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Short communication

Synthesis and characterisation of crown ether based azo dyes

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Abstract

Five new azo dyes derived from *trans*-diaminodibenzo-18-crown-6-ether have been synthesised. The physico-chemical properties and the application of these dyes on cotton fiber are discussed, and results from dye evaluations in paints and inks are presented. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Crown ethers; Azo dyes; Physico-chemical properties

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1. Introduction

Macrocyclic compounds are commonly used in phase transfer reactions, biomimetic studies, and as specific and selective complexing agents for metals. Recently, crown ether derivatives with ethereal or anionic groups on the periphery of the macrocycles have been developed, in order to increase metal selectivity and complex stability in analytical and separation methods as well as in biological membranes [1–7].

Several workers have reported modified crown ethers with chromogenic groups [8–11] and it is known that varying the size of the crown ether ring or the chromophoric side arm can modify the properties of these compounds. Such changes produce agents with different sensitivities and selectivities for metal ions, including crown ether based dyes possessing a potential anionic site attached to the chromophore [12]. These structures form intermolecular ion-pair complexes with various metal cations [12]. Other types of crown ether dyes are those that do not contain ionic groups in the vicinity of the chromophore. The color value of both types of crown ether dyes is influenced considerably by the size of the crown ether cavity, the complexed metal cations, and the charge density of the cation. Thus, crown ether derivatives bearing chromophores are promising analytical reagents for colorimetry and metal ion indicators.

Considerable attention has been focused on crown ether dyes containing a chromophore such as picrylamine (**I**; Fig. 1) [13,14] that can be used for photometric determination of alkali and alkaline earth metal ions. Azo dyes such as the *p*-dimethylaniline-based crown dyes (**II**; Fig. 1) [15–19] have also been employed for complexing alkali and alkaline earth metal ions. Generally, dyes with styryl functional groups (cf. **III**) exhibit *cis–trans* photoisomerization [20,21]. The synthesis of crown ether based azo dyes in which an aniline derivative was diazotized and coupled with a phenol residue in a crown ether moiety (cf. **IV**) has also been reported [22]. In other studies, Shinkai and coworkers have synthesized a variety of bis-(crown

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ethers) made by connecting two benzo crown ethers through an azo linkage (cf. **V**) [23].

While chromogenic crown ethers have been used for molecular recognition of alkali and alkaline earth metals, no work has been reported on the use of crown ether-based dyes as dyeing and pigmenting agents. With the latter point in mind, the present investigation pertains to dibenzo-18-crown-6 dyes as organic colourants.

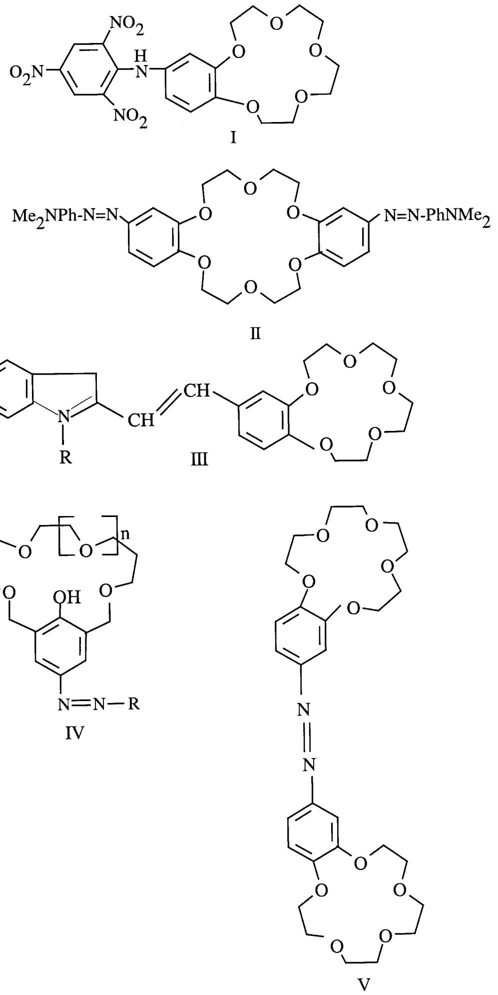

Fig. 1. Crown dyes.

2. Experimental

2.1. General

All chemicals used were obtained from Merck (India) or BDH Company (London) unless otherwise specified. Raney nickel catalyst type W-2 was prepared by the method of Mozingo [24]. DMF was purified under reduced pressure according to method of Weissberger [25].

N.P.L. certified grade A graduated apparatus (pipettes, volumetric flasks) were used for volume measurements. Melting points were determined on a Kfler melting point apparatus and are uncorrected. Elemental analysis was carried out on a 1106 analyzer, FT–IR spectra were recorded on a JASCO 410 FT–IR spectrophotometer as KBr pellets, visible spectra were recorded on a Hitachi U-3210 UV–visible spectrophotometer, and ESI mass spectra were recorded on a Micromass Quattro 2 triple quadruple mass spectrometer. The ESI capillary was 3.5 KV, the cone voltage was 25–50 V, and the flow rate was 0.4 ml/h. Proton NMR spectra were recorded on a 300 MHz Varian T-60 spectrophotometer in DMSO-d_6 with TMS as the internal standard.

Homogeneous paint and ink formulations were prepared using a Marshal MV614 Vibroshaker. The resultant formulations were applied to gloose paper using a Marshal automatic film applicator. The reflectance of the dyed material was measured using an Elico CL-26 reflectance meter.

2.2. Synthesis

Bis(2-chloroethyl)ether (**VII**) was synthesised from diethylene glycol (**VI**) [26] and dibenzo-18-crown-6-ether (**IX**) was synthesised from catechol (**VIII**) and bis(2-chloroethyl)ether (**VII**) [27]. Nitration of (IX) gave the corresponding "*cis*" (**Xa**) and "*trans*" (**Xb**) isomers. The "*trans*" isomer (**Xb**) was insoluble in the reaction mixture and could be removed by filtration, while the "*cis*" isomer was isolated by evaporation of the filtrate with the aid of a rotatory evaporator [28]. The "*trans*" isomer was used for the present study.

2.2.1. *trans-Diaminodibenzo-18-crown-6 (XI)*

A mixture of *trans* **Xb** (0.99 g, 2.2 mmol), Raney nickel (1.5 g) and anhydrous ethanol (100 ml) was stirred under reflux as hydrazine hydrate (0.40 g, 8.0 mmol) was added over 20 min. The reflux was continued for 2 h to ensure complete removal of ammonia and the mixture was filtered hot to recover the catalyst. Excess solvent was removed under reduced pressure and on cooling, 0.51 g (60%) product was obtained as a white solid, mp 197–203 °C [28].

*2.2.2. Synthesis of crown ether dyes **VII***

Compound **XI** (1.95 g, 5 mmol) was suspended in an HCl (70 ml, 4.5 M) and the mixture was cooled to −5 °C. Cold NaNO$_2$ (10 ml, 1.2 mmol) was added dropwise and the reaction mixture was stirred for 20 min. Residual HNO$_2$ was destroyed by adding *n*-hexylamine and the reaction mixture was further stirred for 15 mm. The resultant solution was added over 15 min to aqueous solution of 0.01 mol β-naphthol, resorcinol, 8-amino-l-naphthol-3,6-disulfonic acid (H acid), 7-amino-1-naphthol-3-sulfonic acid (gamma acid), or 8-amino-1-naphthol-3,5-disulfonic acid (K acid) in NaOH (150 ml, 2 M) at −5 °C [29]. Each reaction mixture was adjusted to pH 8 using HC1 (0.1 M), stirred for 40 min, adjusted to pH 6.5–7.0 with HCl (0.1 M) and stirred for 5 h.

For **XIIa** and **XIIb**, the precipitates were collected by filtration, washed with cold water, and dried in vacuo, while dyes **XIIc–e** were obtained by salting out with NaC1 (100 ml, 40%).

*2.2.2.1. 4,4′-Bis(2-hydroxynaphthylazo)-2,3,11,12-dibenzo-1,4,7,10,13,16-hexa-oxacyclooctadeca-2,11-diene (**XIIa**).* Orange powder; mp 260 °C; λ_{max} 472 nm (DMF); IR (KBr) 3400 (O–H), 1355 (C–N), 1110 (C–OC), and 1595 cm^{-1} (aromatic nuclei); ^{1}H NMR (DMSO-d_6) δ 7.4 (18H, *m*, Ar–H), 8.7 (2H, *s*, OH), 4.1 (16H, *t*, OCH$_2$CH$_2$O); ^{13}C NMR (DMSO-d_6) δ 67.9, 68.9, 133.4, 116.4, 103.4, 144.0, 103.3, 137.0, 119.0, 128.1, 126.3, 124.9; ESI MS (*m/z*) 701 (M + 1), 684, 670, 542, 418, 404, 390, 375,362, 183, 166, 138, 110.

*2.2.2.2. 4,4′-Bis(2, 4-dihydroxyphenylazo)-2, 3,11, 12-dibenzo-1,4, 7,10,13,16-hexa-oxacyclo-octadeca-2,11-diene (**XIIb**).* Reddish yellow powder; mp 210 °C *d*; λ_{max} 435 nm (DMF); IR (KBr) 3400 (O–H), 1355 (C–N), 1115 (C–O–C), 1600 cm^1 (aromatic-nuclei); ^{1}H NMR (DM50-d_6) δ; 7.0 (12H, *m*, Ar–H),8.07 (4H, *s*, OH), 4.0 (16H, *t*, OCH$_2$CH$_2$O); ^{13}C NMR (DMSO-d_6) δ; 148.8, 145.2, 132.3, 118.2, 103.4, 103.0, 69.0, 68.2; ESI MS (*m/z*) 633 (M + 1), 568, 495, 403, 390, 362, 181, 166, 138, 124, 114.

*2.2.2.3. 4,4′-Bis(l-hydroxy-8-amino-3,6-disulfo-2-naphthylazo)-2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclo-octadeca-2,11-diene (**XIIc**).* Violet powder; mp > 300 °C *d*; λ_{max} 550 nm (DMF); IR (KBr) 3400 (O–H), 1355 (C–N), 3250 (N–H), 1110 (O–C–O), 1610 cm^1 (aromatic nuclei); ^{1}H NMR (DMSO-d_6) δ 7.2 (12H, *m*, Ar–H), 7.88 (2H, *s*, OH), 3.40 (4H, *s*, NH$_2$), 3.9 (16H, *t*, OCH$_2$CH$_2$O); ^{13}C NMR (DMSO-d_6) δ 148.2, 145.2, 143.3, 137.1, 136.9, 133.0, 128.4, 122.0, 113.5, 111.7, 108.6, 101.3, 68.7, 67.3; ESI MS (*m/z*) 1138 (M +), 1106, 1077, 974, 872, 770, 671, 543, 419, 403, 390, 375, 362, 183, 166, 138, 124, 110.

*2.2.2.4. 4,4′-Bis(l-hydroxy-7-amino-3-sulfo-2-naphsylazo)-2,3,11,12-dibenzo-1,4,-7,10,13,16-hexaoxacyclo-octadeca-2,11-diene (**XIId**).* Reddish brown powder; mp > 300 °C δ; λ_{max} 545 nm (DMF); IR (KBr) 3450 (O–H), 1355 (C–N), 1100 (O–C–O), 3250 (N–H), 1600 cm^1 (aromatic nuclei); ^{1}H NMR (DMSO-d_6) δ; 7.5 (14H, *m*, Ar–H), 8.4 (2H, *s*, OH), 4.16 (16H, t, OCH$_2$CH$_2$O), 3.43 (4H, *s*, NH$_2$); ^{13}C NMR (DMSO-d_5) δ; 146.9, 146.1, 141.3, 139.4, 132.3, 129.3, 128.5, 117.2, 115.7, 111.9, 107.4, 102.4, 68.7, 67.6; ESI MS (*m/z*) 934 (M +), 832, 730, 715, 684, 668, 557, 543, 418, 404, 390, 375, 362, 183, 166, 138, 124, 110.

*2.2.2.5. 4,4′-Bis(l-hydroxy-8-amino-3,5-disulfo-2-naphthylazo)-2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclo-octadeca-2,11-diene (**XIIe**).* Yellowish orange powder; mp > 300 °C *d*; λ_{max} 390 nm (DMF); IR (KBr) 3450 (O–H), 1355 (CN), 1100 (C–O–C), 3250 (N–H), and 1600 cm^1 (aromatic nuclei); ^{1}H NMR (DMSO-d_6) δ 7.0 (12H, *m*, Ar–H), 9.15 (2H, *s*, OH), 4.08 (16H, *t*, OCH$_2$CH$_2$O), 3.44 (4H, *s*, NH$_2$); ^{13}C NMR (DMSO-d_6) δ 151.0, 146.0, 144.1, 141.0, 134.0, 132.5, 127.5, 124.1, 111.6, 108.9, 102.0, 68.8, 67.1; ESI MS (*m/z*) 1138 (M +), 974, 872, 770, 671, 541, 418, 404, 391, 375, 362, 183, 166, 138, 124, 110.

2.3. Preparation of paint formulations

To a mixture of dye (2 g) and TiO_2 (7.5 g) in a vibroshaker container, polyepoxy resin (30 g), mineral turpentine oil (20%, w/w) and glass beads (7.5 g) were added, and the mixture was shaken for 1 h. The resultant mixture was transferred to gloose paper via an auto applicator using rod No. 2. The paint draw-down was allowed to dry for 3–4 h at 35 °C.

2.4. Preparation of inks

To a mixture of dye (1 g) and polyamide resin (25 g) in a vibroshaker container was added toluene (50 ml) and glass beads (80 g) and the mixture was shaken for 20 min. The resultant ink was transferred to gloose paper via an auto applicator, using rod No. 2, and then allowed to dry for 3–5 min at 35 °C.

2.5. Pigment studies

2.5.1. Light fastness

Light fastness testing was performed in a chamber containing a carbon arc light source. The colored gloose papers were exposed for 10 h and the colour stability of the particular pigment was rated against unexposed samples according to a standard test method [30].

2.5.2. Opacity

The opacity of the dye layers was determined by applying ink formulations to a substrate with different coloured patches. The patches consisted of black stripes on a white background or a combination of commonly used white with black stripes or brown with grey stripes [31]. The opacity was greatest when the layer of test colorant just effectively masked visual differences in colour between the different coloured stripes on the substrate surface.

2.5.3. Dispersibility, brightness, texture

These properties were assessed using a published method [31]. In this regard, texture was the measure of smoothness of the applied pigment formulation on gloose paper.

2.6. Scouring of cotton

A cotton hank (3.5 g) was added to a solution of NaOH (2 g) and common detergent (2 g) in water (200 ml) and the whole was boiled for 3 h. The cooled hank was washed thoroughly with water to remove residual NaOH and detergent and dried (35 °C).

2.7. Dyeing of cotton

The water-soluble dyes **XIIc–XIId** (0.25 g) were added to water (35 ml) and the solutions were heated to 50 °C. The scoured cotton hanks (3.5 g) were added to the dye baths and dyed at 90 °C for about 15 min. After cooling the baths to room temperature the dyed hanks were rinsed with cold water and dried (35 °C).

2.8. Fastness testing involving dyed cotton

2.8.1. Wetfastness [32]

Pairs of dyed and undyed cotton hanks were immersed together in water for 30 min, drained and placed in a perspirometer. The hanks in each pair were dried separately and the change in colour of the dyed hanks and the staining of the undyed hanks were assessed by means of the standard grey scale, where a rating of 5 is excellent and 1 is poor.

2.8.2. Wash fastness [32]

The dyed hanks were divided into two groups. The resultant groups were combined with the corresponding number of undyed cotton or wool hanks, added to aq. detergent solution (0.5%), and agitated for 30 mm at 40–45 °C. The samples were removed, rinsed three times with water and then dried by pressing with a warm iron. Change in colour of the dyed samples and staining of the undyed samples were assessed using the standard gray scale, where a rating of 5 is excellent and 1 is poor.

2.8.3. Perspiration fastness [32]

Acidic and alkaline solutions were used in this test. Each litre of solution contained NaC1 (10 g) and Na_2HPO_4 (1 g). The acidic solution (pH

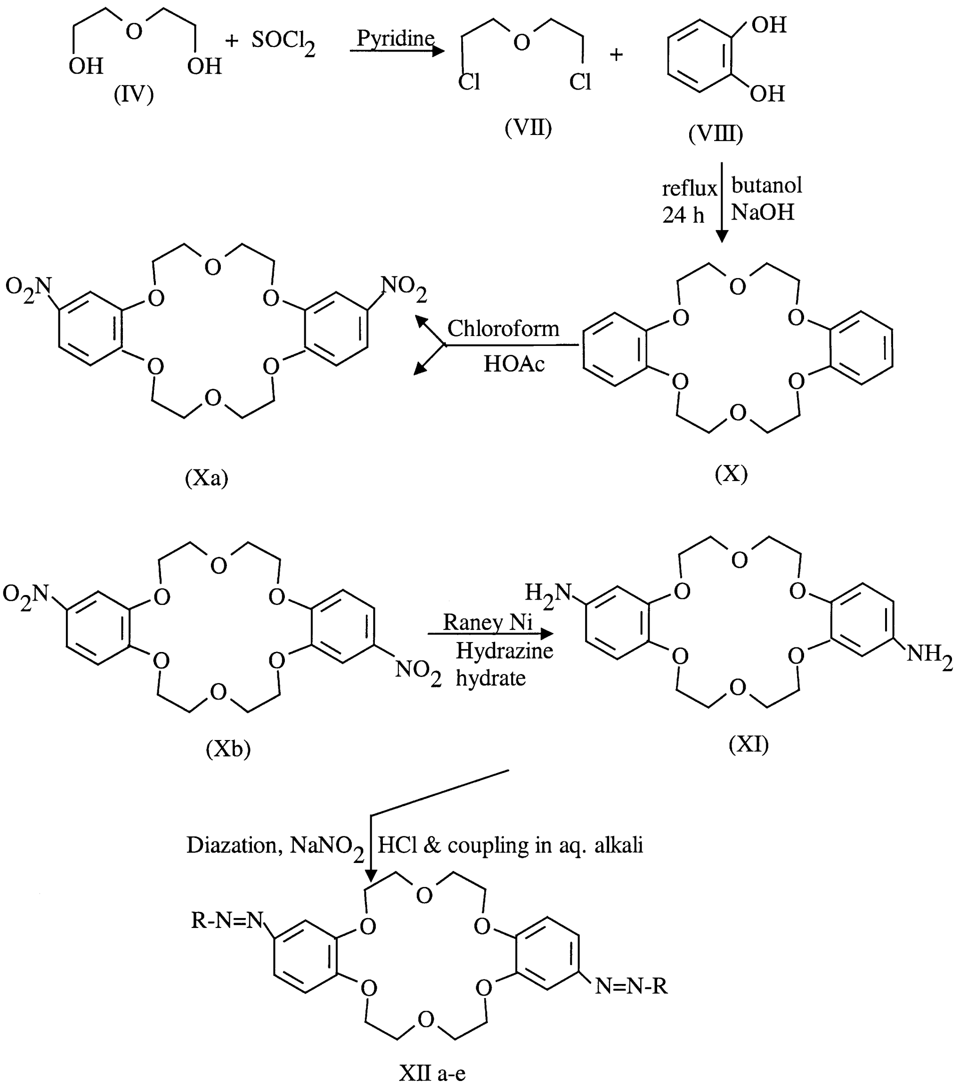

Fig. 2. Synthetic scheme for crown ether-based dyes.

5) also contained lactic acid (1 g) and the alkaline solution (pH 8) had $(NH_4)_2CO_3$ (4 g). Testing was carried out in glass test tubes placed in a drying oven at 38–40 °C. The test samples consisted of a piece of dyed knitted hank rolled together with an undyed hank in such a way that the role just fit into the tubes. Four tests corresponding to grades 1–4 differed only in the time of treatment: 40 min, 2, 6 and 16 h. The dyed and undyed samples were thoroughly wetted with the acidic or alkaline media and inserted in a glass tube, with one-third of the roll remaining outside the tube. Colour change and staining were assessed.

2.8.4. Light fastness [32]

The dyed cotton samples and wool standard were exposed to light in a Xenotest weathering machine for 10 h at 30 °C. The samples were then evaluated for colour loss using the standard grey scale, where a rating of 8 is excellent and 1 is poor.

3. Results and discussion

3.1. Synthesis and analyses

The crown ether-based azo dyes were synthesized according to Fig. 2. This route includes a modified approach to the synthesis of *trans* diamino-dibenzo-18-crown-6 (**XI**) using hydrazine hydrate and Raney nickel, which gave a better yield (60%) than that previously reported (50%) [28].

NMR analysis of **XI** showed a strong singlet at δ 3.25 [33], which was absent in the spectrum of *trans* dinitrodibenzo-18-crown-6 (**Xb**). The IR spectrum of **XI** showed a band for the NH_2 group at 3200–3000 cm^{-1}, which was also absent in the spectrum of **Xb**.

All dyes are readily soluble in DMF and DMSO, and sparingly soluble in organic solvents viz., ethanol, methanol, acetone, and benzene. Dyes **XIIc**, **XIId**, and **XIIe** were soluble or sparingly soluble in water. The colours of our dyes varied from orange to brown.

Table 1
Characteristic properties of crown dyes in paints[a]

Properties	Crown dyes				
	XIIa	**XIIb**	**XIIc**	**XIId**	**XIIe**
Dispersibility	8	5	5	8	ND
Light fastness	8	8	8	8	ND
Texture	5	5	8	8	ND
Opacity	3	5	3	5	ND
Brightness	8	3	8	8	ND

ND, not dispersible.

[a] Rating scale = 1 (poor)–8 (excellent).

Table 2
Characteristic properties of crown dyes in ink[a]

Properties	Crown dyes				
	XIIa	**XIIb**	**XIIc**	**XIId**	**XIIe**
Dispersibility	8	5	8	8	ND
Light fastness	8	8	8	8	ND
Texture	5	5	8	8	ND
Opacity	3	3	3	8	ND
Brightness	5	5	8	8	ND

ND, not dispersible.

[a] Rating scale = 1 (poor)–8 (excellent).

3.2. Paint and ink properties

The properties of the dyes in paint and ink formulations are summarised in Tables 1 and 2. The data reveal that the paint prepared using dye **XIId** was better than that containing dyes **XIIa** and **XIIb**, and that dye **XIIe** was not suitable in paint formulations since it would not disperse well. Dyes **XIIc** and **XIId** were better for inks than **XIIa,** and **XIIb** was not suitable due to poor opacity.

3.3. Dyeing and fastness properties

Only the water-soluble dyes **XIIc–e** were used for dyeing cotton, the most suitable fiber for our application. Figs. 3 and 4 show the effects of dye concentration, salt and pH on shade. The results in Fig. 3 show that increasing dye bath concentration

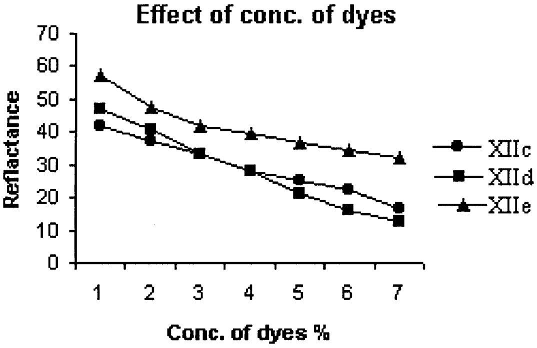

Fig. 3. Effect of dye concentration on reflectance.

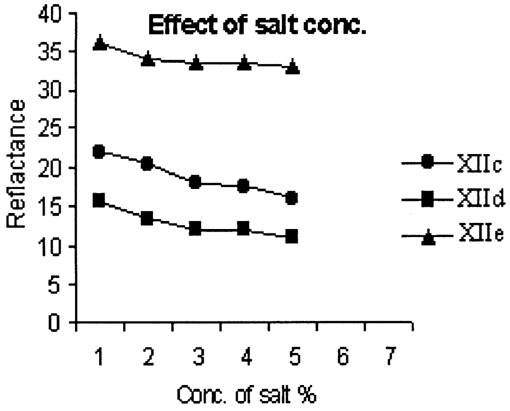

Fig. 4. Effect of salt concentration on reflectance.

Table 3
Fastness of dyes[a]

Dye	Water			Washing			Acid perspiration			Alkaline perspiration			Light fastness
	Alteration in shade of dyed fabric	Degree of staining of undyed		Alteration in shade of dyed fabric	Degree of staining of undyed		Alteration in shade of dyed fabric	Degree of staining of undyed		Alteration in shade of dyed fabric	Degree of staining of undyed		
		Cotton	Wool		Cotton	Wool		Cotton	Wool		Cotton	Wool	
XIIc	4	4	4	4	3–4	4	4	4	4	4	4	4	5–6
XIId	4	4	4–5	4	3–4	4	4	4	4–5	4	4	4–5	5–6
XIIe	4	4–5	4–5	4	4	4–5	4	4–5	4–5	4	4–5	4–5	5–6

[a] Rating scale = 1 (poor)–8 (excellent).

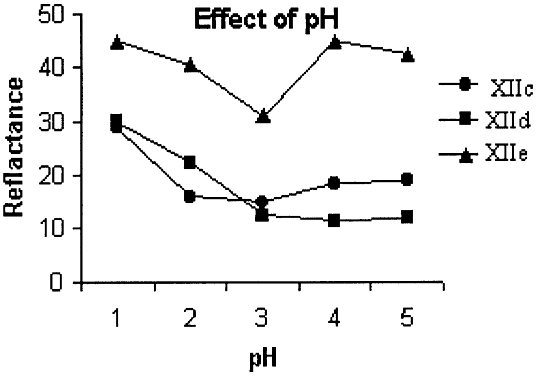

Fig. 5. Effect of pH on reflectance.

from 0.1 to 0.7% gave a corresponding increase in colour strength on the fiber, indicating that the dyes build well on cotton.

When the salt concentration was varied from 1.0 to 5.0% it was clear that salt concentration above 3% did not have much of an effect on shade depth (Fig. 4). When cotton was dyed at pH 3–10.5 the results summarised in Fig. 5 indicate that dyeing was unsatisfactory at acidic pH levels and at pH >7. As would be expected optimum shade depths were obtained at pH 7. This assures that the basic and acidic groups in the dye structures are not in their ionic forms, which increases water solubility and decreases exhaustion.

The fastness of the dyed yarns to washing, water, and perspiration are summarised in Table 3. The light fastness ratings on cotton were at the 5–6 levels. The results also show that fastness to water, washing, and perspiration were at level 4, indicating a noticeable alteration in shade depths. Similar results were obtained in the case of staining of undyed fibers, as the ratings were at the 3–4 levels.

Acknowledgements

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