Synthesis and Studies of Some Disperse Dyes Derived from 5-Pyrazolone-3-methyl-1-(*m*-nitrophenyl)

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Summary: The synthesis of a series of disperse dyes derived from 5 –pyrazolone-3-methyl-1-(m-nitrophenyl) is described. The colour fastness of these dyes to washing, dry-heat and to artificial light (Xenon arc fading lamp) are reported and found to depend on the influence of the substituents on the electron density around the azo-group. The visible absorption spectra of all the dyes showed that the colours of these dyes lie in the range of yellow – orange – red.

Introduction

The first azo dye of the pyrazolone series, tartrazine was made by Ziegier in 1884 by condensation of phenylhydrazine with a β-Ketone ester. Disperse dyes were initially developed for dyeing of cellulose acetate fiber (first regenerated cellulose fiber) during the first world war [1]. Dyestuffs commonly known at that time were unable to dye this newly invented fiber. The primary reason being compactness of structure (due to acetylated methylol group of parent cellulose residue) resulting in hydrophobicity and execessive repulsion of negative acetyl group with similar charged dyes. Trials were thereafter conducted to dye the fiber from aqueous dispersion of disperse dyes (i.e.simple amino and phenol azo derivatives, without any solublizing group) at 80 – 85^{0}C. The results of these trials were quite encouraging and the fiber was found to readily absorb these dyes [2]. Later on these dyestuffs enjoyed extensive utilization in dyeing of other synthetic fibers specially polyester. In polyester fiber, the compactness/hydrophobicity is even more than that of cellulose acetate. It is due to extensive orientation of the liner polymers employed during spinning of the fiber. Moreover the hydrogen bonding between the polymeric fibre hinders the dye penetration in the polyester fabric. In this context, the suitable disperse dyes are applied only via structural modification (i.e. swelling) of fiber either by temperature alone (thermosole dyeing process at 180 to 200°C) or by both pressure and temperature (high temperature dyeing at 130°C). The dye itself slips molecule by molecule through narrow pores in the fibre, and then attaches itself to the fibre by non-polar Van-der Waal forces, also acting as dispersion force. This phenomenon occurs between the hydrophobic surface of the dye and of the fibre and factors like larger fibre area and lesser distance between the fibre and the dyes enhance the effect of Van der Waal dispersion forces.

These factors also positively contribute in dislodging water molecules associated with the fibre chain by the dye molecule [3,4].

Disperse dyes from aryl diazoniums coupled to 5-amino-3-alkyl-(aryl)-pyrazoles give yellow to scarlet shades on polyester. In general the presence of chlorine, bromine and electron withdrawing groups

Science is the hub of modern life. The aim and object of science is to reduce human suffering and pain. It has made our lives comfortable, easy and beautiful. In fact science has confirmed great booms of mankind. Scientists are the greatest benefactors of humanity.

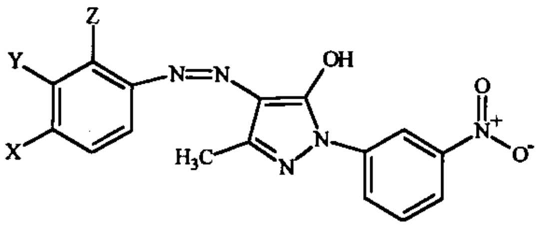
Our honorable Minister for Science and Technology Prof. Dr. Atta-ur-Rahman is one of the most distinguished member of our community of scientists. Every nation has produced great men. They are great by their work or deeds. Our nation has produced Prof. Dr. Atta-ur-Rahman, a great scientist, a man of superhuman qualities, who has done so much outstanding and marvelous work for our country.

He is the author of several internationally acclaimed books and hundreds of papers in prestigious international scientific journals. In the light of hid dedicated services for our country, Govt. of Pakistan has bestowed several honours and awards to him.

We want to dedicate our research paper, a meager attempt for the cause of science and technology, to Honourable Prof. Dr. Atta-ur-Rahman, due to his selfless and dedicated services for the cause of science, technology and education in our developing country. We further heartily congratulate Dr. Saheb on the happy occasion of his 60th birthday. May Allah Almighty bestow him a long and happy life.

Tanzil Haider Usmani and all the co-authors such as NO_2 and CN in diazo component tends to cause a shift of λ_{max} absorption towards the longer wavelength (bathochromic effect). [5]. This effect is enhanced and further intensified by variations in nuclear substituents and non-nuclear substituents attached to nitrogen. Many authors have described the effect of certain functional groups in the fastness properties of disperse dyes. D. Marion indicated that the presence of certain groups such as – OH, - $CONH_2$, - SO_2N, ON, O-Alkyl in the dye nucleus confer affinity and fastness properties on disperse dye-fibre combinations [6].

In the present work, studies are made on certain disperse dyes in which aryl diazoniums were coupled with –5-pyrazolone-3-methyl-1-(m-nitrophenyl). The work depicted in this study describes the synthesis of some monoazo dyes of general structure shown in Scheme-1 used as disperse dyes, and evaluation of their fastness properties on polyester fibres.



i). 1a =X = NO_2, Y=Z=H
ii). 1b=X=Y=H, Z=NO_2
iii). 1c=X=Z=H, Y=NO_2
iv). 2a=X=Y=H, Z=OH
v). 2b=X=OH, Y=Z=H
vi). 2c=X=Z=H, Y=OH
vii). 3a=X=Y=H, Z=OCH_3
viii). 3b=X=Z=H, Y=OCH_3
ix). 3c=X=OCH_2, Y=Z=H

Scheme-1:

The conventional structure of dyes containing pyrazolone.

Results and Discussion

Disperse dyes (1a-3c) were obtained by coupling the appropriate diazonium ion with 5-pyrazolone –3-methyl –1- (m-nitrophenyl), purified and their λ_{max} in visible regions were determined. The data presented in Table-I, shows the effect of

Table–1:Data on characterization of disperse dyes prepared from 5-pyranzolone –3- methyl –1- (m-nitrophenyl)

Sample Code	Mol. Formula	M.P [^{0}C]	Mol. wt.	% Yield
1 a	$C_{16}H_{12}N_6O_5$	214	368	92
1 b	$C_{16}H_{12}N_6O_5$	148 – 150	368	74
1 c	$C_{16}H_{12}N_6O_5$	126 – 128	368	83
2 a	$C_{16}H_{13}N_5O_4$	150 – 152	339	62
2 b	$C_{16}H_{13}N_5O_4$	216	339	48
2 c	$C_{16}H_{13}N_5O_4$	200 – 212	339	85
3 a	$C_{17}H_{15}N_5O_4$	178 – 180	353	68
3 b	$C_{17}H_{15}N_5O_4$	115 – 117	353	72
3 c	$C_{17}H_{15}N_5O_4$	140 – 142	353	89

subsituents in the diazo component and the absorption spectra of the dyes derived from 5-pyrazolone-3-methyl-1-(m-nitrophenyl). The higher absorbency of 1a as compared to 1b and 1c might be due to the electron withdrawing effect of $-NO_2$ group, which is more effective at para position, which results in quinonid structure. The relative stable resonance structure increases the absorbency, eventually resulting in bathochromic effect in the dye system.

The hydroxyl group at ortho position to azo-group of dye 2a causes effective activation of the benzene ring as compared to meta position (dye 2c), and thus results in higher absorbency.

The electron withdrawing effect of dye 3b is less than the negative induction effect of dye samples 3a and 3c, and this eventually leads to a comparative lesser de-activation of benzene ring and hence quite higher absorbency in sample 3b is observed. (Bathochromic shift).

Dyeing Mechanism

As disperse dyes are sparingly soluble in water, the absorption of dye into the substrate is somewhat different from common dyeing mechanism. The dyeing mechanism can be interpreted in two ways i.e. as these are applied from diluted dye liquor (due to little water solubility), hence the dyes greater part of the dye remains dispersed. As the adsorption of the dye molecules into the substrate proceeds, some more dye passes from dispersed phase into solublized phase to maintain an equilibrium concentration of the dye in the solution and on the fiber surface.

Another hypothesis elucidating this phenomenon explains the partition of solute between

Table – 2:Effect of Light, Washing and Dry Heat on Various Disperse Dyes Prepared from 5-Pyrazolone-3-methyl-1-(m-nitrophenyl)

Sample Code	λmax (n.m)	Absorbence	log ε	Fastness To Light	Fastness to Washing			Fastness to Dry Heat		
					Change in colour	Staining cotton	Staining polyester	Change in colour	Staining cotton	Staining polyester
1a	480	1.1	3.308	5	5	4-5	4-5	5	4-5	4-5
1b	500	0.5	2.301	4-5	4-5	4	4	4-5	4	3-4
1c	500	0.565	2.618	4	5	5	5	5	4-5	4
2a	500	1.8	3.00	4-5	5	5	5	4-5	4-5	4
2b	500	0.8	2.963	4	4-5	5	4-5	4	4	3-4
2c	500	1.35	3.206	5	4-5	5	5	4-5	4-5	4
3a	510	1.08	2.869	4-5	5	4-5	4	4-5	4	4
3b	500	1.3	2.856	3-4	4	4	4	4	3-4	3
3c	510	1.18	3.054	4-5	5	4-5	5	4-5	4	4

two-imiscible solvents. Disperse dyes being more soluble in substrate than water, henceforth the dyes make "solid solution" within the substrate under elevated temperature and pressure.

Dyeing Properties

The 100% polyester knitted fabric (Design-pique) was dyed with different disperse dyes shown in Scheme – 1, by using the dispersing agent lycol-0-.

All dyes exhibited very good level of dyeing on polyester fibre with a good build – up and all round fastness. The shades were generally bright and vary from yellow to light brown, depending on the nature of the substituent groups present in the diazo – components, as depicted in Table-2.

Table-2 details the properties of fastness to washing and to dry-heat of these dyes, and it shows that all the dyes have good fastness properties, which are in the range of 3-5. Light fastness properties of these dyes are also quite good and are in the range of 4-5, which depends on the influence of the substituents and it further changes the electron density around the azo-group.

Experimental

Synthesis of Dyes

The dyes were obtained by coupling the appropriate diazonium ion with 5-pyrazolone-3-methyl-1-(m-nitrophenyl). All the amines were diazotised in aqueous hydrochloric acid by conventional means [7,8] and then gradually added to a well stirred dispersion of 5-pyrazolone-3-methyl-1-(m-nitrophenyl) in weakly basic systems and are listed as 1a – 3c. The dyes were separated from the reaction mixture by filtration and then purified by dissolving them in a minimum quantity of chloroform. The melting points and λ_{max} of these dyes are presented in Table-1 & Table-2 respectively.

Dyeing and Fastness Properties

Polyester knitted fabric (Design-Pique) was dyed with different disperse dyes at a temperature of about 130°C using a dyeing machine by the following procedure: -Dyeing of 1% depth of each dye was carried out on 5 gm fabric at 130°C for 75 minutes, using high temperature dyeing bath containing 2 gm / l dispersing agent (lyocol-o), 3 ml/l acetic acid to maintain pH at 4.5 – 5.5 and fibre-liquor ratio of 1:20. After this period, the bath temperature was lowered and the specimens were removed from the dyeing bath and rinsed with cold water and finally dried at 60°C in an electric oven.

Reduction clearing was thereafter carried out in an aqueous solution of sodium hydrosulfite (2-3 gm/l) and sodium hydroxide (2 gm/l), using a fibre liquor ratio of 1:20 at 60°C for 10 minutes. Treated samples were then rinsed with water and dried.

Colour Fastness to Washing

The colour fastness of polyester specimens, dyed with different samples of disperse dyes to washing, was carried out by ISO-PO5 Standard Procedure [9]. Each specimen of polyester fabric (6cm x 5cm) in contact with specified cotton fabric was mechanically agitated under specified conditions of time and temperature in a soap solution and then rinsed and dried. The change in colour of specimen and staining of the adjacent fabric were assessed with the Grey scale. The results are being summarized in Table-2.

Colour Fastness to Dry-heat

The fastness to dry heat (excluding pressing) of polyester sample, dyed with different disperse dyes, was carried out by ISO-PO1 Standard Procedure [9]. The composite specimen (8 cm x 4 cm) in contact with specified adjacent fabric was heated in close contact with a medium at a temperature of 210°C for 30 seconds. The change in colour of the test specimen and the staining of the adjacent fabric were assessed with the grey scale and the results are presented in Table-2.

Colour fastness to Artificial Light (Xenon Arc Fading Lamp Test):

The colour fastness to artificial light of the various specimens dyed with different disperse dyes, was carried out by ISO-BO2 Standard Procedure [9]. The test specimen of the dyed polyester fabric was exposed to artificial light (Xenon arc fading lamp), under standard conditions, using sample of Blue Wool as a reference.

The colour fastness of the test specimens was then assessed by comparing the change in colour with that of the reference blue wool sample. The results obtained in case of different test specimens are tabulated in Table-2.

Conclusions

Different disperse dyes of type 1a to 3c were synthesized to observe their dyeing and colour fastness properties on 100% polyester fabric. The dyed samples of fabric showed a range of brilliant yellow to brown colours with good fastness properties to artificial light (Xenon arc fading lamp), washing and dry heat. It has further been inferred, that the λ_{max} of a particular dye depends upon the nature of the substituent group present in the diazo component.

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