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Dyeing of multiple types of fabrics with a single reactive azo disperse dye

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Three novel reactive azo disperse dyes were prepared using 7-acetamide-4-hydroxy-2-naphthalene sodium sulphate as the precursor. The structure of the dyes has the combined characteristics of reactive, disperse, and cationic dyes. Under alkaline conditions (pH 9), the dyes can be applied to cotton, silk, wool, and nylon. Under neutral conditions, they can be used to dye polyester. Under acidic conditions (pH 4.5), they can colour acrylic fabric after conversion of the tertiary amine group to the quaternary ammonium cation. The colour-fastness of the dyed fabrics were also evaluated.

Keywords: reactive dye, disperse dye, cationic dye, synthesis of dye, coloration, affinity

Introduction

For any given type of fabric, only a limited range of dyes can be applied to obtain the desired aesthetic effect with satisfactory exhaustion values and fastness properties (Gordon & Gregory, 1987). Owing to the distinctive properties of each dye, different dyeing processes are necessary and multiple types of dyeing facilities are needed. In addition, each dyeing process produces its own effluent, which requires unique treatment prior to discharge into the environment. All these factors contribute to increasing the cost of dyeing. If one dye can be applied to all types of fabrics, both the dyeing process and the effluent treatment can effectively be simplified. Moreover, as the dye bath may be reused, the amount of dyeing effluent can be reduced substantially. It is evident that the development of a novel type of dyes that can be applicable to multiple types of fabric will not only reduce the dyeing cost but will also provide an environmental advantage.

As conventional dyeing processes have already attained their mature stage, the modification of fabric and the modification of dye are regarded as two feasible approaches to achieving this goal. Lewis and Broadbent (1997) modified the structure of wool and cotton by the benzoylating reaction and used a disperse dye to colour wool and cotton. They also investigated the coloration properties of benzoylated cotton with a disperse dye in supercritical carbon dioxide (Özcan et al., 1998). In these cases, disperse dyes were used to dye hydrophilic fabric instead of the hydrophobic one, which clearly extends the application range of disperse dyes. The effect of this treatment on the wearability of fabric remains uncertain, and this method has not achieved significant commercial success to date. In parallel, various approaches have been proposed to modify the structure of dyestuffs. Lee and Kim (1999) and Lee et al. (2002) used temporarily solubilised disperse dyes to dye polyester in the absence of a dispersing agent and they further extended the application of this kind of dyestuff to wool (Lee et al., 2001). Sokolowska-Gajda and Freeman (1990) and Suwanruji et al. (2004) incorporated a dichlorotriazine reactive group to the structure of acidic dye, and applied the resultant dye to poly(ethyleneterephthalate), polyester, and acrylic fibres. They noted that the presence of naphthalene sulphonamide might account for the good sublimation fastness on polyester, and ascribed the low exhaustion on cotton to the hydrophobic nature of the dye molecules.

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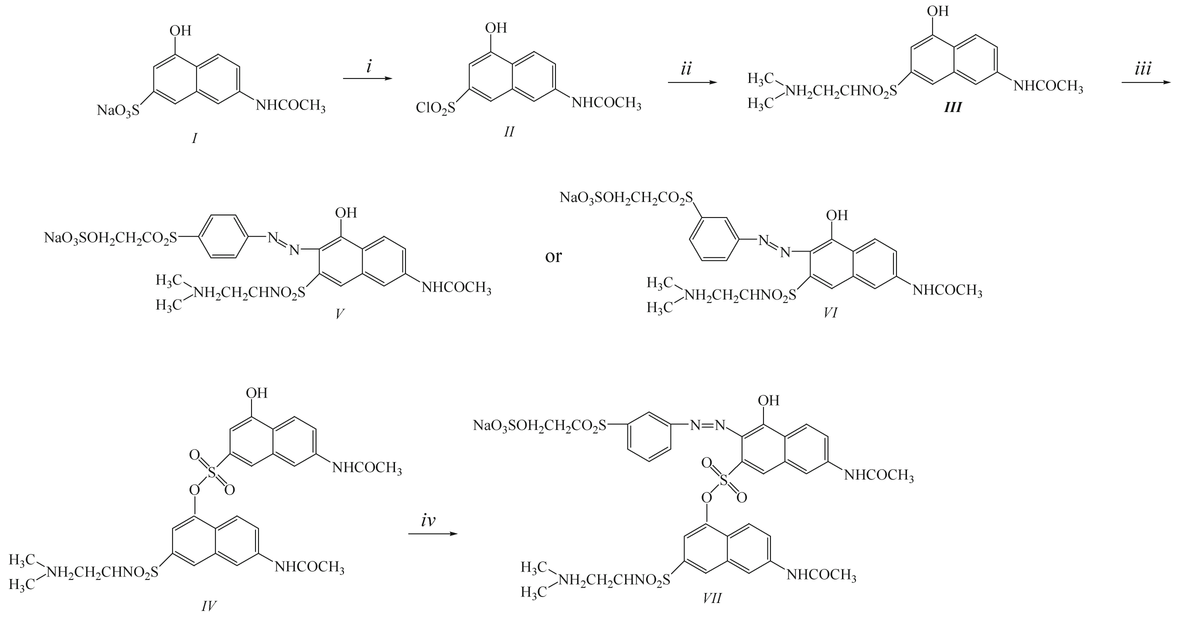

Fig. 1. Synthesis route for reactive azo disperse dyes: *i*) $POCl_3$, DMA, CH_3CN, 55–60 ℃, 4 h, 92 %; *ii*) *N,N*-dimethylethylenediamine, K_2CO_3, acetone, 40 ℃, 4 h, 61 %; *iii*) diazonium salt of *p*-amino-benzene-β-hydroxyethylene sulphonate (diazonium salt of p-amino-benzene-β-hydroxyethylene sulphonate), H_2O, < 5 ℃, 1 h, 65 % (68 %); *iv*) diazonium salt of *m*-amino-benzene-β-hydroxyethylene sulphonate, H_2O, < 5 ℃, 1 h, 81 %.

In light of the above, this work seeks to synthesise reactive azo disperse dyes with a naphthalene sulphonamide structure. To improve the water solubility of dye, the sodium salts of β-sulphatoethylsulphonyl and *N,N*-dimethylethylenediamine moieties are imparted simultaneously. It is probable that these novel structured dyes may be applied to all types of fabrics.

Experimental

General

All chemical reagents were commercial products of analytical grade (Tianjin Chemical Reagent, China). The mass spectra were obtained on a HP 1100 System of HPLC/MSD or HP6890 Series GC System/5973 Mass Select Detector (Hewlett Packard, USA). The IR spectra (the sample was formed into a KBr pellet) were recorded on an FT/IR-430 infrared spectrophotometer (JASCO, Japan). UV-VIS spectra were recorded on a UV-VIS-NIR scanning spectrophotometer (Cary 5000, Varian, UK). A quartz cuvette with 10 mm optical path length (CXA-145-055M, Fisher Scientific, UK) was adopted as the solution-holder. The dyeing of polyester was performed on a Roaches TFO (Roaches, UK) and the light-fastness was tested on a Xenotest150s (Heraeus, Germany).

Synthesis of dye and intermediate

Fig. 1 illustrates the synthesis routes for the three reactive azo disperse dyes and the related intermediates.

Synthesis of N,N-dimethylethylenediamine

N,N-dimethylethylenediamine were synthesised using ethanol amine in accordance with the reference (Akihiro et al., 1983).

Synthesis of II

Phosphorus oxychloride (4.9 mL, 0.050 mol) was added to the mixture of *I* (5.4 g 0.018 mol), *N,N*-dimethylacetamide (DMA; 6.6 mL, 0.090 mol), and acetonitrile (28 mL) The resultant mixture was stirred at 55–60 ℃ for 4 h and poured into cold water. *II* (5.0 g) was then collected by filtration.

Synthesis of III and IV

III and *IV* were synthesised by a similar procedure (Zhang, 2013). Take *III* as an example: in a typical procedure, a suspension of *II* (4.9 g, 0.016 mol) in acetone (100 mL) was added dropwise into *N,N*-dimethylethylenediamine (0.6 g, 0.007 mol), K_2CO_3(4.2 g, 0.030 mol), and acetone (30 mL). The mixture was stirred at 40 ℃ for 4 h. After extraction with ethyl acetate, *III* (3.5 g) was obtained.

Synthesis of dye V, VI, VII

The diazotisation of *p*-aminophenyl sulphatoethyl sulphone was performed in accordance with the literature (Biolchi et al., 2006). Under stirring, a solution of *III* (2.0 g, 0.006 mol) in *N,N*-dimethylformamide (DMF; 10 mL) was slowly added into water (200 mL). Then, the diazonium salt of *p*-amino-benzene-β-

Table 1. Spectral data of synthesized dyes and intermediates

Dyes	Spectral data
I	IR, $\tilde{\nu}/\text{cm}^{-1}$: 3480 (–SO$_2$–OH), 3387 (–NH–), 1672 (–C═O)
II	IR, $\tilde{\nu}/\text{cm}^{-1}$: 3383 (–NH–), 1677 (–C═O), 1358 (–S═O), 1167 (–S═O)
III	MS, m/z (I_r/%): 352.1 (100) $(M + H)^+$, 353.1 (19), 374.1 (12) $(M + Na)^+$
IV	MS, m/z (I_r/%): 615.1 (69.6) $(M + H)^+$, 637.1 (100) $(M + Na)^+$
V	MS, m/z (I_r/%): 546.1 (100) (M – NaHSO$_4$) UV, $\lambda_{\max}$, 465nm, $\varepsilon \cdot 10^{-4}$ (L mol^{-1} cm^{-1}): 2.1
VI	MS, m/z (I_r/%): 546.2 (100) (M – NaHSO$_4$) UV, $\lambda_{\max}$, 472nm, $\varepsilon \cdot 10^{-4}$(L mol^{-1} cm^{-1}): 1.5
VII	MS, m/z (I_r/%): 929.0 (80) $(M + H)^+$, 827.2 (100) (M – NaHSO$_4$) UV, $\lambda_{\max}$: 408nm, $\varepsilon \cdot 10^{-4}$(L mol^{-1} cm^{-1}): 1.2

hydroxyethylene sulphonate (1.9 g, 0.006 mol) was added drop-wise and the mixture was stirred under 5 °C for 1 h, giving 2.6 g of red brown *V*. Similarly, *VI* (2.71 g) was synthesised when the diazonium salt of *m*-amino-benzene-β-hydroxyethylene sulphonate (1.9 g, 0.006 mol) was used as the diazo component. Using *IV* (1 g, 0.002 mol) as the coupling component, *VII* (1.2 g) was prepared.

Application of dye to fabric

Since the dyeing processes for *V*, *VI*, and *VII* are similar, *VII* is selected as an example to show how the dyes are applied to different types of fabrics. The mass of fabrics used was 3.0 g. Unless specified, the liquid ratio (the ratio between the volume of dyeing solution and the mass of fabric) was 60 : 1 and the quantity of dispersing agent was twice that of the dye. After dyeing, the coloured fabric was rinsed with water and air-dried.

Cotton

NaCl (6 g, 0.100 mol) in water (20 mL) was added to a dye bath containing *VII* (0.03 g, 0.03 mmol) and pH was then adjusted to 9 using 10 mass % Na$_2$CO$_3$. The temperature of the dye bath was increased to 80 °C at 1 °C min^{-1} and maintained for 1 h.

Silk and wool

The pH of *VII* (0.09 g, 0.10 mmol) dye bath was adjusted to 4.5 using formic acid. The temperature of the dye bath was increased to 95 °C and maintained for 1 h, then cooled to 90 °C. The pH of the dye bath was adjusted to 9 by 10 mass % Na$_2$CO$_3$ and maintained for 15 min.

Nylon

The pH of the dye bath containing *VII* (0.15 g, 0.16 mmol) was adjusted to 4.5 using formic acid, then the dye bath was allowed to boil for 1 h and then cooled to 90 °C. The pH of the dye bath was adjusted to 9 by 10 mass % Na$_2$CO$_3$ and maintained for 1 h.

Polyester

The dye bath consisting of *VII* (0.15 g, 0.16 mmol, liquid ratio 20 : 1) was heated to 130 °C at 2.5 °C min^{-1}, maintained for 3 h and cooled to ambient temperature at 3 °C min^{-1}.

Acrylic

The pH of the *VII* (0.15 g, 0.16 mmol) dye bath was adjusted to pH 10 by 10 mass % Na$_3$PO$_4$, then to pH 4.5 by formic acid. The dye bath was allowed to boil for 1 h, then cooled to ambient temperature.

Results and discussion

Structure characteristics of dyes

To examine the optical properties, the UV-VIS spectra of the synthesised dyes were recorded and the maximum absorption ($\lambda_{\max}$) and molar extinction coefficient (ε) are listed in Table 1.

By β-elimination reaction, the β-sulphatoethysulphone group can be converted to the vinylsulphone group, which is the active reactant for nucleophilic addition. As a consequence, the reactive azo disperse dyes thus prepared may be used as reactive dyes to colour hydrophilic fabrics, for instance cotton, wool, silk, and nylon, that can provide nucleophile species. The tertiary amine group can be converted to quaternary ammonium salt and the dyes thereby obtained can be used as cationic dyes to colour acrylic by the formation of salt- bonding. As no strong hydrophilic group is present in the aromatic rings, the water solubility of the dyes is limited and the dyes can be employed as disperse dyes to colour hydrophobic fabrics like polyester. In essence, the dyes thus prepared possess the combined characteristics of reactive, disperse and cationic dyes and may be applied to multiple types of fabrics, as illustrated in Fig. 2.

Coloration performance of dyes

By measuring the absorbance of the dye solution prior to and after dyeing, the dyeing exhaustion values were calculated and are plotted in Fig. 3. It is clear

Table 2. Fastness properties of dyed fabrics

Compound	Fabric	o.m.f./%	Light-fastness[a]	Wash-fastness[a]		
				Colour change	Staining on fabric	
					Cotton	Other
V	Wool	3	3–4	3–4	4	4–5[b]
	Silk	3	2–3	4–5	4	3[c]
	Nylon	5	2	4–5	4–5	4[d]
	Acrylic	5	4	3	4	4–5[e]
VI	Wool	3	4	4	4–5	4–5[b]
	Silk	3	3–4	4–5	4–5	3–4[c]
	Nylon	5	2	4–5	4–5	4[d]
	Acrylic	5	3–4	3–4	4	4–5[e]
VII	Wool	3	2	3	4	4–5[b]
	Silk	3	2	3–4	4	4–5[c]
	Nylon	5	1–2	4	4–5	4–5[d]

a) Grey scale ratings ranged from 1 (poor) to 5 (excellent); if the depth of shade is light, the fastness of the dyed fabrics is not included; *b*) wool; *c*) silk; *d*) nylon; *e*) acrylic.

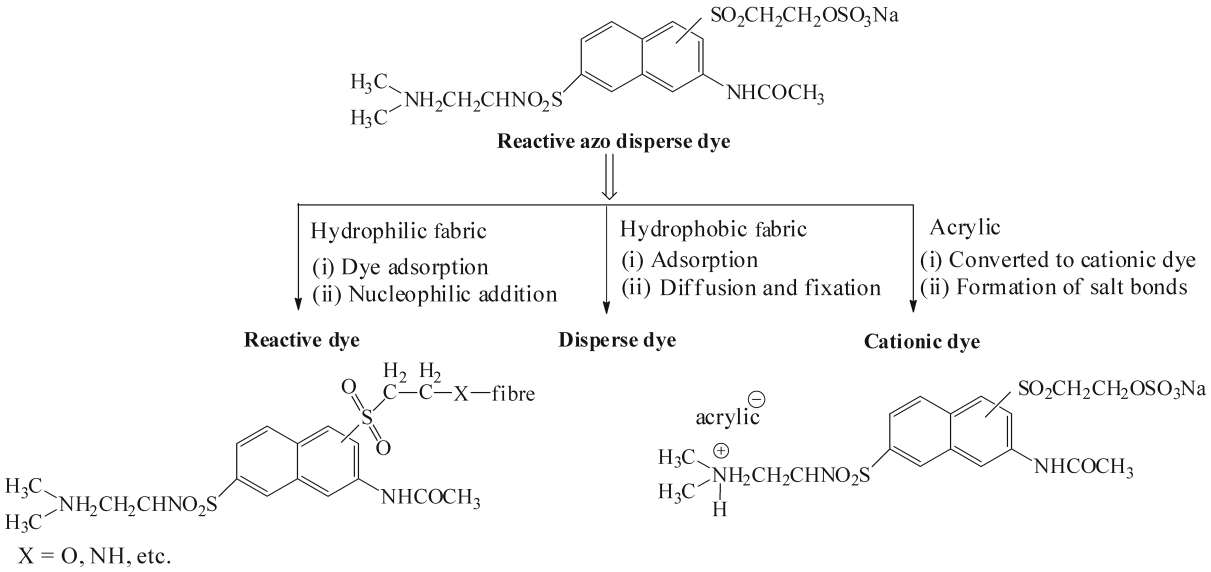

Fig. 2. Application of dye to various types of fabrics.

that dyes *V*, *VI*, *VII* have a reasonable affinity for wool, silk, and nylon, but a poor affinity for cotton and polyester. As far as acrylic is concerned, only dyes *V* and *VI* have a good affinity.

After washing with reference to the method denoted by Standards Association of China (1997), the wash-fastness of the dyed fabrics was examined by the method denoted by Standards Association of China (1998) and the results are given in Table 2. All the dyed fabrics exhibit moderate to excellent properties in respect of fastness to laundering, as the grey scale values are all over 3, in some cases up to 5. The dyed fabrics also exhibit reasonable staining properties on undyed fabrics: the scale of the cross-staining of fabrics is over 3, indicating insignificant dye transfer from

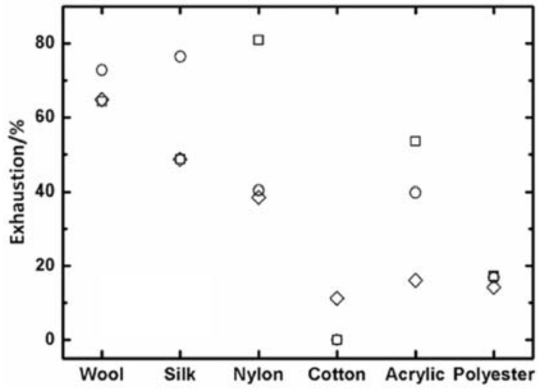

Fig. 3. Dyeing exhaustion values of reactive azo disperse dyes on different fabrics: □ – *V*; ○ – *VI*; ◇ – *VII*.

Table 3. Elemental composition of dyes

Compound	$(M^+)_{calculated}$	$(M^+)_{found}$	Formula	Content of $-SO_3Na$ in molecule/%
V	665.6914	546.2^a	$C_{24}H_{28}N_5NaO_{10}S_3$	15.5
VI	665.6914	546.1^a	$C_{24}H_{28}N_5NaO_{10}S_3$	15.5
VII	928.9606	929.0	$C_{36}H_{37}N_6NaO_{14}S_4$	11.1

a) Found as ($M - NaHSO_4$).

the dyed fabrics. The dyed fabrics have low to moderate colour-fastness, which is presumably due to the scarcity of electron-withdrawing groups in diazonium salt (Yang & Zhang, 1989).

Effect of dye composition and structure on coloration

The macro dyeing properties of a dye molecule are highly dependent on its composition and microstructure. If a dye is to be applied to multiple types of fabrics, several factors need to be taken into account and balanced: (i) the dye molecule should be neither too hydrophilic nor too hydrophobic; either extreme will repel the opposite type of fabric; (ii) molecular mass is another concern. A low molecular mass dye is preferable for the coloration of hydrophobic fabrics as the diffusion of the dye molecule into the fabric is strengthened. However, a low molecular mass dye is likely to show poor substantivity for hydrophilic fabrics; (iii) a further issue affecting the dyeing performance is the planarity of the dye molecule. In general, good planarity facilitates penetration of the dye into the fabric, and the occurrence of hydrogen-bonding and van der Waal's forces due to the close contact between the dye molecule and the fibre, resulting in good substantivity to the fabric. The atomic composition, molecular mass, and percentage of the sodium sulphonate group ($-SO_3Na$) in the molecules for dyes *V*, *VI*, and *VII* are listed in Table 3.

Fig. 3 shows that dyes *V*, *VI*, and *VII* have reasonable dyeing exhaustion values on wool, silk, and nylon; this means that the dyes as prepared have a good affinity for these fabrics. Table 2 indicates that the coloured fabrics have good fastness to laundering, which may be ascribed to the formation of covalent bonding through operation of the nucleophilic addition between the vinylsulphone group of the dye molecule and functional groups such as hydroxyl (–OH) and amine ($-NH_2$) of the fibre: see Fig. 2. For acrylic, dyes *V* and *VI* have good exhaustion values but *VII* has a poor one. This may be related to the higher molecular mass of *VII* (Table 3). Under acidic conditions, the tertiary amine group in dyes can be converted to the quaternary ammonium cation, which may form salt bonds with anionic dyeing sites, hence the acrylic fabric is dyed. However, once adsorbed, the bulky *VII* molecule may shield the adjacent anionic dyeing sites and, in turn, reduce the amount of dye molecule adsorbed, resulting in a reduced exhaustion value.

Although *VII* displays an exhaustion value of 11.2 %, the promotion of the affinity for cotton is still desirable. This may be explained in terms of the low hydrophilicity of the dye molecules. The strong hydrophilic group ($-SO_3Na$) is attached to the aromatic ring via an alkyl bridge and its percentage in the dye molecules is lower than 16 % (Table 3); this means that its contribution to the improvement of hydrophilicity is limited. Compared with *V* and *VI*, dye *VII* has a higher exhaustion to cotton (Fig. 3). This may stem from the presence of one extra naphthalene ring in the *VII* molecule, which leads to the increase in molecular mass (Table 3) and is beneficial for the improvement of substantivity to cotton. This is consistent with the results reported by Smith et al. (2006) and Lewis and Siddigue (2006). The exhaustion values of *V*, *VI*, and *VII* to polyester range from 14.2 % to 17.3 %, which may be associated with the high molecular mass and poor planarity of the dye molecules.

The key issue in the design and synthesis of a single dye molecule that is applicable to multiple types of fabrics is to calculate the balanced points between hydrophilicity and hydrophobicity. In addition, the dye molecule should have a suitable molecular mass and good planarity. For the dyes obtained here, further structural modification is needed; this will focus on increasing the hydrophilicity by the incorporation of moderate hydrophilic groups and improving the molecular planarity.

Conclusions

The synthesised dyes possess the characteristics of a reactive dye (containing β-sulphatoethysulphone group), a disperse dye (without the strong hydrophilic group present in the aromatic rings), a cationic dye (containing the tertiary amine group, which can be converted to the quaternary ammonium group); hence, they have the potential to be applied to multiple types of fabrics. The dyes thus obtained demonstrate a reasonable performance on wool, silk, nylon, and acrylic. Their performance on cotton and polyester needs to be improved by enhancement of their hydrophilicity and molecular planarity.

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