to having alkyl chain. Steric hindrance may be an important factor. Usually, ε_{max} is a widely accepted measurement of tinctorial strength. However, assessing the tinctorial strength of dyes is quite difficult and, in some cases, controversial results could be obtained. As a general rule, steric hindrance always causes a reduction in tinctorial

Table 1. The characteristics of compounds and dyes

Sample Name	Mp (°C)	λ_{max} (nm)	ε_{max} (dm^{3}mol^{-1}cm^{-1})
Compound **2**	Decompose at 250	-	-
Compound **3**	Decompose at 274	-	-
Compound **7**	Decompose at 286	-	-
Dye 1	Decompose at 385	552	25620
Dye 2	Decompose at 381	512	21767
Dye 3	Decompose at 400	536	22931
Dye 4	Decompose at 400	500	20019

Table 2. FTIR, ^{1}H NMR and elemental analysis of compounds

Compound	FTIR, ^{1}H MNR and Elemental Analysis
2	FTIR (KBr, ν, cm^{-1}): 3444 (-OH); 1407 (C-N); 1039 (C-Cl); 1189 (S=O Stretching). ^{1}H NMR (500 MHz, D_2O, δ, ppm): 1.8-2.7 (3 singlet, 3H, $-SO_3H$), 2.85 (singlet, 1H, benzene C-NH), 3.27 (singlet, 1H, naphthalene C-NH), 4.6 (singlet, 1H, aromatic C-OH), 6.5-8 (broad peak, 4H, 1-naphthalene), 8-8.5 (complex, 4H, 1-benzene). Anal Calcd for $C_{19}H_{14}ClN_5O_{10}S_3$: C, 37.78%; H, 2.34%; N, 11.60%; found: C, 37.2%; H, 2.86%; N, 11.78%.
3	FTIR (KBr, ν, cm^{-1}): 3420, 1629 ($-NH_2$). ^{1}H NMR (500 MHz, D_2O, δ, ppm): 3.9 (singlet, 2H, $-NH_2$), 4.62 (singlet, 2H, $-CH_2Br$), 6.3-7.1 (complex, 4H, benzene). Anal Calcd for C_7H_8N: C, 45.19%; H, 4.33%; N, 7.53%; found: C, 44.56%; H, 4.38%; N, 7.40%.
7	FTIR (KBr, ν, cm^{-1}): 3408 ($-NH_2$); 2922, 2851 ($-CH_2(CH_2)_{10}CH_3$). ^{1}H NMR (500 MHz, D_2O, δ, ppm): 0.8-0.82 (triplet, 3H, $-(CH_2)_{11}-CH_3$); 1.2 (singlet, 18H, $-N+(CH_3)_2-(CH_2)_2-(CH_2)_9-CH_3$); 1.5 (complex, 2H, $-N^+(CH_3)_2-CH_2-CH_2-C_{10}H_{21}$); 1.8 (triplet, 2H, $-N^+(CH_3)_2-CH_2-C_{11}H_{23}$); 2.7 (singlet, 6H, $-N^+(CH_3)_2-C_{12}H_{25}$); 3.9 (singlet, 2H, aromatic C-NH_2); 4.3 (singlet, 2H, $-CH_2-N^+(CH_3)_2-C_{12}H_{25}$); 6.5-7.2 (complex, 4H, 1-benzene). Anal Calcd for $C_{21}H_{39}BrN_2$: C, 63.14%; H, 9.84%; N, 7.01%; found: C, 63.59%; H, 10.03%; N, 7.25%.

Table 3. The FTIR, ^{1}H NMR and Elemental Analysis of dyes

Dye	FTIR, ^{1}H MNR and Elemental Analysis
1	FTIR (KBr, ν, cm^{-1}): 3442 (-OH); 1622 (N=N); 1043 (C-Cl). ^{1}H NMR (500 MHz, D_2O, δ, ppm): 1.9 (singlet, 3H, $-SO_3H$); 4.1 (singlet, 2H, aromatic C-NH); 4.68 (singlet, 2H, CH_2Br); 5.1 (singlet, 1H, aromatic C-OH); 7-9 (complex, 11H, aromatic ring). Anal Calcd for $C_{26}H_{16}BrClN_7Na_3O_{10}S_3$: C, 36.02%; H, 1.86%; N, 11.31%; found: C, 36.07%; H, 1.9%; N, 11.26%.
2	FTIR (KBr, cm^{-1}): 3446 (-OH); 1618 (N=N); 1042 (C-Cl). ^{1}H NMR (500 MHz, D_2O, δ): 1.9 (singlet, 2H, $-SO_3H$); 4.1 (singlet, 2H, aromatic C-NH); 4.6 (singlet, 2H, CH_2Br); 5.2 (singlet, 1H, aromatic C-OH); 7-8.4 (complex, 12H, aromatic ring). Anal Calcd for $C_{26}H_{17}BrClN_7Na_2O_7S_2$: C, 40.83%; H, 2.24%; N, 12.82%; found: C, 41.02%; H, 2.31%; N, 12.75%.
3	FTIR (KBr, ν, cm^{-1}): 3453 (-OH); 2923, 2853 ($CH_3(CH_2)_{10}$ CH_2-); 1619 (N=N); 1401 ($-N^+(CH_3)_2-$); 1041 (C-Cl). ^{1}H-NMR (500 MHz, D_2O, δ, ppm): 0.54 (broad peak, 3H, $-(CH_2)_{11}-CH_3$); 0.88 (broad peak, 18H, $-N^+(CH_3)_2-(CH_2)_2-(CH_2)_9-CH_3$); 1.2 (broad peak, 2H, $-N^+(CH_3)_2-CH_2-CH_2-C_{10}H_{21}$); 1.75 (triplet, 2H, $-N^+(CH_3)_2-CH_2-C_{11}H_{23}$); 1.85 (singlet, 6H, $-N^+(CH_3)_2-C_{12}H_{25}$); 2.62 (broad peak, 3H, $-SO_3H$); 4.02 (singlet, 2H, aromatic C-NH); 4.68 (singlet, 2H, $-CH_2-N$); 4.88 (singlet, 1H, aromatic C-OH); 6.5-9 (broad peak, 11H, aromatic ring). Anal Calcd for $C_{40}H_{47}ClN_8Na_3O_{10}S_3$: C, 47.97%; H, 4.70%; N, 11.19%; found: C, 47.80%; H, 4.81%; N, 11.25%.
4	FTIR (KBr, ν, cm^{-1}): 3427 (-OH); 2923, 2854 ($CH_3(CH_2)_{10}$ CH_2-); 1574 (N=N); 1405 ($-N^+(CH_3)_2-$); 1039 (C-Cl). ^{1}H-NMR (500 MHz, D_2O, δ, ppm): 0.62 (broad peak, 3H, $-(CH_2)_{11}-CH_3$); 0.98 (broad peak, 18H, $-N^+(CH_3)_2-(CH_2)_2-(CH_2)_9-CH_3$); 1.4 (broad peak, 2H, $-N^+(CH_3)_2-CH_2-CH_2-C_{10}H_{21}$); 1.7 (triplet, 2H, $-N^+(CH_3)_2-CH_2-C_{11}H_{23}$); 1.86 (broad peak, 2H, $-SO_3H$); 2 (singlet, 6H, $-N^+(CH_3)_2-C_{12}H_{25}$); 3.6 (singlet, 2H, aromatic C-NH); 4.55 (singlet, 2H, $-CH_2-N$); 5.2 (singlet, 1H, aromatic C-OH); 7-9 (broad peak, 12H, aromatic ring). Anal Calcd for $C_{40}H_{48}ClN_8Na_2O_7S_2$: C, 53.48%; H, 5.39%; N, 12.47%; found: C, 53.41%; H, 5.48%; N, 12.43%.

strength,[6] which readily explains our experimental results, as shown in Table 1. The structure of dyes 1 and 2 is small, providing little steric hindrance, and thus absorption did not decrease due to alkyl chain.

The FTIR spectra of the dyes show the absorbance bands at wavenumbers, ν, of 1039, 1407, 3444, and 1182 cm^{-1}, which can be attributed to the C–Cl, C=N, OH, and S=O stretching vibrations, respectively. The results correspond with the literature data. Also, there is only one peak in the region of 1575-1630 cm^{-1} for the dyes, which can be attributed to stretching vibration of N=N group. Asymmetric and symmetric stretching vibrations for alkyl chain are shown at wavenumbers 2920-2960 cm^{-1} and 2830-2880 cm^{-1}, respectively. These peaks only can be observed in the FTIR spectra of the dyes 3 and 4.

The chemical structures of the synthesized dyes were also confirmed by ^{1}H NMR analysis. By comparing the ^{1}H NMR spectra of the dyes, there are peaks at chemical shift, δ, 0.54-1.85 ppm at the spectrum of dye 3, 0.62-1.7 ppm at the spectrum of dye 4, which confirms the presence of the alkyl chain group. The physical and chemical properties of the abovementioned intermediates such as the yields (Y%), melting points and appearance of the crystals were reported at the end of each preparation section. The FTIR, ^{1}H NMR spectra and elemental analysis of intermediates and dyes are given in Tables 2 and 3, respectively.

Evaluation of technical properties of dyes

The change in shade for effect of variation in the alkali and salt concentration of the dyes at 1% o.m.f depth of shade were assessed (Figs. 2 and 3). In aqueous solutions, depending on the pH within the fiber, hydroxyl groups of cellulose will be ionized to a greater or lesser extent, also the soda ash affects on the fixation and hydrolyses of dyes; therefore determination of optimum concentration for soda ash is necessary. Fig. 3 reveals that the dyes show a maximum colour yield at 20 g/l alkali.

As shown in Fig. 2, the colour yield of dyes initially increases with salt concentration, reaching a 'plateau' in the presence of 40 g/l. The role of salt in the dyeing process is to suppress the repulsion between the negative charge on the surface of the cellulose and the anionic dye, thereby increasing its substantivity for the cotton. This effect will progressively increase as the concentration of salt is increased, leading to a higher colour yield.

Dyeing properties of the dyes

In order to predict the likely (level) dyeing and fastness properties of the dyes under (bulk) exhaust dyeing conditions, the SER_5F profiles of the dyes were measured and compared. The results are shown in Table 4. Dyes 2 and 4 both exhibit higher substantivity (%S, 78% and 81%, respectively) and higher exhaustion (%E, 85% and 87%, respectively) levels than dyes 1 (65%) and 3 (82%). High substantivity and exhaustion are desirable properties of dyes for environmental and an economical point of view. This may be attributed to the fact that dyes 2 and 4 have lower solubility than dyes 1 and 3, which have extra sulphonic acid groups present in their H acid coupling component.

Table 4. SER_5F profile for the novel dyes

Dye	1	2	3	4	3 (with urea)	4 (with urea)
%S	65	78	68	81	61	70
%E	72	87	82	85	76	81
%R5	67	70	58	60	53	50
%F	70	75	63	67	59	64
E-F	2	12	19	18	17	17

S: substantivity, E: exhaustion, R_5: reactivity after 5 min, F: fixation.

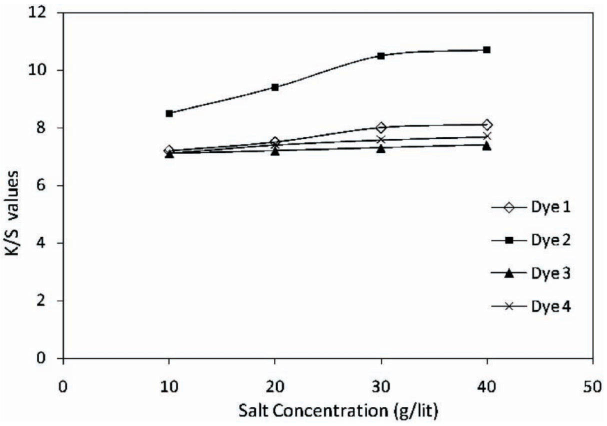


Fig. 2. Effect of salt concentration on colour yield.

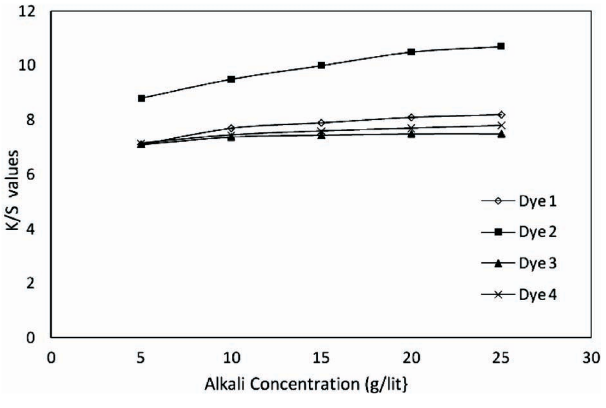


Fig. 3. Effect of alkali concentration on colour yield.

The comparison of substantivity (%S) and exhaustion (%E) of dyes 1 and 2 with those of dyes 3 and 4 (quarernized dyes) shows that dyes 3 and 4 carrying cationic group in dye structure led to higher substantivity and exhaustion. This observation can be attributed to a corresponding increase in the attractive ion-ion interaction operating between the cationic groups in the dye molecule and the anionic groups (ionized hydroxyl groups) present in the fiber. On the other hand, there is a decrease of solubility due to the presence of hydrocarbon chain group in the molecular structures of dyes 3 and 4.

The fixation (%F) levels of dyes 3 (63%) and 4 (67%) are lower than those of dyes 1 (70%) and 2 (75%). This may be attributed to the fact that these dyes contain hydrocarbon chain group, and this group prevents the dyes to be adsorbed on substrate.

Urea is commonly used for dyeing and printing. It is capable of the bursting the aggregation and associate the dye being adsorbed on the fabric. In the presence of urea, results in Table 4 show that the substantivity, exhaustion and fixation of dyes 3 and 4 which are the cationic reactive dye decreased on cotton. The reduction in colour yield when the urea is added to dye bath could be due to decrease aggregation of the dye molecules in the dyebath, leading to increase of solubility and prevention of the dye being adsorbed on to the cotton.

A useful indicator of the ease of washing off of the hydrolysed reactive dye, in order to achieve good wet fastness properties, can be obtained by examination of the difference between the exhaustion (E) and fixation (F) values.[11,13] A high 'E-F' value means a large amount of hydrolysed dye needing to be washed out during the rinsing and 'soaping' stages. This will result in potentially lengthy washing sequences, especially if the dye possesses a high substantivity (S).

Comparing the E-F values for the dyes indicate that dye 1 due to small structure offer lower E-F value (2%) than the others (12-19%), indicating less amount of hydrolysed to be removed from the substrate. This could be attributed to higher solubility of dye 1 due to more sulphonic acid groups present on its structure (3 suphonic acid group on dye 1 and 2 sulphonic acid group on dye 2). Dyes 3 and 4 show higher E-F values (18-19%) in compared with dyes 1 and 2. This could be attributed to the cationic alkyl chain present on their structure. The use of urea decreased the E-F values of dyes 3 and **4** (17%), indicating that urea facilitated the removal of the hydrolysed dyes.

Migration indices of dyes

The migration index (MI) of a dye is often a reflection of its substantivity; highly substantive dyes exhibiting a low migration index and vice versa. Table 5 shows that the migration indices of dyes 1 (77%) and 2 (72%) is much better than dyes 3 (61%) and 4 (59%). These observations could be attributed to the high solubility of dyes 1 and 2 in dyebath. Hence, dyes 1 and 2 likely represent better level dyeing properties than the other two novel dyes.

Fastness properties of dyes

The results of fastness tests for dyes 1-4 on cotton fabric were summarized in Table 5. The wash fastness of the dyes was assessed using the ISO105-C01:1993(E) and ISO105-C04:1993(E) wash fastness test at 40 °C and 95 °C. The change in shade and the degree of cross-staining were assessed visually using grey scales. The wash fastness, as expected, of each dye fixed to cotton fabrics was very good at each of the four depths of shade employed. The light fastness of dyes was assessed using the ISO105-B02:1994(E). The change in shade was assessed visually using blue scale. Results indicated the light fastness of dyes is moderate. These results also reveal that quarternization of the dyes has no significant effect on the fastness properties of the dyes.

Softening properties

Finishing is a comprehensive term referring to processes in which fabric is treated with chemical agents after production. Textile softener is a result of chemical technology; they give feeling of softness and slick hand in fabrics. Consensus of the studies discussed below suggests that regular use of a fabric softener results a reduction of friction between the fabric components; therefore it would increase fabric flexibility, reduce wrinkling and abrasion resistance, increase fiber elongation and improve tear strength. Since quaternary ammonium salts are extremely important softener derivatives, the above mentioned tests were employed for dyed fabric. The results are summarized in Table 6. For evaluation purpose, two comparisons have been chosen: 1. Comparing softness properties of dyed fabrics with cationic reactive dyes only; 2. Comparing softness properties of dyed fabrics with cationic reactive dyes 1 and 2, then the dyed fabric finished with cationic softening agent.

Table 5. Migration indeces and fastness properties of the novel dyes

Dye	Migration index (MI)	Wash fastness	Wash fastness	Light fastness
		ISO105-C01:1993(E)	ISO105-C04:1993(E)	ISO105-B02:1994(E)
1	77	5	5	5
2	72	5	4-5	5
3	61	5	5	5
4	59	5	4-5	5

Table 6. Softening properties of the novel dyes

Dye	1	2	3	4	1*	2*
E (%)	31.55	30.52	32.46	36.70	35.28	35.06
TS (N)	14.5	14.12	14.82	15.05	14.9	14.77
RFM (g)	0.002	0.002	0.004	0.002	0.004	0.004
BL (cm)	2.6	2.6	2.6	2.55	2.35	2.35
FR (mg/cm)	0.29	0.26	0.26	0.25	0.2	0.2
CRA	95	92	102	104	100	100

E: Elongation, TS: Tear Strength, RFM: Reduction of Fabric Mass, BL: Bending Length, FR: Flexural Rigidity, CRA: Crease Recovery Angle.
*Finished.

Tear strength

Table 6 shows the tear strength of the fabrics dyed with cationic reactive dyes. As can be seen, dyes 1 and 2 provide lower tear strength in compared to dyes 3 and 4. This effect could be attributed to quaternary ammonium moiety of the dyes. Samples dyed only with dyes 1 and 2 were compared with samples dyed with dyes 1 and 2, then finished with cationic softener agent. The results show that tear strengths of the samples are almost the same, confirming the role of quaternary ammonium moiety of dyes 3 and 4. Finally, it proves the effectiveness of simultaneous dyeing and finishing of the novel cationic reactive dyes.

Abrasion Resistance

Table 6 shows the abrasion resistance of the fabrics dyed with cationic reactive dyes. As can be seen, dyes 1 and 2 offer lower mass reduction in compared to dyes 3 and 4, revealing more softening property for the novel cationic reactive dyes.

Flexibility

Table 6 shows flexibility results for the fabrics dyed with cationic reactive dyes. Dyes 1 and 2 offer higher flexibility rigidity than dyes 3 and 4. Furthermore, samples dyed with dyes 1 and 2 and then finished with cationic softening agent lowers the flexibility rigidity.

Crease Recovery Angle

Table 6 shows crease recovery angle results for the samples dyed with cationic dyes. Dyes 3 and 4 offer higher crease recovery angle in compared with dyes 1 and 2. In addition, even samples which were separately dyed with dyes 1 and 2 then followed by finishing with cationic softening agent do not provide the same crease recovery angle as dyes 3 and 4 offer.

CONCLUSIONS

Four novel dyes were synthesized in good yield. Two of them have quaternary ammonium salt in their structures. Replacement of H-acid with J-acid in the molecular structures of the dyes offered bathochromicity in visible spectra. Incorporating the QAS alkyl chain on dye structure led to hypsochromic shift in visible absorption spectra. Cotton fabrics were dyed using the novel cationic reactive dyes. The technical properties of the dyes were evaluated with SER_5F profile and migration properties. These tests showed that dyes 2 and 4 offer high substantivity and exhaustion because they have lower solubility than dyes 1 and 3. Dyes 3 and 4 exhibited low fixation due to having big structure, resulting in low adsorption on fabric. Dyes 3 and 4 have lower migration indices than dyes 1 and 2 due to their low solubility. The results show that the cationic reactive dyes either improve or affect fabric properties.

Incorporation of quaternary ammonium group to dye structure of dyes 1 and 2 imparts softening properties in the dyed fabric. Also several properties of the substrate dyed with these dyes could be mentioned as being similar or top of those for separately dyed and then cationic softener finished substrate. It is concluded that dyeing and softening finishing are simultaneously employed in one step. These dyes have excellent wash fastness, whilst their light fastness on fabric is moderate.

REFERENCES

1. Xie, K.; Liu, Y.; Li, X. *Mater. Chem. Phys.* **2007**, *105*, 199.
2. Xie, K.; Liu, Y.; Li, X. *Mater. Chem. Phys.* **2007**, *105*, 204.
3. Liu, J.; Sun, G. *Dyes Pigm.* **2008**, *77*, 380.
4. Liu, S.; Ma, J.; Zhao, D. *Dyes Pigm.* **2007**, *75*, 255.
5. Freeman, H. S.; Hauser, P. J.; Chen, X.; Nakpathom, M. Annual Report. *National Textile Center*; November 1999, C98-S04. http://www.ntcresearch.org (Accessed March 7, 2012)
6. Ma, M.; Sun, Y.; Sun, G. *Dyes Pigm.* **2003**, *58*, 27.
7. Fox, M. R.; Sumner, H. H. In *The Dyeing of Cellulosic Fibres*; Preston, C., Ed.; The Dyers' Company Publication Trust: Bradford, 1986; Chapter 4, pp 142-195.
8. Christie, R. M. *Colour Chemistry*; The Royal Society of Chemistry: Cambridge, 2001; pp 45-46.
9. Gao, Y.; Cranston, R. *Text. Res. J.* **2008**, *78*, 60.
10. Suwanruji, P. *The Design, Synthesis and Application of Easy Wash off Reactive Dyes*; A Dissertation Submitted to the Graduate Faculty of North Carolina State University 2004.
11. Mokhtari, J.; Phillips, D. A. S.; Taylor, J. A. *Dyes Pigm.* **2004**, *63*, 51.
12. Bent, C. J.; Davies, P. A.; Phillips, D. A. S. *J. Soc. Dye. Colour.* **1982**, *98*, 326.
13. Mokhtari, J.; Phillips, D. A. S.; Taylor, J. A. *Dyes Pigm.* **2005**, *64*, 163.
14. Cockett, K. R. F.; Rattee, I. D.; Stevens, C. B. *J. Soc. Dye. Colour.* **1969**, *85*, 461.
15. Bradbury, M. J.; Collishaw, P. S.; Phillips, D. A. S. *J. Soc. Dye. Colour.* **1992**, *108*, 430.
16. Gordon, P. F.; Gregory, P. *Organic Chemistry in Colour*; Springer-Verlag: New York / Berlin / Heidelberg, 1983; pp 96-104.