

Synthesis and Application of Some Alkali-clearable Azo Disperse Dyes Based on Naphthalimide Derivatives

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A series of naphthalimide-based alkali-clearable azo disperse dyes containing a fluorosulfonyl group was synthesized. 4-Fluorosulfonylaniline, 4-fluorosulfonyl-2-nitroaniline and 6-chloro-4-fluorosulfonyl-2-nitroaniline as the diazo components were prepared from N-acetylsulfanilyl chloride and were subsequently coupled with 4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide. The synthesized dyes and their intermediates were characterized by the use of DSC, FTIR, ¹H NMR, ¹³C NMR, Mass spectroscopy and UV-visible spectroscopic techniques. Spectrophotometric investigations of prepared dyes in different solvents were carried out in order to obtain their absorption maxima, molar extinction coefficients and solvatochromic effects. The obtained dyes were applied to polyester fabric by the HT method and exhibited good leveling, wash and sublimation fastnesses and moderate light fastness. The synthesized dyes showed that incorporated fluorosulfonyl group to these dyes can be converted to the dyes containing a water soluble sulfonate group in the relatively mild alkaline conditions.

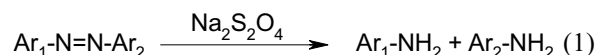
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1. INTRODUCTION

In recent decades, production and requirements of new synthetic dyes for dyeing textile fibers have been considerably decreased because of three reasons. Firstly, the massive increase in oil prices and subsequent recession of recent years has hit the dye and textile industries particularly severely.¹ Secondly, the introduction of stringent toxicological test requirements for new products and severe regulations for protecting environment, have made the introduction of new dyes a much less attractive proposition. Finally, there is the unavoidable fact that there is a natural limit to the number of dyes needed by the textile industry, and the current status of dye development is such that further improvements in performance and economics of existing dyes are likely to be minimal.¹ These limitations, which have been performed by the world organizations for decreasing pollution of environment, have caused increasing requirements for manufacturing environmentally friendly dyes.

Disperse dyes are slightly soluble in water, and they can be applied as a dispersion in water on polyester fibers. Since disperse dyes have a limited solubility in water, some particles of dyes may be remained on the fiber surface after

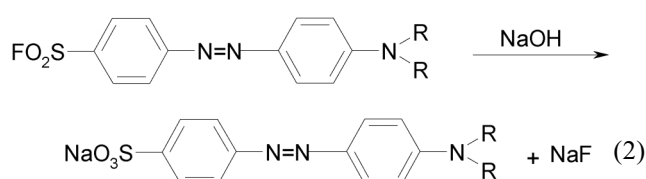
the dyeing is completed. These particles, which have remained on the surface of the fibers, cause reduction of the shade brightness as well as the wash and rubbing fastnesses.^{2,3} Therefore, the conventional method of reduction clearing is necessary for removing these particulates. In this process the dyed fabric is treated by a solution containing sodium hydrosulfite, sodium hydroxide and detergent. Treatment of reduction clearing causes environmental pollution, and increases BOD of the effluents.^{4,5} Disperse dyes containing azo groups can also be broken and generate toxic and carcinogenic aromatic amines according to Eq. 1. Therefore, elimination of treatment of reduction clearing in the dyeing polyester process with disperse dyes can significantly reduce pollution of environment as well as the costs of effluent treatments.



Pioneering work on disperse dyes has been researched to obtain the dyes which leads to the elimination of reduction clearing process in dyeing polyester fibers.⁴ Synthesized disperse dyes based on diester, phthalimide and thiophene derivatives are groups of these dyes which can be

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converted to water soluble or colourless compounds in alkali media.⁵⁻⁸ Therefore, for substrates which have been dyed with these dyes, reduction-cleared process can be replaced by alkali-cleared process. Another group of this type is fluorosulfonyl-based alkali-clearable dyes.^{2,3} In this type, the fluorosulfonyl group can be converted to the water soluble SO_3Na group according to Eq. 2. Different substituents with different dyeing properties of these dyes have been synthesized. In these dyes the diazo component was an aromatic amine containing of $-\text{SO}_2\text{F}$ group and the coupling component was a tertiary aromatic amine.



In the present study, a novel series of monoazo disperse dyes based on naphthalimide derivatives containing of fluorosulfonyl group has been obtained utilizing 4-fluorosulfonylaniline, 4-fluorosulfonyl-2-nitroaniline and 6-chloro-4-fluorosulfonyl-2-nitroaniline, as the diazo components and 4-hydroxy-N-3-propyl-1,8-naphthalimide constituted the coupling component (Fig. 1). The dyes were then purified and characterized together with their corresponding intermediates by the use of spectroscopic techniques. The prepared dyes were subsequently dyed on polyester fabric and finally their optical, dyeing and alkali-clearable properties were determined.

2. EXPERIMENTAL

2.1. Materials

All compounds used in this study were of analytical grade unless otherwise stated.

2.2. Procedures

(i) Preparation of 4-fluorosulfonylaniline was carried out by the use of N-acetylsulfanilyl chloride and then subsequent processes such as fluorination, hydrolysis, nitration and chlorination were carried out according to the method of Koh et al.⁹

FTIR (cm^{-1}): 1595 (C=C str.), 3397-3492 (N-H str.); ^1H NMR (CDCl_3): δ (ppm): 4.40 (2H, NH_2), 6.72-6.75 (2H, 3-H, 5-H), 7.76-7.79 (2H, 2-H, 6-H), Yield = 63%, m.p = 70 °C.

(ii) Preparation of 4-fluorosulfonyl-2-nitroaniline and 6-chloro-4-fluorosulfonyl-2-nitroaniline were carried

out by the use of the same methods mentioned above.

4-Fluorosulfonyl-2-nitroaniline:

FTIR (cm^{-1}): 1201 (C-N str.), 1403-1514 (NO_2 str. sym. and unsym.), 1559 (C=C str.), 3368-3481 (N-H str.); ^1H NMR (CDCl_3): δ (ppm): 1.59 (2H, NH_2), 7-7.03 (1H, 6-H), 7.78-7.9 (1H, 5-H), 8.86 (1H, 3-H); Yield = 33%, m.p = 150.3 °C.

6-Chloro-4-fluorosulfonyl-2-nitroaniline:

FTIR (cm^{-1}): 759 (C-Cl str.), 1208 (C-N str.), 1409-1526 (NO_2 str. sym. and unsym.), 1552 (C=C str.), 3342-3449 (N-H str.), ^1H NMR (CDCl_3): δ (ppm) 1.58 (2H, NH_2), 8.09-8.1 (1H, 3-H), 8.81-8.83 (1H, 5-H); Yield = 64%, m.p = 132 °C.

(iii) Preparation of 4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide as the coupling component was carried out by the use of acenaphthene as a starting material and then subsequent reactions such as sulfonation, oxidation, imidation and hydroxylation were carried out.¹⁰

FTIR (cm^{-1}): 1586 (C=C str.), 1642-1688 (C=O str. sym. and unsym.), 3276 (OH str.); ^1H NMR (CDCl_3): δ (ppm) 2.01-2.03 (2H, CH_2), 3.37 (3H, OCH_3), 3.42-3.59 (2H, CH_2O), 4.27-4.32 (2H, NCH_2), 6.73 (1H, O-H), 6.98-7.01 (1H, 3-H), 7.7-7.75 (1H, 6-H), 8.41-8.44 (1H, 2-H), 8.54-8.58 (1H, 5-H), 8.62-8.64 (1H, 7-H); Yield = 71%, m.p. = 225 °C.

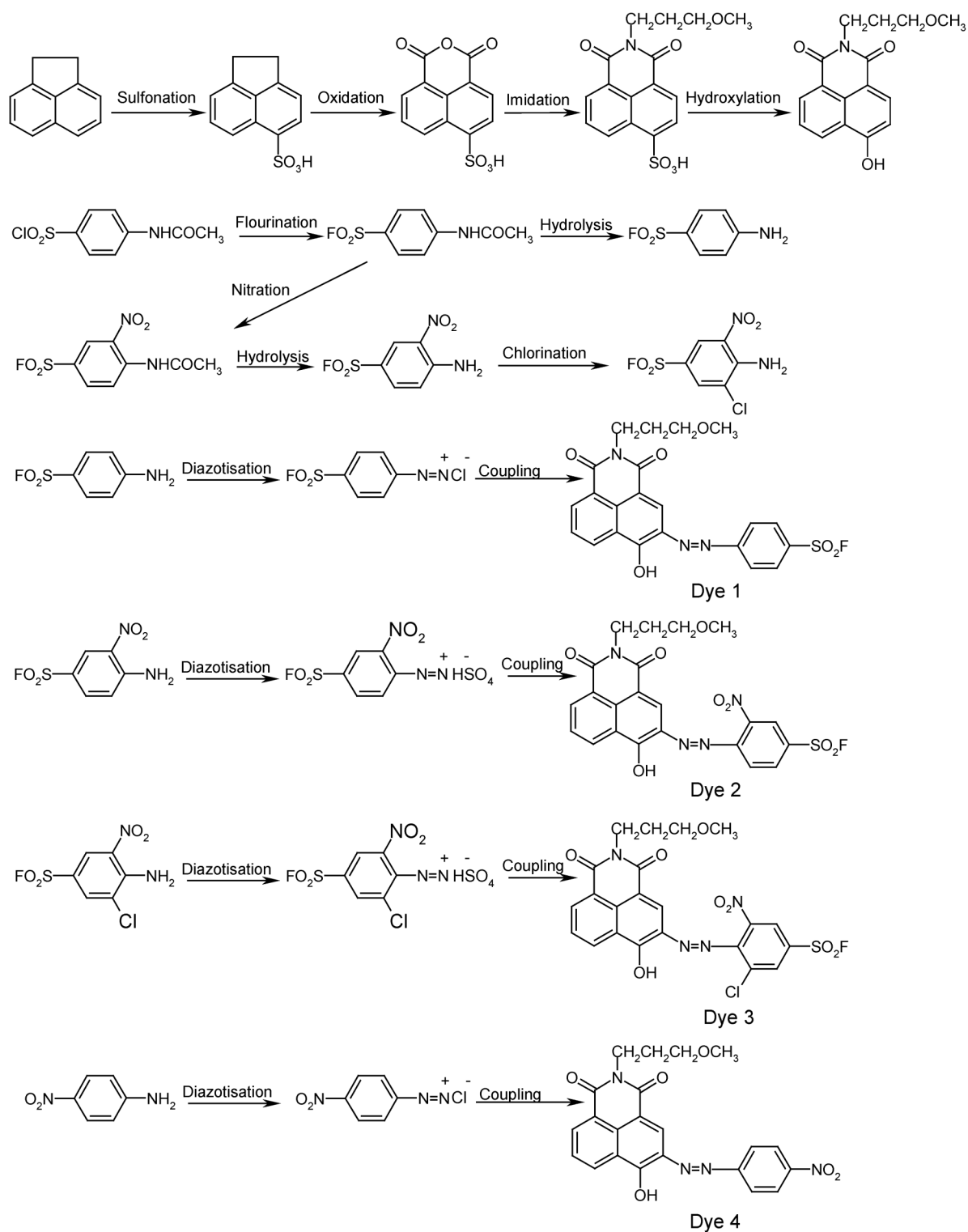
Preparation of the dyes

(i) Dye 1

4-Fluorosulfonylaniline (10 mmol, 0.175 g) was diazotized in solution of hydrochloric acid (3.45 mL) and water (35 mL) and sodium nitrite (10 mmol, 0.07 g) at a temperature of 0-5 °C. The saturated of sodium acetate was added to this solution and the pH value of the diazo liquor was adjusted to 5-6. The reaction mixture was stirred for 5 hours to complete the reaction.

The diazotized 4-fluorosulfonylaniline was added to a solution containing 10 mmol (0.285 g) of coupling component (4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide) in 20 mL of methoxyethanol. After 4-5 hours the reaction was completed and the precipitated dye was filtered, washed with water and dried. The dye was purified by TLC and column chromatography methods.

FTIR (cm^{-1}): 1402 (N=N str.), 1498 (C-N str.), 1620, 1657 (C=O str. Carbonyl sym. and unsym.), 3443 (O-H str.); ^1H NMR (CDCl_3): δ (ppm) 2.0-2.05 (2H, CH_2), 3.35 (3H, OCH_3), 3.51-3.55 (2H, CH_2O), 4.25-4.30 (2H, NCH_2), 7.73-7.78 (H, 6-H), 7.89-7.92 (2H, 3'-H, 5'-H), 8.15-8.17 (2H, 2'-H, 6'-H), 8.44 (1H, 2-H), 8.65-8.66 (1H, 5-H),



8.67-8.69 (1H, 7-H), 16.39 (1H, OH); ¹³C NMR (CDCl₃): δ (ppm) 21.3, 24.7, 37.2, 41.6, 62.5, 75.8, 94.1, 119.3, 126.7 (2C), 130.1, 133.9 (4C), 137.5, 141.4, 150.8, 152.2, 163.1, 172.4, 176.9; Yield = 57%, m.p = 216 °C, Mass: 471 m/z.

(ii) Dye 2

Diazotization of 4-fluorosulfonyl-2-nitroaniline was carried out with nitrosylsulphuric acid. For this purpose, 4-fluorosulfonyl-2-nitroaniline (10 mmol, 0.22 g) was dissolved in the solution of acetic acid and propionic acid (4:1, 50 mL) and then it was added to the solution of sodium nitrite (10 mmol, 0.07 g) and sulfuric acid (15 mL) at a temperature of 5–10 °C. The reaction mixture was stirred at this temperature for 3 hours. The obtained clear diazonium salt solution was used immediately in the coupling reaction. The pH of the diazonium salt solution was adjusted to 5–6 by adding sodium acetate solution.

The diazotized 4-fluorosulfonyl-2-nitroaniline was added to a solution containing 10 mmol (0.285 g) of coupling component (4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide) in 20 mL of methoxy ethanol. After 13 hours the reaction was completed and the precipitated dye was filtered, washed with water and dried. The dye was purified by TLC and column chromatography methods.

FTIR (cm^{-1}): 1408 (N=N str.), 1486 (C-N str.), 1403, 1556 (NO_2 str. sym. and unsym.), 1607, 1660 (C=O str. Carbonyl sym. and unsym.), 3427 (O-H str.); ^1H NMR (CDCl_3): δ (ppm) 1.98–2.07 (2H, CH_2), 3.35 (3H, OCH_3), 3.51–3.55 (2H, CH_2O), 4.25–4.30 (2H, NCH_2), 7.79–7.88 (2H, 6'-H, 6-H), 8.28 (1H, 2-H), 8.31–8.34 (1H, 5'-H), 8.66–8.7 (2H, 3'-H, 5-H), 9.02 (1H, 7-H), 16.78 (1H, OH); ^{13}C NMR (CDCl_3): δ (ppm) 22.7, 25.3, 38.5, 42.2, 63.1, 74.6, 93.2, 120.8, 127.4 (2C), 128.4, 129.7 (2C), 131.5, 137.9, 138.4, 142.2, 151.7, 154.6, 162.5, 168.1, 177.4; Yield = 64%, m.p = 202 °C, Mass: 516 m/z .

(iii) Dye 3

Diazotization of 6-chloro-4-fluorosulfonyl-2-nitroaniline was carried out with nitrosylsulphuric acid. For this purpose, 6-chloro-4-fluorosulfonyl-2-nitroaniline (10 mmol, 0.254 g) was dissolved in the solution of acetic acid and propionic acid (4:1, 50 mL) and then it was added to the solution of sodium nitrite (10 mmol, 0.07 g) and sulfuric acid (15 mL) at a temperature of 5–10 °C. The reaction mixture was stirred at this temperature for 3 hours. The obtained clear diazonium salt solution was used immediately in the coupling reaction. The pH of the diazonium salt solution was adjusted to 5–6 by adding sodium acetate solution. The diazotized 6-chloro-4-fluorosulfonyl-2-nitroaniline was added to a solution containing 10 mmol (0.285 g) of coupling component (4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide) in 20 mL of methoxy ethanol. After 13 hours the reaction was completed and the precipitated dye was fil-

tered, washed with water and dried. The dye was purified by TLC and column chromatography methods.

FTIR (cm^{-1}): 800 (C-Cl), 1420 (N=N str.), 1620, 1657 (C=O str. Carbonyl sym. and unsym.), 1409, 1531 (NO_2 str. sym. and unsym.), 3435 (O-H str.); ^1H NMR (CDCl_3): δ (ppm) 2.01–2.03 (2H, CH_2), 3.34 (3H, OCH_3), 3.55 (2H, CH_2O), 4.27–4.29 (2H, NCH_2), 7.79–7.82 (1H, 6-H), 8.26–8.31 (1H, 2-H), 8.67–8.72 (3H, 3'-H, 5'-H, 5-H), 9.03 (1H, 7-H), 16.78 (1H, OH); ^{13}C NMR (CDCl_3): δ (ppm) 20.4, 23.5, 36.2, 40.3, 61.4, 73.1, 91.9, 118.7, 125.2 (2C), 124.5, 128.6, 133.7, 132.9, 134.1, 137.2, 140.5, 149.8, 151.9, 160.1, 171.3, 175.8; Yield = 61%, m.p = 215 °C, Mass: 550 m/z .

(iv) Dye 4

4-Nitroaniline (10 mmol, 0.175 g) was diazotized in solution of hydrochloric acid (3.45 mL) and water (35 mL) and sodium nitrite (10 mmol, 0.07 g) at a temperature of 0–5 °C. The reaction mixture was stirred at this temperature for 30 min. The obtained clear diazonium salt solution was used immediately in the coupling reaction.

The diazotized 4-nitroaniline was added to a solution containing (10 mmol, 0.285 g) of coupling component (4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide) in 20 mL of methoxy ethanol. After 4–5 hours, the reaction was completed and the precipitated dye was filtered, washed with water and dried. The dye was purified by TLC and column chromatography methods. FTIR (cm^{-1}): 1395 (N=N str.), 1334–1497 (NO_2 str. sym. and unsym.), 1605–1653 (C=O str. Carbonyl sym. and unsym.), 3440 (OH str.); ^1H NMR (CDCl_3): δ (ppm): 2–2.07 (2H, CH_2), 3.35 (3H, OCH_3), 3.51–3.56 (2H, CH_2O), 4.25–4.3 (2H, NCH_2), 7.73–7.78 (1H, 6-H), 7.83–7.86 (2H, 3'-H, 5'-H), 8.4–8.47 (3H, 2'-H, 6'-H, 2-H), 8.65–8.69 (2H, 5-H, 7-H), 16.48 (1H, OH); ^{13}C NMR (CDCl_3): δ (ppm) 23.5, 27.1, 40.3, 43.7, 60.9, 72.7, 95.2, 121.4, 125.3 (2C), 128.6 (2C), 129.4 (2C), 135.1, 139.3, 150.2, 154.9, 157.1, 164.8, 173.6, 178.1. Yield = 65%, m.p = 225 °C, Mass: 434 m/z .

2.3. Instrumentation

The purified dyes and their corresponding intermediates were characterized by the following instruments:

1. FTIR measurements were carried out on a Bomem, Canada instrument (by the KBr method).
2. ^1H NMR and ^{13}C NMR measurements were carried out on a 300 MHz brucker instrument.
3. DSC thermal analyses were carried out on a DuPont 2000 DSC instrument.
4. UV-visible spectrophotometry was carried out on a

Cecil double beam transmission spectrophotometer. The λ_{\max} , ϵ_{\max} and solvatochromic effects were also determined.

5. Mass spectroscopy was carried out on an Agilent technology (hp), model 5973, Ion Source: electron impact 70 ev.

2.4. Application and dyeing properties

Polyester fabric (1 g) was pretreated with a nonionic detergent, (5 g/l) at 80 °C for 20 min prior to being used for dyeing. The samples were dyed in a rotadyer apparatus (Nasaj sanat yazd) using acetic acid (pH = 4-5) and L.G = 50:1. The build up properties of the synthesized dyes on polyester fabrics obtained by dyeing with dye dispersions were 0.1, 0.3, 0.5, 0.7, 1, 1.5, 2 and 4% (omf). Dyeing was carried out by raising the dye bath temperature from 30 °C to 90 °C at 2 °C/min, followed by 90 °C to 130 °C at 1 °C/min and keeping it at this temperature for 60 min and cooling to 70 °C at 3 °C/min.

Some of the dyed samples were reduction cleared using the solution of sodium hydrosulfite (2 g/l), sodium hydroxide (1 g/l) and detergent (1 g/l). Other samples were alkali cleared by utilizing sodium carbonate (20 g/l) and detergent (1 g/l) at liquor to goods ratio of 50:1 (Fig. 2).

The light fastness, wash fastness, rubbing and sublimation fastness of each dye was determined according to ISO 105/B, ISO 105/C, ISO 105-X12 and ISO 105 P01 standards, respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis of the diazo components

Preparations of the diazo components were carried out by the use of N-acetyl sulfanilyl chloride and then subsequent reactions such as fluorination, hydrolysis, nitration and chlorination were carried out respectively.⁵ The yields, melting points, FTIR and ¹H NMR spectra of the diazo components and coupling component are given in previous part.

The diazotization of 4-fluorosulfonylaniline was carried out with the hydrochloric acid and sodium nitrite, but the diazotization of its nitro and chloro derivatives were carried out with the aid of nitrosylsulphuric acid. The dissolution of sodium nitrite in concentrated sulphuric acid followed by slow addition of the given amine to the pre-

pared nitrosylsulphuric acid at below 10 °C until the diazonium salt was formed (note: at higher temperatures the diazonium salt of the series will decompose and nitrogen gas will be evolved).¹¹ However, basic strength of the amine will be reduced; due to the presence of nitro and chloro group in the aromatic amine derivatives, therefore, the reaction needs stronger NO⁺HSO₄⁻ group.

3.2. Synthesis of the coupling component (4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide)

Preparation of the coupling component was carried out by utilizing acenaphthene as a starting material and then subsequent processes such as sulfonation, oxidation, imidation and hydroxylation were carried out.¹⁰ The yield, melting point, FTIR and ¹H NMR of the 4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide is given in previous part.

Solution of the coupling component namely 4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide was prepared to which the diazonium salts were added gradually in acidic medium to yield different dyes (1-4). It is notable that dye 4 is made from diazotized p-nitroaniline coupled with the 4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide as a comparison sample. The yield percentage, DSC, FTIR, ¹H NMR, ¹³C NMR and Mass spectra of synthesized dyes are given in previous part.

3.3. Spectral Characteristics of the dyes

A colour-structure relationship plays a remarkably dominant role in producing the desirable dyes. In view of the commercial importance of producing dyes the relationship between colour and molecular structure is very important. Due to this matter dye manufacturers have a considerable interest in producing azo dyes.^{12,13} In this respect, the wavelength of maximum absorption (λ_{\max}), extinction coefficient (ϵ_{\max}) and half-band width ($\Delta\nu_{1/2}$) of dyes are all important. The λ_{\max} of the visible band indicates the hue of the dyes and the quantity of the intensity of the visible band is of economic importance as it is a measure of the strength of the dye. The ϵ_{\max} should be above ca. 20,000 l mol⁻¹cm⁻¹ for acceptable commercial purposes.¹

A series of dyes having different substituents were synthesized and the wavelength of maximum absorption and ϵ_{\max} of the dyes were measured in the chloroform solution. The dyes had hues from red to red-orange as given in Table 1.

All the synthesized dyes (1-4) have two λ_{\max} between



Fig. 2. Profile of reduction and alkali-clearing.

Table 1. The λ_{\max} and the ϵ_{\max} of the synthesized dyes in CHCl_3

Dye	Chloroform λ_{\max} (nm)	$\Delta\nu_{1/2}$ (nm)	ϵ_{\max} ($1 \text{ mol}^{-1} \text{cm}^{-1}$)
1	505.7	91	35480
	359.6		
2	507.5	100	37217
	374.0		
3	501.8	117	31038
	365.9		
4	513.6	104	36928
	364.2		

300-700 nm. In the UV range, there are only naphthalene bands, characteristic for simple naphthalene derivatives which are ascribed to the absorption of the benzeneazo-naphthalene (BAN) chromophore and in the visible range bands characteristic for azo dyes.¹⁴⁻¹⁷ The chromophore in the 340-375 nm range and in the visible range the K-band ($\pi \rightarrow \pi^*$ shifts) appears in the region 500-589 nm, characteristic for azo dyes.¹⁸ The present considerations are limited to a discussion of bands within 206-589 nm, where the known K and R bands ($n \rightarrow \pi^*$ shifts) appear and show characteristic changes depending on the solvent used.¹⁹

Introduction of the phenylazo chromophore into the 3-position of 1,8-naphthalimides results in a large bathochromic shift in the absorption maxima in chloroform (Table 1) compared with the usual yellow colour of 4-nitro-N-substituted-1,8-naphthalimides and the usual orange colour of 4-amino-N-substituted-1,8-naphthalimides.^{15,16}

The visible absorption maxima of several donor-substituted azobenzenes were considered²⁰ and it is clear that for a monosubstituted dye the bathochromic shift depends on the expected manner of the electron donating strength of the substituent. Since the electronic transition in these compounds involves a general migration of electron density from the donor group towards the azo group, it is not surprising that electron withdrawing groups in the diazonium component ring exert a bathochromic effect and electron donating groups in the coupling component ring exert a bathochromic effect.²⁰ It is found that the bathochromic shift in these series of disperse dyes is related roughly to the Hammett σ -constant for the electron withdrawing group.²⁰ Similar investigations have been carried out on naphthalimides series of disperse dyes.^{15,16,21}

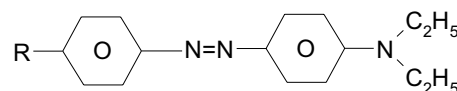
In the present study as illustrated in Fig. 1, the naphthalimide residue acts as a coupling component, due to having two withdrawing carbonyl groups which are weak donor groups and following the same lines of reasoning, the

mentioned dyes 1, 2, 3 and 4 have nearly the same λ_{\max} given in Table 1.

The hydroxyl group in the coupling component ring gives intramolecular hydrogen bond with the nitrogen in the β -position leading to the brightness in all synthesized dyes (Table 1).

Analogously substituted 4-aminoazobenzenes, e.g. structure I which ($R = \text{SO}_2\text{F}$), having λ_{\max} at 469 nm⁹ is still 36.7 nm, 38.5 nm, 32.8 nm and 44.6 nm more hypsochromic compared with dyes 1-4, respectively. Therefore, the effect of the naphthyl residue and the carbonyl groups are apparent and the dyes 1-4 are bathochromic with respect to the analogous aminoazobenzenes I.

Structure I



3.4. Investigation of the solvatochromic effects

The spectrophotometric properties of the prepared alkali-clearable disperse dyes in various solvents were examined.

The λ_{\max} shifts of the prepared dyes in various solvents are brought about by the solvatochromic effect resulting from changes in the dielectric constant of the solvent ($\pi \rightarrow \pi^*$ transition) (Table 2).²

Solvent-solute interactions can have various influences on an absorption spectrum. Thus the position and intensity of a band may vary, as may the band width. In many dyes, however, the ground state is less polar than the excited state, thus a polar solvent will tend to stabilize the excited state more than the ground state, giving rise to a bathochromic shift.²⁰

Solvatochromic effects of the synthesized dyes in different solvents such as toluene, DMF and chloroform were measured. The results indicated that the λ_{\max} in the toluene solvent is 4-6 nm more than chloroform solvent (Table 2).

A considerable change was observed in changing the polarity of the solvents from toluene to DMF; these changes are 58.8 nm, 96 nm, 79.2 nm and 73 nm for the dyes 1-4 respectively. The most change is ascribed to the dye 2 and the least change is ascribed to the dye 1 (Table 2). These observations are in accord to the other results.^{15,16,21-25} In all cases, positive solvatochromic effect is observed from the changing solvent polarity.

Table 2. The λ_{\max} of the synthesized dyes in the different solvents

Dye	Chloroform (nm)	DMF (nm)	Toluene (nm)
1	505.7	569.9	511.1
2	507.5	607.4	511.4
3	501.8	586.7	507.5
4	513.6	588.5	515.5

3.5. Investigation of the dyeing of polyester fabric

The prepared dyes were subsequently dyed on polyester fabrics and finally their optical and dyeing properties, light fastness, wash fastness and sublimation fastness were determined. The synthesized dyes were applied to polyester fabric by the high temperature dyeing method. The results showed that the dyeings were red-yellow to red-blue and the colour of naphthalimide dyes depends on the delocalization of electrons through the conjugated azo chromophore. The leveling properties of the dyes were very good. The fastness properties on the polyester fabric showed that the dyes 1 and 4 have very good light fastness, and the dyes 2 and 3 have moderate light fastness (Table 3). The sublimation fastness of all dyes was excellent. The naphthalimide derivatives show exceptionally excellent thermal stability and their dyeings have good fastness properties.^{15,16,23,24} These dyes tended to undergo association in the crystalline state which was confirmed by their IR spectra and high melting points.²³ This propensity for association provides dyes with good thermal stability as reflected in the sublimation fastness of the dyes. The light fastness, wash fastness and sublimation fastness of all dyes are shown in Table 3.

Wash fastness evaluation of the dyeings on polyester fabrics showed that uncleared samples possess relatively low wash fastness. In comparison to the uncleared samples both alkali-cleared and reduction-cleared samples have an increase in wash fastness (except dye 4). This case indicates that the dyes containing of fluorosulfonyl group is converted to a water soluble sulfonate group by alkali-hydrolysis (Fig. 3) and can be easily washed-off. Thus, the

Table 3. Fastness properties of the synthesized dyes

Dye	Wash fastness ^a			L.F	S.F (180 °C)
	None	Alkali-clearing	Reduction-clearing		
1	3	5	5	6	5
2	3-4	4-5	4-5	4	5
3	4	4-5	4-5	3-4	5
4	2	2-3	5	7	5

^a Staining on cotton, L.F: Light fastness, S.F: Sublimation fastness

wash fastness will increase, and the reduction-cleared can be replaced by the alkali-cleared.

4. CONCLUSION

A novel series of naphthalimide-based alkali-clearable azo disperse dyes containing a fluorosulfonyl group has been prepared by using 4-fluorosulfonylaniline, 4-fluorosulfonyl-2-nitroaniline and 6-chloro-4-fluorosulfonyl-2-nitroaniline as the diazo components and 4-hydroxy-N-3-methoxypropyl-1,8-naphthalimide constituted the coupling component. The diazo components were synthesized from N-acetylsulfanilyl chloride, and then subsequent processes such as fluorination, hydrolysis, nitration and chlorination were carried out. The coupling component was prepared from acenaphthene as a starting material and then subsequent reaction such as sulfonation, oxidation, imidation and hydroxylation were carried out. Diazotization and coupling reactions were carried out in order to obtain the final dyes. Maximal yields were sought after and the reaction conditions were varied accordingly.

The final dyes were recrystallised in order to be attained in a purified form. The obtained dyes and their corresponding intermediates were characterized by the use of DSC, FTIR, ¹H NMR, ¹³C NMR, UV-visible and Mass spectroscopic techniques.

Spectrophotometric investigations of the prepared dyes in different solvents were carried out in order to obtain their absorption maxima, intensities and solvatochromic

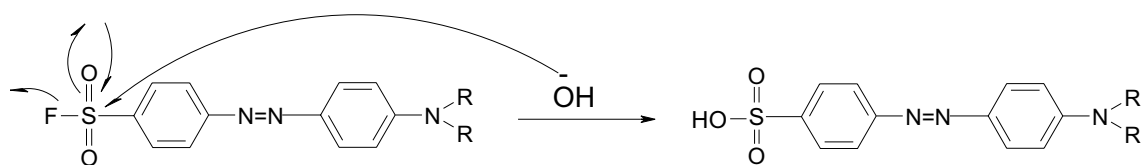


Fig. 3. The reaction mechanism of hydrolysis of dyes in alkali medium.

effects. The dyes were finally dyed on polyester fabrics in order to investigate their dyeing properties and the obtainable colour gamut.

The aim of preparing azo disperse alkali-cleared dyes incorporating fluorosulfonyl group was to convert them under relatively mild alkaline conditions and temperature to the dyes containing a water-soluble sulfonate group without breaking the azo bond.

The use of fluorosulfonyl group in these types of disperse dyes shows a desirable build up, excellent wash fastness and offers the selection of alkali clearance to obtain high wash fastness, displacing reductive clearing and elimination sodium hydrosulfite, which has a very high BOD on conventional disperse dyeing wastewater and generates aromatic amines.

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