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Synthesis and application of a temporarily solubilised alkali-clearable azo disperse dye and analysis of its conversion and hydrolysis behaviour

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Abstract

A temporarily solubilised alkali-clearable azo disperse dye containing both a β-sulphatoethylsulphone group and carboxylic acid ester groups was synthesised and applied to polyester for the purpose of the dispersant-free dyeing and alkali-clearability. The disperse dye containing only a β-sulphatoethylsulphone group or that containing only carboxylic acid ester groups were also synthesised and their dispersant-free dyeing properties and alkali-clearability was compared with the temporarily solubilized alkali-clearable dye prepared. In order to investigate the feasibility of dispersant-free polyester dyeing and alkali-clearability, conversion behaviour, alkali-hydrolysis behaviour and colour fastness were assessed. The results showed that the temporarily solubilised alkali-clearable disperse dye could be successfully applied to polyester without the use of dispersants and has reasonable alkali-clearability; the dye exhibited good levelling and fastness properties on polyester.

Keywords: Temporarily solubilised alkali-clearable azo disperse dye; β-Sulphatoethylsulphone group; Carboxylic acid ester groups; Dispersant-free polyester dyeing; Alkali-clearability; Conversion behaviour

1. Introduction

The development of new disperse dyes must take into account the effect that dyeing effluent will have on the environment, and aim to minimise such pollution. These objectives are not mutually exclusive but interrelated; they must all be taken into account in any dye development program [1].

Temporarily solubilised dyes containing β-sulphatoethylsulphone group have been investigated for the dispersant-free dyeing of polyester [2,3]; the sodium sulphonate group of the dye structure gives sufficient water solubility at the early stage of dyeing without any dispersant. As dyeing proceeds the soluble dye molecules are gradually converted to the vinylsulphone form by β-elimination reaction at the proper pH and temperature, and then this water-insoluble form is adsorbed onto the polyester fabric. Therefore, the temporarily solubilised dyes can obviated the need for the dispersing agent not only in

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dyeing process but also in dye manufacturing process.

Also, alkali-clearable disperse dyes have been studied for the last 30 years in order to reduce the impact of dyeing processes on the environment through reductions in effluent discharge as well as in the use of energy and materials [4–8]; the alkali-clearable disperser dyes enable an alkaline treatment to be substituted for costly and environmentally damaging reduction clearing process since the dyes can be easily hydrolysed and washed-off under relatively mild alkaline condition.

In this study, a temporarily solubilised alkali-clearable azo disperse dye (**1**) was synthesized and its conversion and hydrolysis behaviours were investigated. Aminophenyl-4-(β-sulphatoethylsulphone) was used as a diazo component to give temporary solubility to the dyes and alkali-clearability was conferred by the carboxylic acid ester in terminal amino group of the coupling component. Also, for the comparative purpose, the 4-(*N,N*-diethylamino) analogue (**2**) and the 4′-nitro analogue (**3**) were synthesised and their levelling properties and colour fastness properties on polyester were also compared.

2. Experimental

2.1. Synthesis of dyes

2.1.1. 4-(N,N-di(β-methoxycarbonylethyl)amino)-4′-(β-sulphatoethylsulphone)azobenzene dye (1)

Aminophenyl-4-(β-sulphatoethylsulphone) (0.02 mol) was diazotised in 4.8 ml of conc. HCl and 200 ml of water, by adding 0.02 mol of $NaNO_2$ at a temperature of 0–5 °C. After 4–5 h, the completion of diazotization was checked using a solution of 4-(*N,N*-dimethylamino)benzaldehyde and the pH value of the diazo liquor was then adjusted to pH 5–6 by adding sodium acetate. The diazonium liquor was added to a solution containing 0.02 mol of *N,N*-di(β-methoxycarbonylethyl)aniline, 20 ml of methanol and 20 g of ice. After 4–5 h, the pH value of the mixture was adjusted to pH 5–6 by adding sodium acetate and the reaction product was salted out of solution by adding solid NaCl, filtered and dried. The dye was purified by column chromatography. UV/Vis (H_2O) λ_{max}; 460 nm, ε_{max}; 28 000. M.p. 97–100 °C. ^{1}H-NMR (d_6-DMSO): δ = 6.8–8.0 (m, 8H, aromatic protons), 3.97 (t, 2H, O–CH_2–C), 3.73 (t, 4H, N–CH_2–C), 3.67 (t, 2H, C–CH_2–S), 3.62 (s, 6H, O–CH_3), 2.65 (t, 4H, C–CH_2–COO) ppm. Elemental analysis calcd for $C_{22}H_{26}N_3O_{10}S_2 + 2.5\ H_2O$: C; 42.3 H; 5.00; N, 6.73, found: C, 42.3; H, 5.13; N, 6.86.

2.1.2. 4-(N,N-Diethylamino)-4′-(β-sulphatoethylsulphone)azoboenzene dye (2)

N,N-Diethylaniline was used as a diazo component and the dye (**2**) was prepared by the same procedure as Section 2.1.1. The dye was purified by column chromatography. UV/vis (H_2O) λ_{max}; 486 nm, ε_{max}; 31 000. M.p. 139–142 °C. ^{1}H-NMR (d_6-DMSO): δ = 6.8–8.0 (m, 8H, aromatic protons), 3.97 (t, 2H, O–CH_2–C), 3.66 (t, 2H, C–CH_2–S), 3.49 (q, 4H, N–CH_2–C), 1.17 (t, 6H, C–CH_3) ppm. Elemental analysis calcd for $C_{18}H_{22}N_3O_6S_2 + 2.5\ H_2O$: C, 42.51; H, 5.35; N, 8.26; found: C, 42.55; H, 4.74; N, 8.82.

2.1.3. 4-(N,N-di(β-methoxycarbonylethyl)amino)-4′-nitroazoboenzene dyes (3)

p-Nitroaniline (0.02 mol) was diazotised and coupled with 0.02 mol of *N,N*-di(β-methoxycarbonylethyl)aniline dissolved in 20 ml methanol. After 3 h, the pH value of the mixture was adjusted to pH 5–6 by adding sodium acetate and the precipitated dye (**3**) was filtered, water-washed and dried. The dye was purified by column chromatography. UV/vis (DMF) λ_{max}; 476 nm, ε_{max}; 29 000. M.p. 105–108 °C. ^{1}H-NMR (d_6-DMSO): δ = 6.8–8.4 (m, 8H, aromatic protons), 3.74 (t, 4H, N–CH_2–C), 3.62 (s, 6H, O–CH_3), 2.66 (t, 4H, C–CH_2–COO) ppm. Elemental analysis calcd for $C_{20}H_{22}N_4O_6$: C, 57.97; H, 5.35; N, 13.52; found: C, 58.23; H, 5.35; N, 13.01.

2.1.4. Vinyl forms of dyes 1 and 2 (6, 7)

Ten grams of aminophenyl-4-(β-sulphatoethylsulphone) (**4**) was dissolved in 500 ml distilled water and 20 g of sodium hydroxide was added to the solution at room temperature. After 30 min the precipitated vinyl form of a diazo component (**5**) was water-washed and filtered.

This diazo component was diazotised and coupled with *N,N*-di(β-methoxycarbonylethyl)aniline and *N,N*-diethylaniline to give the vinyl forms of the dyes 1 and 2, respectively (Scheme 1). The dyes were purified by column chromatography.

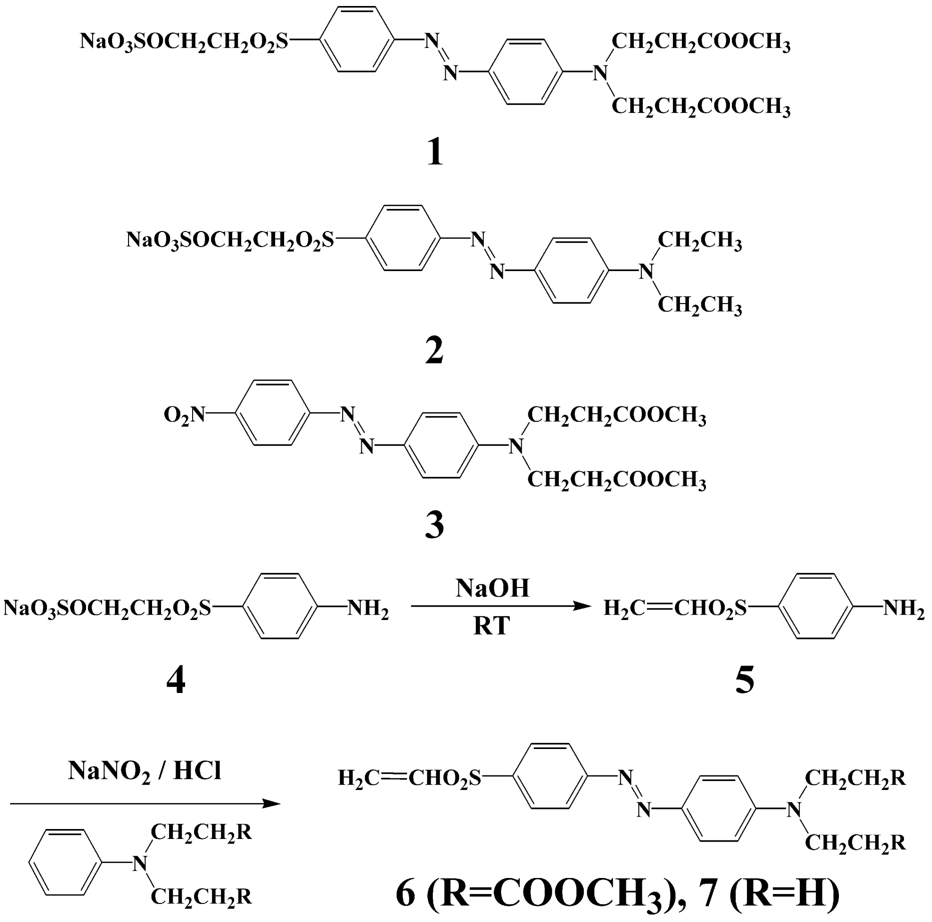
Dye **6**, ^{1}H-NMR (d_6-DMSO): δ = 6.8–8.0 (m, 8H, aromatic protons), 7.15 (t, 1H, C=CH–S), 6.2~6.4 (d, 2H, CH_2=C), 3.73 (t, 4H, N–CH_2–C), 3.62 (s, 6H, O–CH_3), 2.65 (t, 4H, C–CH_2–COO) ppm. Elemental analysis calcd for $C_{22}H_{25}N_3O_6S$: C, 57.50; H, 5.48; N, 9.14; found: C, 57.10; H, 5.19; N, 9.32.

Dye **7**, ^{1}H-NMR (d_6-DMSO): δ = 6.8–8.0 (m, 8H, aromatic protons), 7.15 (t, 1H, C=CH–S), 6.2~6.4 (d, 2H, CH_2=C), 3.49 (q, 4H, N–CH_2–C), 1.17 (t, 6H, C–CH_3) ppm. Elemental analysis calcd for $C_{18}H_{21}N_3O_2S$: C, 62.95; H, 6.16; N, 12.23; found: C, 63.02; H, 6.11; N, 12.13.

2.2. *Analysis of conversion and hydrolysis behaviour*

2.2.1. *Conversion behaviour*

Analysis of conversion behaviour of the dye **1** was carried out using HPLC (Young-Lin, M930 reverse-phase column). A mixture of methanol and water (65:35) was used as the mobile phase with flow rate of 1 ml/min. In order to analyse the conversion behaviour of dye **1**, blank dyeing was performed using an Ahiba dyeing machine. The dyebath was prepared at room temperature with 50 ml buffer solution (pH 4–7) and 20 mg dye, heated to 70 °C and then up to 130 °C by 1 °C/min. The pH of dyebath was controlled by using buffer solution; pH 4 and 5 with sodium acetate (0.05 M)/acetic acid (60%) and pH 6 and 7 with sodium phosphate monobasic (0.05 M)/sodium



Scheme 1. Preparation of vinylsulphone forms of dyes **1** and **2**.

phosphate dibasic. Samples were taken for HPLC analysis every 10 min from 80 to 130 °C. The retrieved samples were diluted with the same volume of methanol and then 1 ml of this solution was diluted again with 9 ml methanol. A 10 μl sample of diluted solution was injected into the HPLC.

2.2.2. Alkali hydrolysis behaviour

Absorbance values of the vinyl forms of the dyes 1 and 2 treated by reducing clearing solution (NaOH 2.0 g/l, $Na_2S_2O_4$ 2.0 g/l) and alkali clearing solution (Na_2CO_3 2.0 g/l) were measured every 10 min while the temperature of the dispersions was raised 60–80 °C using a laboratory dyeing machine (Turbo Color, Ahiba). The hydrolysed form of dyes 1 and 2 were confirmed by FT-IR (Prospect-IR, MIDAC) and Mass (Quattro LC Triple Quadrupole Tandem Mass spectrometer) analysis after alkali-clearing treatment (Na_2CO_3 2.0 g/l, 80 °C, 20 min).

2.3. Dyeing behaviour

Polyester fabric was dyed with the synthesised dyes (1.0% owf) in a Ahiba dyeing machine at a liquor ratio of 25:1. Dyebath temperature was raised from 70 to 130 °C by 1 °C/min and then maintained for 60 min. The pH of dyebath was controlled by using the buffer solution mentioned in 2.2.1. Dispersing agent was not used and the dyed polyester fabric was taken every 10 min from 80 to 130 °C and every 20 min after the dyeing temperature reached the 130 °C, respectively. The colour yield of all specimens was measured using a spectrophotometer (Color-Eye 3000, Macbeth, standard illumination D_{65}, 10° standard observer and specula component excluded).

2.4. Assessment of levelling properties of dyes

In order to investigate the feasibility of dispersant-free dyeing of the synthesised dyes, the levelling property of the dyed polyester fabric was estimated by calculating colour differences; five points on a trial sample were measured at regular intervals, and the mean value of colour differences between the two points, which were systematically chosen out of five points, was calculated [9].

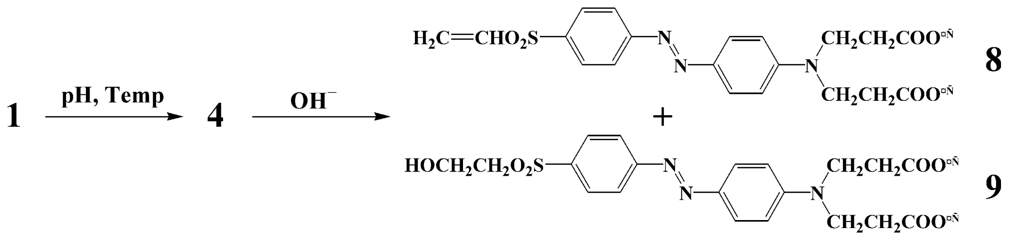
2.5. Colour fastness test

Polyester fabric was dyed at 1.0% owf and heat-set (180 °C, 60 s) for the wash fastness test (ISO 105 C06/C2S) and the sublimation fastness test (ISO 105 X11). In order to evaluate the alkali-clearability of the synthesised dyes fastness tests were carried out for two differently cleared polyester fabric after dyeing; reduction cleared (NaOH 2.0 g/l, $Na_2S_2O_4$ 2.0 g/l, 80 °C, 20 min) and alkali-cleared (Na_2CO_3 2.0 g/l, 80 °C, 20 min).

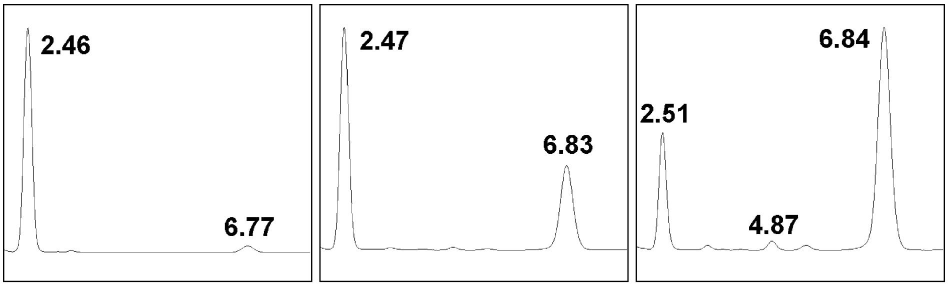
3. Results and discussion

3.1. Conversion behaviour

The β-sulphatoethylsulphone group, which confers solubility to the dyes, can be readily transformed into vinylsulphone group by controlling pH and temperature (Scheme 2) [4,5]. HPLC analysis demonstrated that three types of dye existed in the dyebath during dyeing. Generally, in reverse-phase column chromatography, a more polar substance has a more rapid elution rate. Fig. 1 shows that the β-sulphatoethylsulphone form of the dye **1**, which is the most polar species, was eluted at 2.46–2.51 min. The less polar hydroxyl and vinyl form had 4.87 and 6.77–6.84 min of retention time, respectively. As the temperature of the dyebath was raised, the amount of β-sulphatoethylsulphone form of dye **1** decreased, whereas the amount of vinylsulphone form of dye **1** increased. Fig. 2 shows the degree of the formation of vinylsulphone form as a function of temperature at various pHs. These results confirm that the optimum pH for application with temporarily solubilized dyes should be around 5. At this pH condition, temporarily solubilized disperse dye have a moderate conversion rate. However, above pH 6, the vinylsulphone form was rapidly produced and decreased remarkably at the early stage of dyeing, therefore, the dispersion stability of temporarily solubilized disperse dyes could not be secured and controlled. Conversely, at pH 4, owing to the low conversion rate, it is supposed that the colour yield on the polyester will be decreased although dispersion stability



Scheme 2. β-Elimination and alkali-hydrolysis of dye **1**.



(a) 80°C (b) 110°C (c) 130°C

Fig. 1. HPLC chromatogram of dye **1** at pH 5.

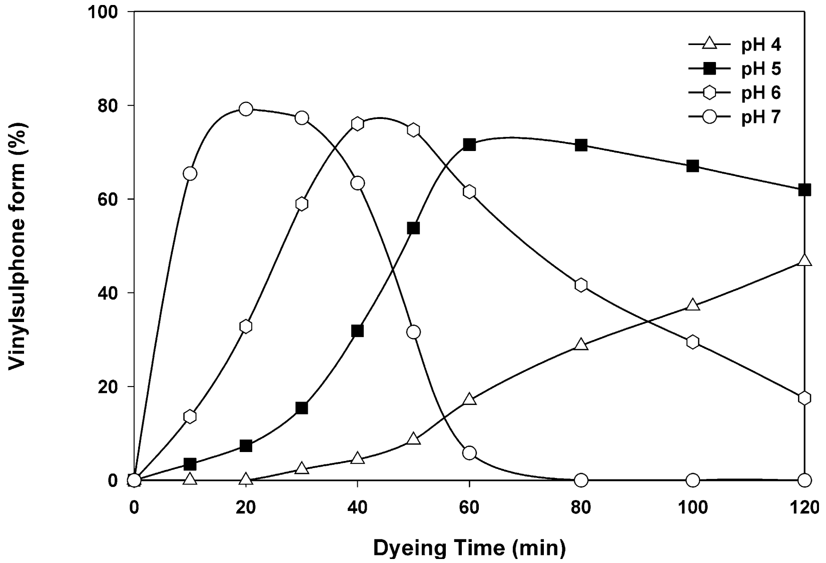


Fig. 2. Effect of pH on the conversion of dye **1** into vinylsulphone form (**6**).

maintained until the end of the dyeing. These overall results concerning the conversion behaviours of temporarily solubilised disperse dyes are consistent with those of reported by Lee and Kim [2,3].

3.2. Alkali-hydrolysis behaviour

Fig. 3 shows the change in absorbance values of dyes **1** and **2** resultant from reduction clearing and alkali clearing. In the case of reduction clearing,

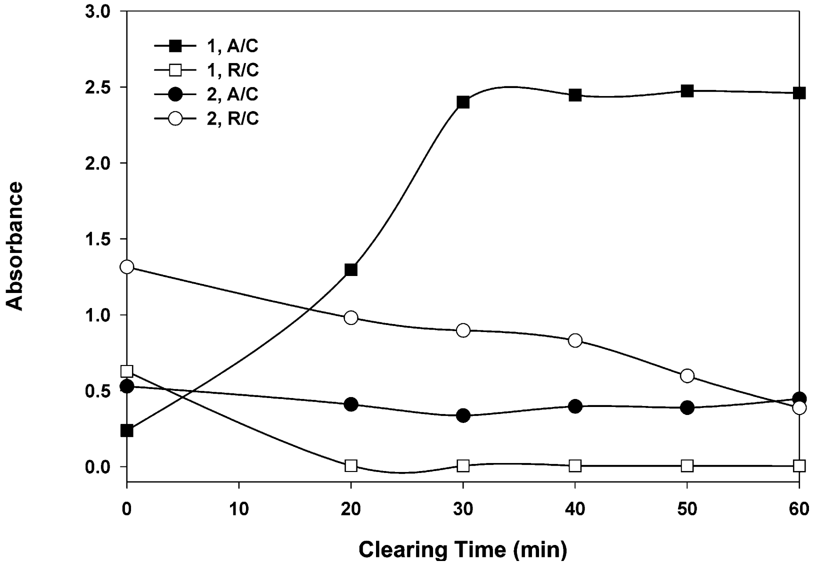


Fig. 3. Change in absorbance of dyes **1** and **2** under each clearing condition (A/C: alkali clearing, R/C: reduction clearing).

the absorbance of dyes **1** and **2** gradually decreased presumably because the azo linkage of the dye was broken by the action of a reducing agent and the dye became colourless. In the case of the alkali clearing, the absorbance of dye **1** increased as the temperature was raised, which implies that dye **1** containing diester groups was hydrolysed and became water soluble under the mild alkaline condition without the breakage of an azo linkage [6]. On the contrary, dye **2** did not show any evident changes in absorbance under the alkali clearing condition (Scheme 2).

Fig. 4 shows the IR spectra of dye **6** (vinylsulphone form dye **1**) before and after alkali-treatment. The characteristic peak of carbonyl group which was observed at 1732 cm^{-1} before alkali-treatment was shifted to 1603 and 1390 cm^{-1} due to asymmetric and symmetric stretching vibration of the carboxylate after alkali-treatment. The characteristic peak of OH group was also observed at 3400 cm^{-1}.

Fig. 5 shows the mass spectra of alkali-hydrolysed dye **1**. The peaks for the carboxylic acid form and carboxylate salt form were observed at 432 ($C_{20}H_{21}N_3O_6S+1$), 450 ($C_{20}H_{23}N_3O_7S+1$), 472 ($C_{20}H_{22}N_3NaO_7S+1$), 454 ($C_{20}H_{20}N_3NaO_6S+1$), 494 ($C_{20}H_{21}N_3Na_2O_7S+1$) and 476 ($C_{20}H_{19}N_3Na_2O_6S+1$).

All the results (Figs. 4 and 5) indicate that the ester groups were hydrolysed and converted to water-soluble carboxylic acids or carboxylate salts and some of the vinylsulphone groups were also converted into hydroxyethylsulphone groups under relatively mild alkaline condition (Scheme 2).

3.3. Dyeing behaviour

The conversion rate of the temporarily solubilised disperse dyes determines their various dyeing properties such as dye exhaustion, dispersion stability, levelness of dyeing and fastness properties [2]; depending on the pH and temperature conditions in the dyebath, soluble dye molecules are gradually converted through β-elimination (Scheme 2) to insoluble derivatives having an affinity to polyester. Some of the insoluble dyes, which are dispersed in the dyebath, are adsorbed on the fibre surface and diffuse into the fibre like a conventional disperse dye. In this process, the dispersion stability of temporarily solubilized disperse dyes is mainly dependent on the amounts of dye converted, especially the amounts of the dispersed in the dyebath, because dispersants are not added. The converted insoluble disperse dye molecules aggregate with one another as a result

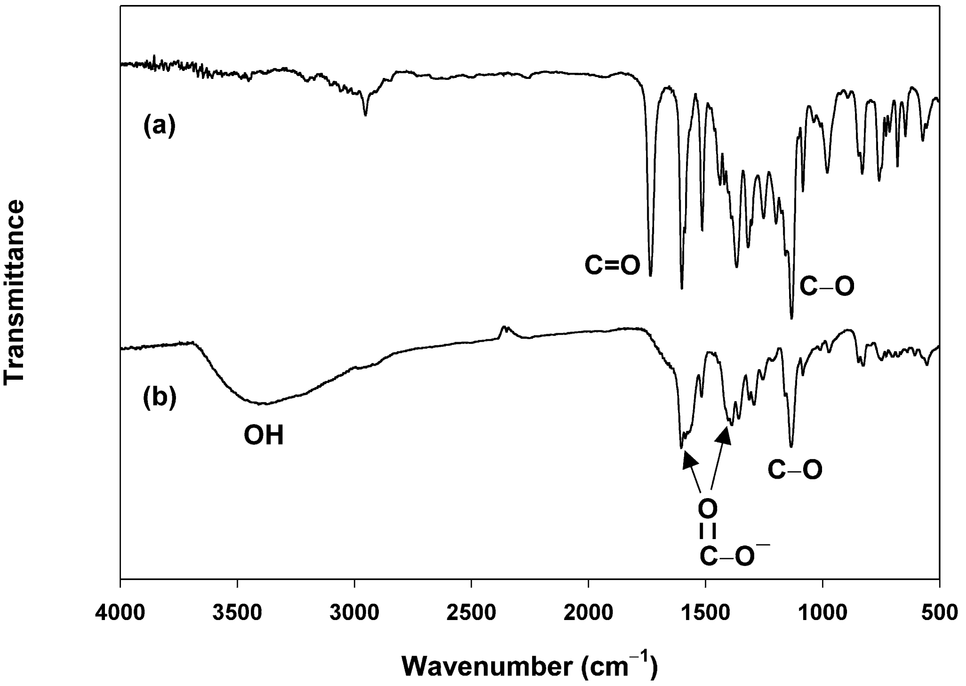


Fig. 4. IR spectra of the dye 6 (a) before alkali-treatment (b) after alkali-treatment.

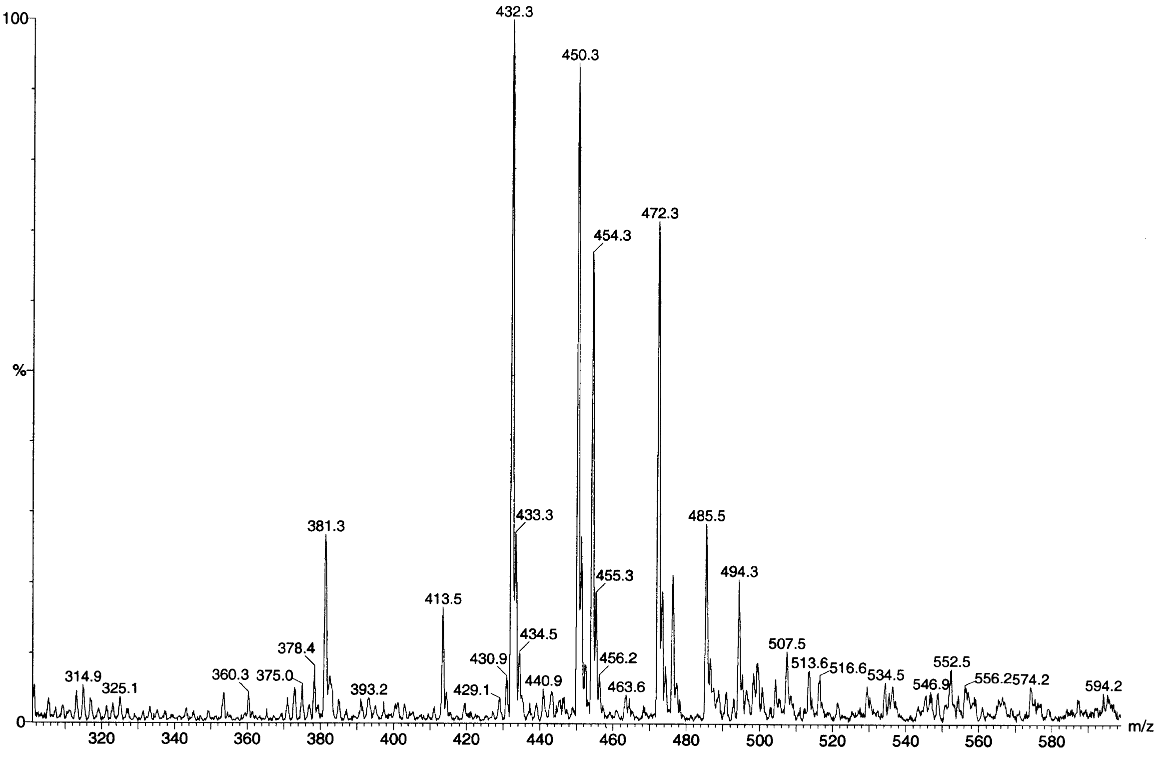


Fig. 5. Mass spectrum of the dye 6 after alkali-treatment.

of hydrophobic interaction, causing a collapse of the dyebath dispersion. Therefore, moderate conversion rate of the dye is required to minimise unfavourable aggregation.

In Section 3.1, we proposed that the optimum pH for dispersant-free polyester dyeing is pH 5 where the temporarily solubilised alkali-clearable disperse dyes were hydrolysed into the insoluble form at a moderate rate with minimising hydrolysis of carboxylic acid ester group. Fig. 6 shows the colour yield of dye **1** on polyester fabric at various pH values, which has the similar patterns to the conversion behaviour of dye **1** as shown in Fig. 2. Indeed, the colour yield of dye **1** at pH 5 showed the highest values. Although the K/S value of dyed fabric at pH 6 was similar to that observed at pH 5, the dyeing produced were unlevelled. However, in the case of pH 8, the K/S value of the dyed fabric started to decrease in the middle of the dyeing probably because the vinylsulphone form was rapidly produced and the dispersion stability of temporarily solubilising disperse dyes could not be maintained properly. Also, at pH 4, the colour yield on the polyester increased very slowly due to the low conversion rate, and it was not high enough even at the end of the dyeing.

3.4. *Levelling properties*

Fig. 7 shows the average colour differences (ΔE in CIE $L^*a^*b^*$ colour coordinates) of the polyester fabric dyed with synthesised dyes. The average ΔE value of the dyed fabric with dyes **1** or **2** which have a temporarily soluble β-sulphatoethylsulphone group was smaller than that of the dyed fabric with dye **3** containing no temporarily soluble groups in its structure when dispersing agent was not used. However, the average ΔE of the polyester fabric dyed with dye **3** was as small as that of the other dyes when dispersing agent was used. These results indicate that temporarily solubilising group gave good levelling property while the conventional disperse dye such as dye **3** cannot achieve a level dyeing without dispersing agent.

3.5. *Colour fastness*

Table 1 shows the results of the wash fastness and the sublimation fastness of the dyed polyester fabric under reduction clearing and alkali clearing, respectively. In the case of dyes **1** and **3** containing carboxylic acid ester groups in their structures, there were no differences in the fastness between the

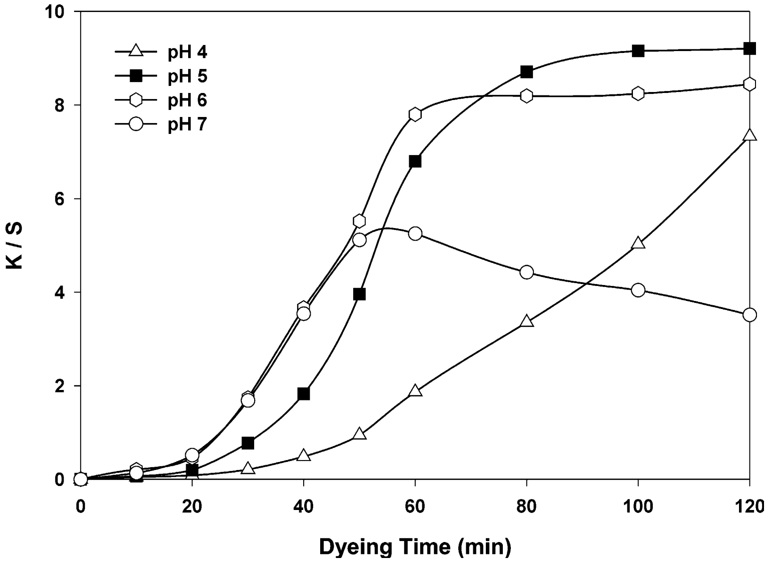


Fig. 6. Effect of pH on the colour yield of dye **1** on polyester fabric (1.0% owf).

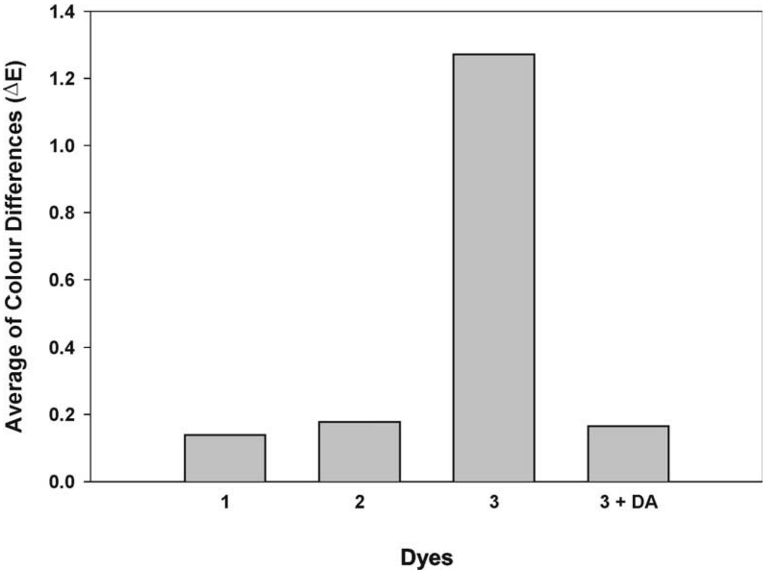


Fig. 7. Average of colour differences (ΔE) of dyed polyester fabric (DA: dispersing agent).

Table 1
Colour fastness of the synthesised dyes (1.0% owf)

Dye	Clearing	Wash fastness (ISO 105 C06/C2S)			Sublimation fastness (ISO 105 X11, 180 °C)		
		Change	Staining		Change	Staining	
			Cotton	Nylon		Dry	Wet
1	A/C	5	5	5	4–5	4–5	4–5
	R/C	5	5	5	4–5	4–5	4–5
2	A/C	5	4–5	4	4–5	4	4
	R/C	5	5	4–5	4–5	4	4
3	A/C	5	5	4–5	4–5	4–5	4–5
	R/C	5	5	4–5	4–5	4–5	4–5

reduction-cleared sample and the alkali-cleared sample, which demonstrates that alkali clearing can give enough wash-off to obtain a high level of colour fatness. These results support the hydrolysis mechanism of carboxylic acid ester groups which was proposed in Scheme 2. On the contrary, in the case of dye **2**, alkali-cleared sample showed lower fastness ratings than the reduction-cleared one since dye **2** cannot give water-soluble dyes on hydrolysis. This finding could be supported by the results of dye hydrolysis behaviour as well (Fig. 3).

4. Conclusions

A temporarily solubilised alkali-clearable azo disperse dye containing both a β-sulphatoethylsulphone group and carboxylic acid ester groups was synthesised and its conversion and alkali hydrolysis behaviour were examined. The synthesised dye showed the best dyeing properties on polyester fabric at pH 5 without dispersing agent and it was confirmed by HPLC analysis.

For the comparative purpose, the disperse dye containing only a β-sulphato-ethylsulphone group or that containing only carboxylic acid ester groups were synthesised and their dispersant-free dyeing properties and alkali-clearability was compared with the temporarily solubilized alkali-clearable dyes prepared.

The levelling property of the dye fabric using the temporarily solubilised dye without dispersing agent was as good as that using the conventional dye with dispersing agent. Also, the dyes having carboxylic acid ester groups showed good alkali-clearability and that was confirmed by the comparison of UV/vis. spectra and colour fatness assessment.

The synthesised disperse dye containing both a β-sulphatoethylsulphone group and carboxylic acid ester groups enabled the dispersant-free polyester dyeing and alkali clearing instead of environmentally damaging reduction clearing, which could meet the demands for environmentally friendly dyes of high wet fastness on polyester.

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