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Synthesis and application of an alkali-clearable azo disperse dye containing a fluorosulfonyl group and analysis of its alkali-hydrolysis kinetics

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Abstract

An alkali-clearable azo disperse dye containing a fluorosulfonyl group was synthesised. 4-Fluorosulfonylaniline, which was used as the diazo component, was prepared from *N*-acetylsulfanilyl chloride and coupled with *N*,*N*-diethyl-*m*-toluidine. Pseudo first-order kinetics were determined by analysis of the dye hydrolysis under alkaline conditions using HPLC. The synthesised dye was also applied to poly(ethyleneterephthalate) and its dyeing and wash fastness properties examined. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali-clearable azo disperse dye; Fluorosulfonyl group; Dye kinetics; Hydrolysis; HPLC; Wash fastness

1. Introduction

The demand for environmentally friendly dyes of high wet fastness on polyester is increasing. In addition, there are rising global legislative pressures 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. Alkali-clearable disperse dyes offer a means of tackling both of these challenges simultaneously [1].

Alkali-clearable dyes, which can be solubilised by the action of alkali, were first introduced for the discharge printing of polyester and exhaust dyeing of polyester alone or blended with cotton in 1976 by ICI [2]. These so-called PC dyes obviated the need for sodium hydrosulfite and significantly reduced the cost of effluent treatment.

In 1977, ICI introduced novel thiophene-based disperse dyes. These dyes were designed to rupture under the action of alkaline after-treatments to produce colourless or only slightly tinted decomposition products [3].

More recently, phthalimide-based alkali-clearable dyes have been reported [4,5]. These dyes, containing a phthalimide moiety, undergo ring opening and convert to water-soluble products under relatively mild alkaline conditions. One advantage of these dyes is the lack of azo bond reduction, which can lead to harmful primary aromatic amine-containing compounds.

In this study an alkali-clearable disperse dye containing a sulfonyl fluoride group is studied.

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The dye was synthesised and alkali-hydrolysis kinetics at various conditions were determined by using HPLC. The synthesised dye was also applied to polyester (PET) and the dyeing and wash fastness properties examined.

2. Experimental

2.1. Materials

All the chemicals used in the synthesis and dyeing were of laboratory-reagent grade. Diwatex 40 and Prestogen W were kindly supplied by BASF (UK), Sandozin NIE was kindly supplied by Clariant. Polyester fabrics (BS EN ISO 105 F04) were used for dyeing.

2.2. Preparation of dye intermediate (3)

Sixty grammes of *N*-acetylsulfanilyl chloride (**1**) was stirred into a solution of 89.5 g KF in 120 ml of water and 120 ml of *p*-dioxane for 3 h under reflux, then drowned onto ice, washed with warm tap water (pH 4–5) and the precipitate (**2**) was collected. This precipitate was refluxed in the mixture of ethanol (50 ml) and 35% HCl (50 ml) for 1 h then drowned onto ice, neutralised with NaOH, and filtered, giving white powder (**3**) (Scheme 1); 23.9 g (53.1%), mp 66–68 °C. ^{1}H-NMR (d_6-DMSO): δ 6.74 (*s*, 2H, C-NH_2), 7.48–7.77 (*d*, 4H, aromatic protons). Mass spectrum (*m*/*z*): 175 (M^+).

2.3. Synthesis of dye containing a fluorosulfonyl group

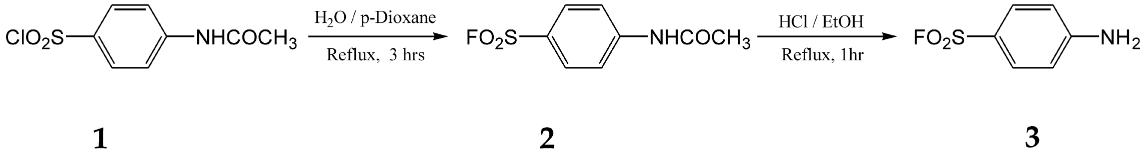
4-Fluorosulfonylaniline (**3**) (0.025 mol) was diazotised in 8.6 ml of 35% HCl and 90 ml of water, by adding 0.025 mol of $NaNO_2$ at a temperature of 0–5 °C. After 4–5 h, the completion of diazotisation was checked using a solution of 4-(dimethylamino)benzaldehyde and the pH value of the diazo liquor was then adjusted to pH 5–6 by adding solid sodium acetate. The diazonium liquor was added to a solution containing 0.025 mol of coupling component (*N*,*N*-diethyl-*m*-toluidine), 50 ml of water and 4.3 ml of 35% HCl. After 4–5 h, completion of coupling was checked by 10% H-acid solution, and the precipitated dye (**4**) was filtered, washed with water and dried (Scheme 2). The dye was purified by crystallization from methanol, giving a red powder 7.58 g (86.8%), mp 113–116 °C, UV–vis (acetonitrile) λ_{max}: 484 nm. ^{1}H-NMR (d_6-DMSO): δ 1.14–1.20 (*t*, 6H, NCH_2CH_3), 3.45–3.53 (*q*, 4H, NCH_2CH_3), 6.67 (*s*, 3H, CCH_3), 7.64–8.23 (*m*, 7H, aromatic protons). Mass (*m*/*z*): 349 (M^+).

2.4. Synthesis of hydrolysed dye containing a sulfonate group

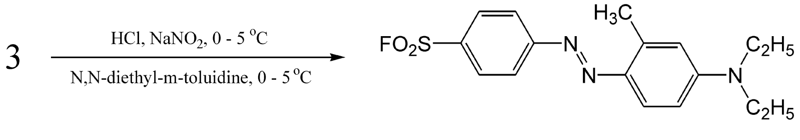
The procedure of 2.3 was repeated except that in place of 4-fluorosulfonylanilie (**3**), sulfanilic acid (**5**) as a diazo component was used to synthesise the hydrolysed form of **4**. After coupling, the reaction product was salted out of solution by adding solid NaCl, filtered and dried (Scheme 3); mp 201–204 °C, UV–vis (acetonitrile) λ_{max}: 521 nm. ^{1}H-NMR (d_6-DMSO): δ 1.13–1.18 (*t*, 6H, NCH_2CH_3), 3.47–3.55 (*q*, 4H, NCH_2CH_3), 6.77 (*s*, 3H, CCH_3), 7.66–7.88 (*m*, 7H, aromatic protons). Mass (*m*/*z*): 369 (M^+).

2.5. Formulation of dye (4)

Synthesised dye (**4**) was formulated as a dispersion prior to application to polyester. The composition comprises dispersing agent (Diwatex 40, 40% on the weight of the dye), wetting agent (Sandozin NIE Liquid, 1 drop) and 1% by the



Scheme 1. Preparation of 4-fluorosulfonylaniline.



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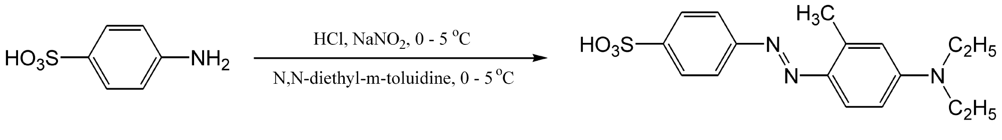
Scheme 2. Synthesis of 4-(4-diethylamino-2-methyl-phenylazo)benzene sulfonyl fluoride.



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Scheme 3. Synthesis of 4-(4-diethylamino-2-methyl-phenylazo)benzene sulfonic acid.

weight of dye in an aqueous medium, buffered at pH 4.0–4.5. The dye dispersion was prepared by milling the composition mixture with pebbles for 1 week until the mean particle size was ~1 μm.

2.6. Alkaline hydrolysis kinetics

Alkaline hydrolysis kinetics were investigated at various pH values (8.0, 9.0, 10.0, 11.0 and 12.0) and temperatures (60, 70, 80, 90 and 100 °C). The buffer solutions used in the experiments were as follows:

(a) pH 8.0: monosodium phosphate (0.25 g/l) and disodium phosphate
(b) pH 9.0: trisodium phosphate (4.0 g/l) and monosodium phosphate
(c) pH 10.0: trisodium phosphate (5.0 g/l) and monosodium phosphate
(d) pH 11.0: trisodium phosphate (2.0 g/l) and disodium phosphate
(e) pH 12.0: sodium hydroxide (0.4 g/l).

The dye liquors were prepared by dispersing 0.02 g of the formulated dye dispersion in 200 ml of buffer solution preheated to proper temperature in water bath. The dye liquor was stirred at the temperature for 40 min and 2 ml aliquots were withdrawn from the dye solution at 5 min intervals and immediately neutralised to pH 4.0–4.5 with equivalent amounts of dilute HCl and cooled to prevent further hydrolysis reactions. Ten millilitres of acetonitrile were added into each withdrawn sample to prepare a sample of the proper composition for HPLC analysis.

Analysis was carried out at room temperature using a HPLC (Varian 5000 Liquid Chromatograph, USA, Varian) with a C18 reverse-phase column and a mixture of acetonitrile and deionised water was used as the mobile phase (acetonitrile: water = 80:20). Ten microlitres of the samples were injected and detected at a wavelength of 484 nm at room temperature.

2.7. Determination of optimum dyeing pH

In order to determine optimum dyeing pH, 0.01 g formulated dye dispersion was added to 50 ml buffer solution containing dispersing agent (0.5 g/l) at a given pH (3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0) and the dye liquors were treated at 130 °C in laboratory dyeing machine (Werner Mathis Labomat, Mathis, Switzerland). After 1 h, dye liquors were diluted with the same amount of acetonitrile and cooled immediately. Four millilitres of the diluted liquor were withdrawn and 6 ml of acetonitrile were added into it to prepare a sample of the proper composition (acetonitrile:water = 80:20) for HPLC. Optimum dyeing pH was determined by comparing the extent of hydrolysis at various pH values. The buffer solutions used in the experiment were as follows:

(a) pH 3.0: sodium acetate (4.0 g/l) and formic acid
(b) pH 3.5: sodium acetate (6.0 g/l) and formic acid
(c) pH 4.0: sodium acetate (3.0 g/l) and acetic acid
(d) pH 4.5: sodium acetate (4.0 g/l) and acetic acid
(e) pH 5.0: sodium acetate (12 g/l) and acetic acid
(f) pH 5.5: sodium acetate (14 g/l) and acetic acid
(g) pH 6.0: monosodium phosphate (7.4 g/l) and disodium phosphate
(h) pH 6.5: monosodium phosphate (5.0 g/l) and disodium phosphate
(i) pH 7.0: monosodium phosphate (2.2 g/l) and disodium phosphate.

2.8. Dyeing procedure

Polyester fabrics were dyed in a laboratory dyeing machine at a liquor ratio of 30:1. Sixty millilitres of dyebath were prepared with formulated dye and a dispersing agent (Diwatex 40, 0.5 g/l) and adjusted to pH 4.0. The polyester fabric (2.0 g) was immersed in the dyebath and dyed for 60 min at 130 °C. After dyeing, the dyed fabric was reduction cleared ($Na_2S_2O_4$ 2.0 g/l, NaOH 2.0 g/l, Sandozin NIE 2.0 g/l) for 20 min at 75 °C.

The percentage dyebath exhaustion on the polyester was estimated colorimetrically by measuring the absorbance value of residual dyebath using an UV/visible-spectrophotometer (UVIKON 860, USA, KONTRON). The build-up property of dye was also investigated by measuring f_k values of dyed fabrics at various dye concentrations. f_k is a colour strength value which is the sum of the weighted K/S values in the visible region of the spectrum; it is calculated using Eq. (1) [6].

$$f_k = \sum_{\lambda=400}^{700} (K/S)_\lambda \left(\bar{x}_{10,\lambda} + \bar{y}_{10,\lambda} + \bar{z}_{10,\lambda}\right) \qquad (1)$$

The colour of the dyed samples was measured using a spectrophotometer (Spectra flash 500, Datacolor, USA, standard light D65, 10° standard observer, SPIN) interfaced with a personal computer.

2.9. Wash fastness test

Polyester fabric was dyed and heat-set (180 °C, 30 s) for the wash fastness test (ISO C06/C2S). Two f_k values (80 for pale depth and 200 for medium-heavy depth) were chosen for wash fastness test. In particular, in order to evaluate alkali-clearability of synthesised dye, these fastness test were carried out for three differently cleared polyester fabrics after dyeing, i.e. alkali cleared (NaOH 0.4 g/l, Sandozin NIE 2.0 g/l, 90 °C, 20 min), oxidation cleared (Prestogen W 1.0 g/l, NaOH 1.0 g/l, 30% H_2O_2 5 ml, 90 °C, 20 min) and reduction cleared ($Na_2S_2O_4$ 2.0 g/l, NaOH 2.0 g/l, Sandozin NIE 2.0 g/l, 75 °C, 20 min).

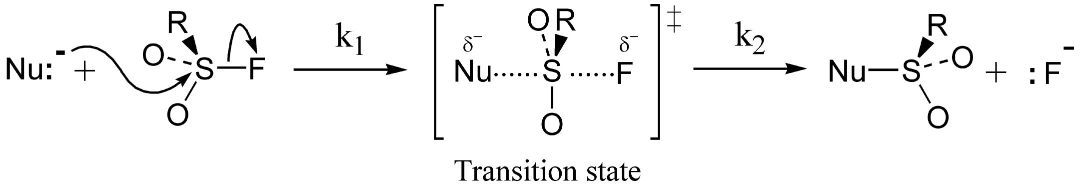
The change in shade and staining of adjacent multifibre (Multifibre DW, adjacent fabric, BS EN ISO 105 F10) were assessed using grey scales.

3. Results and discussion

3.1. Alkaline hydrolysis kinetics

Sulfonyl halides can be hydrolysed to the corresponding sulfonic acids by a nucleophilic bimolecular substitution (S_{N2}) mechanism under alkaline conditions (Scheme 4) [7, 8]. The essential features of the S_{N2} reaction mechanism are that the reaction takes place in a single step without intermediates when the entering nucleophile attacks the substrate from position 180° away from the leaving group. As the nucleophile comes in on one side and bonds to the sulfur atom, the leaving halide group departs from the other side. Therefore, it is presumed that azo disperse dyes containing a fluorosulfonyl group can be hydrolysed under alkaline condition by the S_{N2} mechanism shown in Scheme 4.

Considering that addition of the hydroxide ion to the electrophilic sulfur atom is the rate-determining step of the hydrolysis reaction, and that hydroxide ion concentration is kept constant by



Scheme 4. Nucleophilic bimolecular substitution (S_{N2}) at a sulfur atom of sulfonyl fluoride (Nu, nucleophile).

the use of a buffer or large excess of alkali, the rate of concentration decrease of the parent dye in the alkaline solution can be expressed by Eq. (2) [9]:

$$-\frac{d[p]}{dt} = k_{ps1}[p]t \qquad (2)$$

in which $[p]$ is the concentration of the parent dye at hydrolysis time t, and k_{ps1} is the pseudo first-order rate constant of hydrolysis.

The HPLC chromatograms of the parent dye which were recorded at different times of hydrolysis show the expected decrease in the amount of the parent dye and increase in the amount of the hydrolysed form of the dye (Fig. 1). The figure shows the HPLC retention times of the hydrolysed form of the dye and the parent dye (**4**) to be 1.32 and 7.43 min, respectively. Also, the retention time of synthesised hydrolysed dye (**6a**) was exactly the same as that of the hydrolysed dye from the parent dye (**c**–**f**). There were no traces of any other side reaction products such as (potentially toxic) primary aromatic amines, which are produced during alkaline reduction clearing.

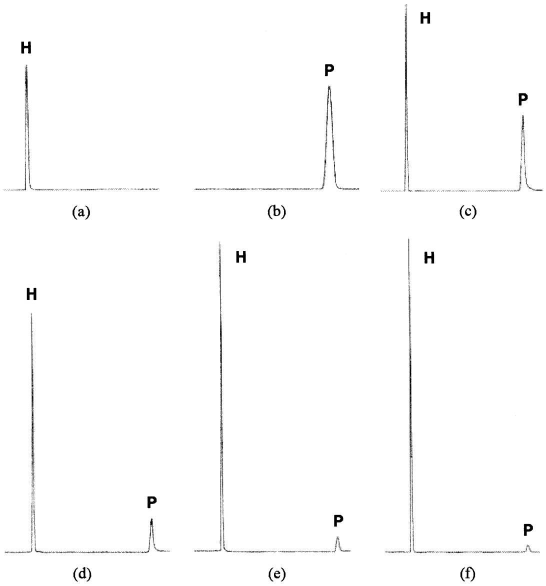


Fig. 1. Chromatogram of the synthesised hydrolysed dye and parent dye in buffer of pH 11 recorded after various times of hydrolysis at 90 °C: (a) synthesised hydrolysed dye, (b) 0 min, (c) 10 min, (d) 20 min, (e) 30 min, (f) 40 min; where components P and H represent parent dye and hydrolysed dye.

Fig. 2 shows the hydrolysis of synthesised dye (**4**) at different pH values and temperatures. It shows the expected increase in the amount of the hydrolysed form of the dye with increase in temperature and pH value. It can also be seen that the amount of parent dye (**4**) exponentially decreases with increasing hydrolysis time especially at the higher temperature.

The values of the peak areas of the components determined from the chromatograms are linearly related to their amount. Replacement of the concentrations of the parent dye with peak areas leads to Eq. (3).

$$\ln\left(\frac{A_0}{A}\right) = k_{ps1}t \qquad (3)$$

where A_0 and A are values of peak areas of the parent dye at the time $t=0$ and at a later time t. This equation shows that if $\ln(A_0/A)$ is plotted against t, then a first-order reaction will give a straight line [10].

The plot of $\ln(A_0/A)$ against time t shown in Fig. 4 yielded a straight line passing through the origin with high correlation coefficients (Table 1). According to Eq. (3) the expected pseudo first-order kinetics were confirmed and the slope of the plot was calculated to determine the rate constant k_{ps1}. In the case of temperature of 100 °C, after a time longer than 20 min, almost all of the parent dye was hydrolysed and, therefore, was not considered

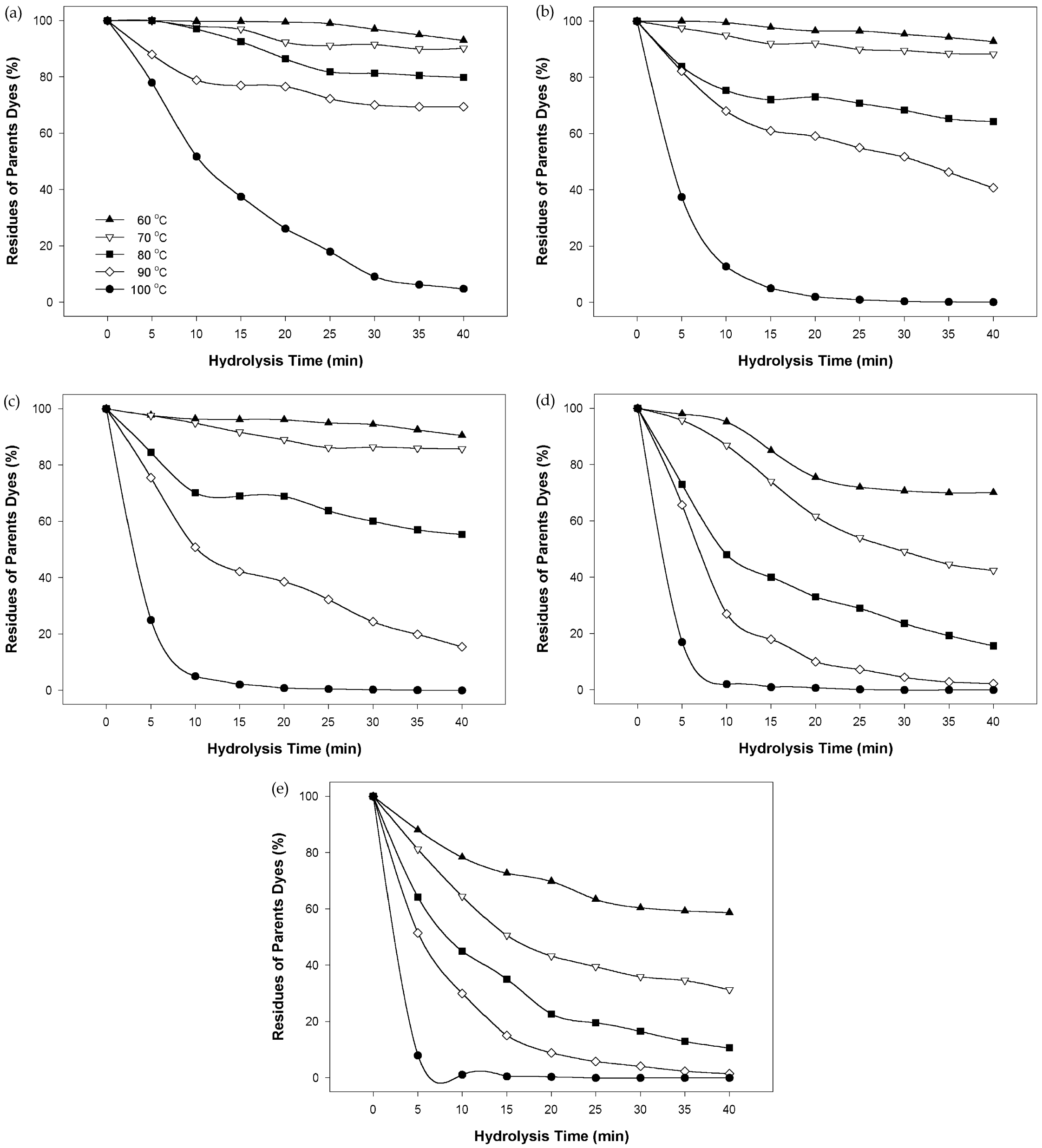


Fig. 2. Residues of parent dyes vs time of hydrolysis *t* at various pH values and temperatures: (a) pH 8.0, (b) pH 9.0, (c) pH 10.0, (d) pH 11.0, (e) pH 12.0.

for determining pseudo first-order hydrolysis constants.

Fig. 5 shows the determined pseudo first-order hydrolysis constants at various pH values and temperatures. The hydrolysis constant range at pH 8 was 0.0012–0.0159 and when the pH was raised by 1.0 the hydrolysis rates increased by 1.24–2.37, 1.20–2.01, 1.27–4.84 and 1.24–1.50 times at pH 9, 10, 11 and 12 respectively. The hydrolysis constant range at 60 °C was 0.0012–

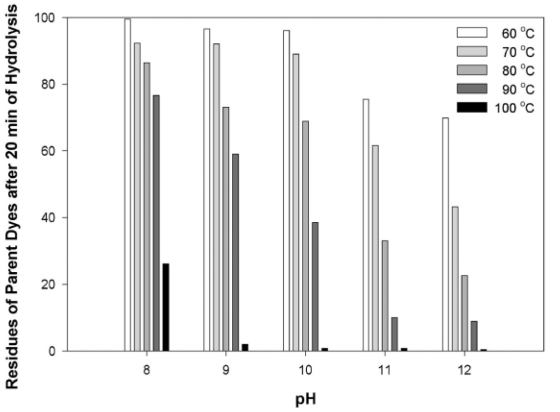


Fig. 3. Residues of parent dyes after 20 min of hydrolysis at various pH values and temperatures.

Table 1
Correlation coefficients (*r*) in the linear regression at different pH values and temperatures

	Temperature (°C)				
pH	60	70	80	90	100
8.0	0.877	0.954	0.964	0.918	0.995
9.0	0.984	0.962	0.907	0.976	0.995
10.0	0.961	0.954	0.945	0.992	0.984
11.0	0.949	0.990	0.988	0.992	0.967
12.0	0.967	0.969	0.988	0.996	0.948

0.0159 and when the temperature was raised by 10 °C the hydrolysis rate increased by 2.06–2.50, 1.83–3.67, 1.78–2.77, and 2.64–7.54 times at 70, 80, 90 and 100 °C, respectively. It is apparent that the effect of pH on hydrolysis rate between pH 10 and 11 and the effect of temperature on hydrolysis rate between 90 and 100 °C, were remarkable. Also, from the overall results, it can be concluded that the effect of temperature on hydrolysis rate was more pronounced than that of pH.

Assuming that any alkali clearing of a polyester dyeing can take no longer than 20 min and that > 90% hydrolysis is required, then it is apparent at temperatures less than 90 °C, the rate of hydrolysis is too slow and insufficient alkali clearance occurs (Fig. 3). In order to guarantee enough alkali clearance to obtain high wash fastness and within 20 min the mildest conditions that are required are 90 °C and pH 11. Alternatively, pH 9 and 100 °C, which gave almost complete (> 98%) would guarantee enough alkali clearance to obtain high wash fastness. The feasibility of any commercial process would obviously need to consider the energy consumption and dyeing effluent together with wash fastness requirements.

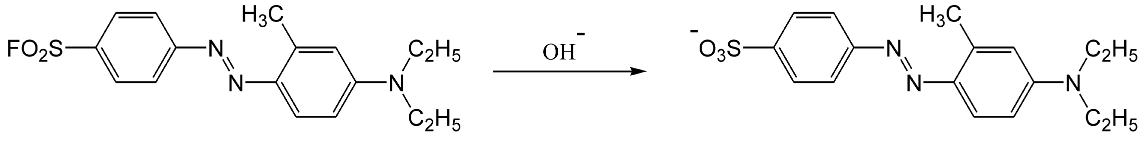
3.2. *Optimum dyeing pH and build-up performance*

The extent of hydrolysis at 130 °C (dyeing temperature) and various pH values is shown in Fig. 6. The synthesised dye (**4**) was the most stable at pH 4.0 while it was almost completely hydrolysed at pH 7.0. Even so, at pH 4 the dye showed some undesirable instability and it is evident that molecular design will play a major role in ascertaining acid stability for dyeing and alkali instability for clearing.

Fig. 7 shows the build-up property of synthesised dye on polyester fabric. The colour strength of dyed fabric reached saturation at the dye concentration ≈ 4.0% o.w.f., which gave a f_k value of around 270.

3.3. *Wash fastness*

Since pH 4 was the optimum dyeing pH, all the dyeing was carried out at this pH. Table 2 shows the ISO CO6 C2S wash fastness test results of dye (**4**) on polyester. These results show that the colour



4 **6**

Scheme 5. Alkali hydrolysis of azo disperse dye (**4**) containing sulfonyl fluoride group.

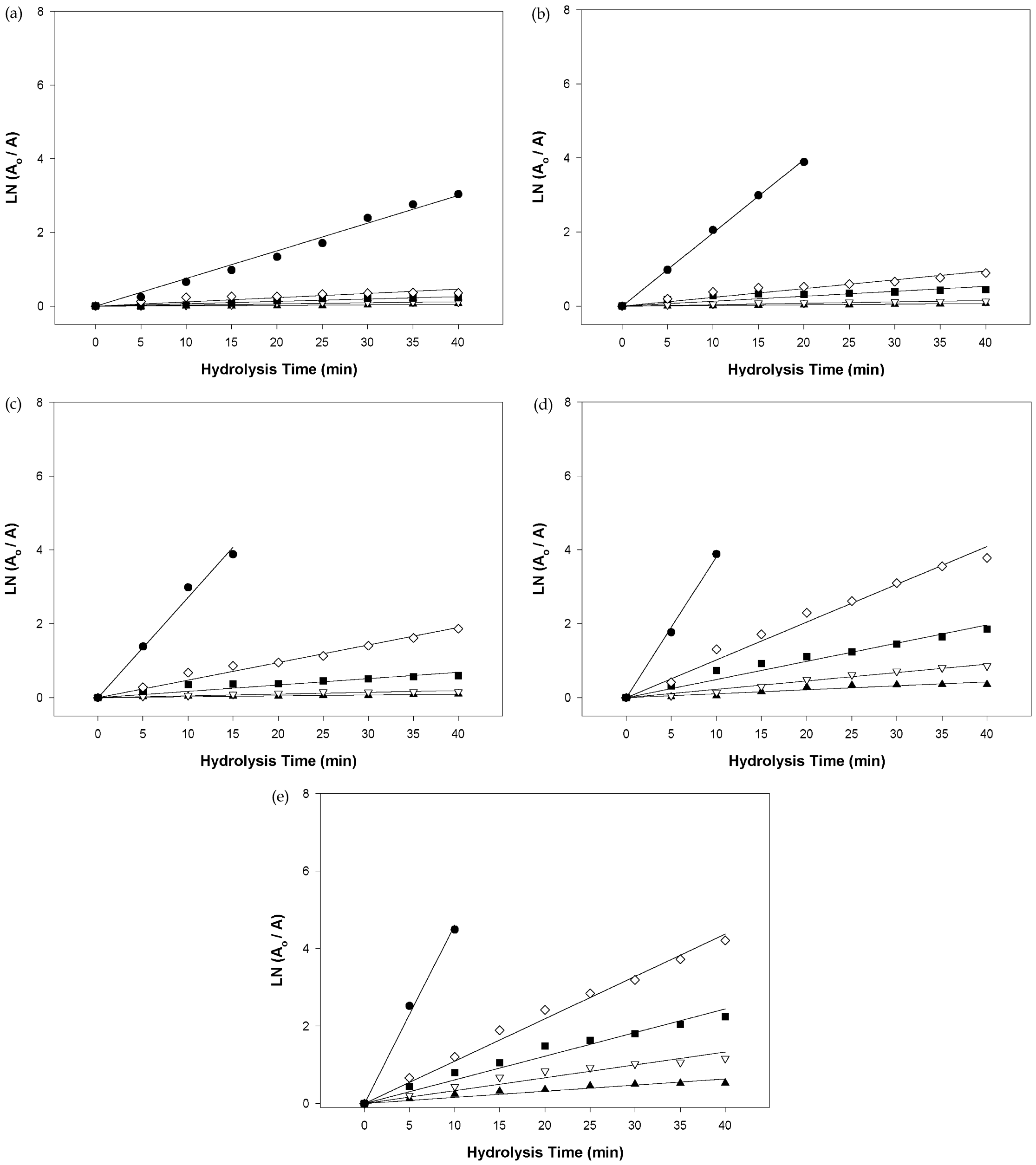


Fig. 4. Plot of $\ln(A_0/A)$ vs time of hydrolysis t at various pH values and temperatures: (a) pH 8.0, (b) pH 9.0, (c) pH 10.0, (d) pH 11.0, (e) pH 12.0 [for key see Fig. 2(a)].

fastness of all the samples was good and within a similar range, irrespective of the clearing process used. The ratings of wash fastness of dyed fabrics which have f_k value of 80 were all 5 and those of dyed fabrics which have f_k value of 200 were in the range 4–5. Clearly, the alkali-cleared fabrics displayed good wash fastness due to clearing properties, attributable to the presence of the fluorosulfonyl group, which was converted to a water soluble sulfonate group by alkali-hydrolysis

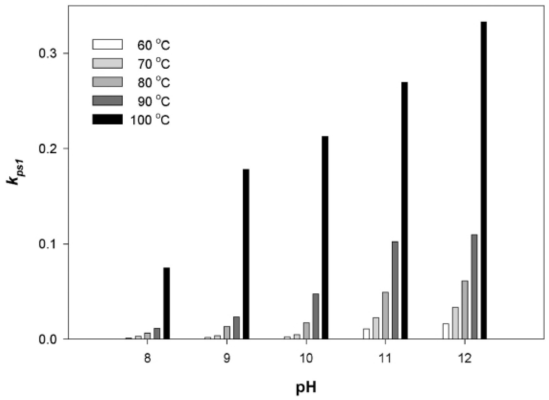


Fig. 5. Pseudo first-order rate constant of hydrolysis at various pH values and temperatures.

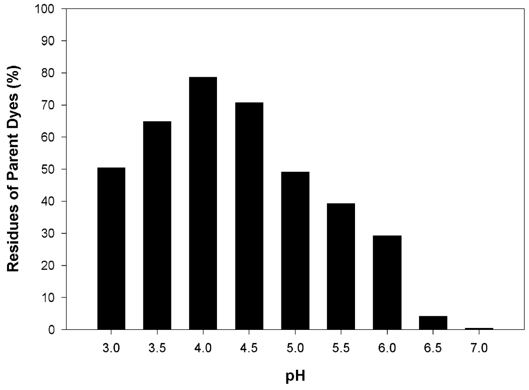


Fig. 6. Hydrolysis of dye at various pH values (130 °C, 60 min).

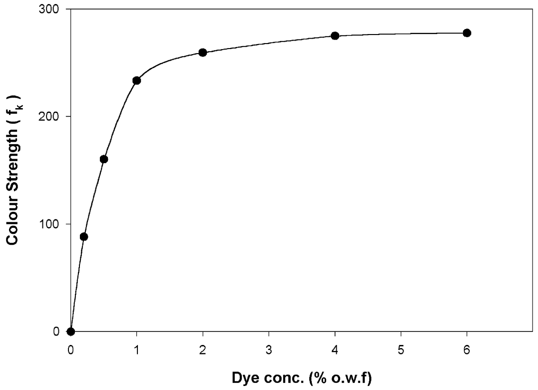


Fig. 7. Build-up property of synthesised dye **4**.

Table 2
Wash fastness (ISO C06 C2S) of synthesised dye at various after treatments

f_k	Clearing process					
	A/C		O/C		R/C	
	80	200	80	200	80	200
Acetate	5	5	5	5	5	4–5
Cotton	5	5	5	5	5	5
Nylon	5	4–5	5	5	5	4–5
Polyester	5	5	5	5	5	5
Acrylic	5	5	5	5	5	5
Wool	5	4–5	5	4–5	5	4–5

and could be easily washed-off (Scheme 5). In addition, it is thought that polyester/cotton blends can be dyed using a one-bath two-step dyeing method, as alkali-clearance enables these dyes to be applied in the same bath with cotton reactive dyes, utilising the alkali fixing conditions stage of reactive dyes as the alkali clearing stage for the disperse dye. High levels of wash fastness even in heavy depths are anticipated.

4. Conclusion

An azo disperse dye incorporating a fluorosulfonyl group hydrolysed under relatively mild alkaline conditions and temperature to a dye containing a water-solubilising sulfonate group, without cleavage of the azo bond. The hydrolysis of the fluorosulfonyl dye in buffered alkaline solution at constant temperature followed pseudo first-order kinetics and the effect of temperature on hydrolysis rate was more pronounced than that of pH.

The use of fluorosulfonyl containing disperse dyes showed a reasonable level of build up, excellent wash fastness and offers the option of alkali clearance to achieve high wash fastness, replacing reductive clearing and particularly sodium hydrosulfite, which places a very high BOD on conventional disperse dyeing effluent and the generates aromatic amines.

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