Synthesis and Studies of Some Acid Dyes

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Summary: Investigations of the adsorption of acid dyes containing acetoacetanilide and pyrazolone by woollen fabric have been carried out. It has been found that the adsorption levels are unexpectedly different for various dyes. Both acetoacetanilide and pyrazolone colorants have good fastness of dyes to washing, light and heat.The light fastness of the dyes was found to depend on the influence of the substituents on the electron density around the azo group. An electron-accepting substituents (*o*-COOH) afforded a good values of light fastness. A correlation between light fastness and dye absorption spectra has been suggested, which showed that π-π^* electronic transition is an important parameter in determining the stability of the system. The visible absorption spectra and Munsell renotations of all the dyes showed that the colours of dyes lie in the range of yellow -red –green.

Introduction

Woollen fibres are most usually dyed with anionic dyes and the mechanism of this process has been the subject of many studies which showed that the amount of anionic dyes taken up by the fibre is dependent on its amino group content. Fuch and co-workers have reported the synthesis of monoazo acid dyes containing acetoacetanilide and studied their properties. They indicated that these dyes gave fast yellow shades on dyeing wool [1]. Other investigators have reported the dyeing and fastness properties of acid dyes. They investigated the influence of the sulphonic acid group position in monosulphonic acid dyes and found that the dyes in which the sulphonic acid group is at the end of the molecule shows a clear overdyeing effect in polyamide fibres.They also presented the objective evaluation of the fading of acid dyes on a wool substrate [2,3].

Many authors have described the synthesis and properties of acid dyes based on different pyrazolones. Ridyard synthesised acid dyes in greenish yellow colour, whereas Mori *et al.*, synthesised disazo acid dyes which dyed wool in the range of yellow to reddish yellow shades [4,5]. Similarly Frank *et al.*, have developed acid dyes from different pyrazolones which dye leather and wool in fast reddish brown shades, whereas Wicki in his patent has presented the method of preparation of acid dyes and their metal complexes containing different pyrazolones which are used to dye wool and leather in orange shades [6,7]. Kovzhina *et al.*, have mentioned the methods for purifying 12 pyrazolone azo dyes by crystallization with different solvent systems [8]. Structural properties of the dyes investigated by Richard revealed that the monoazo

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acid dyes are shown to be hydrazone rather than azo compound, whereas Whitaker in his publication has described the possibility of C-H--O intramolecular bonds in acetoacetanilide colorants. According to him a close relationship between the molecular configuration of Acetacetanilide and pyrazolone colorants has been found [9-10]. Jolly and coworkers reported that certain pyrazolone derivatives have fungicidal and bacteriostatic activity. The synthesis and evaluation of some pyrazolone azo dyes has been described [11].

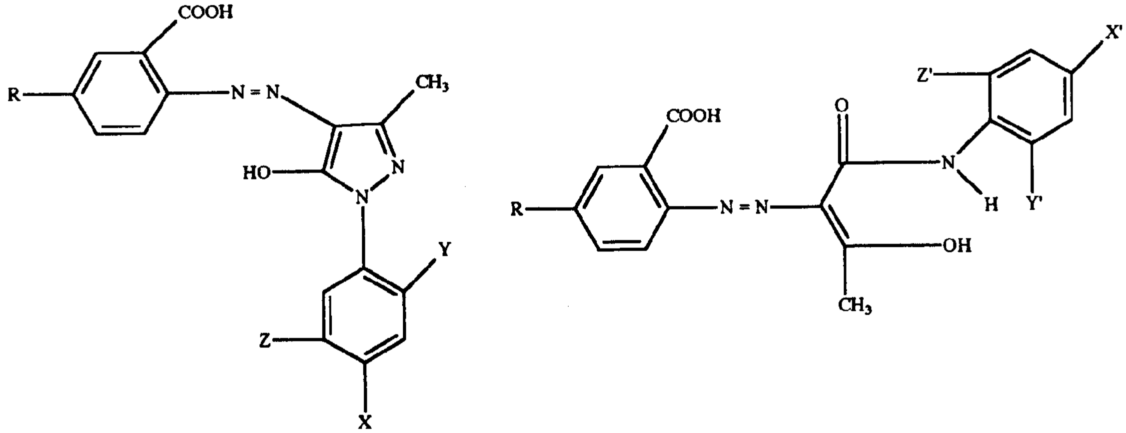
In the present paper studies are made of acid dyes in which acetoacetanilide, pyrazolone and their derivatives were used as coupling components. The work has been carried out with 10 selected monoazo dyes with general formulae shown in Scheme-1. The selected dyes are characterized by different structures that influence their physical and chemical properties

Results and Discussion

Acid dyes (1-5) were synthesised by coupling diazotized anthranilic acid with acetoacetanilide and pyrazolones, whereas for dyes of type 1a-5e diazotized sulphoanthranilic acid was coupled with these coupling agents. The dyes were purified and their λ_{max} in visible regions were determined. The data presented in Table-3 and Table-4 shows the effect of substituents by the coupling components.

Dyeing Properties

The woollen cloth was dyed in acidic bath and the percentage exhaustion was calculated for all the dyed samples by measuring visible absorbance at the given λ_{max} of the dye solution before and after dyeing. The exhaustion percentages of the dyes of 1-5 type lie in the range of 96.2 to 99, whereas exhustion of the dye of 1a-5e series falls in the range of 96.8 % to 98.8% as indicated inTable-3 and Table-4 respectively.



(a) (b)

For 1-5 R = H and 1a-5e R=SO_3H

I. 1, 1a : $X = Z_1 = H$

ii 2, 2b : X SO_3H, Y = Z = H

iii. 3, 3c : X' = Y' = Z' = H

iv. 4, 4d : X' = Cl, Y' = Z' = H

v. 5, 5e : X = SO_3H, Y = Z= Cl

Scheme-1: The conventional structure of dyes containing pyrazolone (a) and of dyes containing acetoacetanilide (b)

The wash fastness properties of all the dyed samples are given in Table-1and Table-2 which show that all the dyes have good fastness properties which are in the range of 3 to 4.0 for dyes of 1-5 type and 4.0 to 5 for 1a-5e dyes having a sulpho group in its molecule .The fastness to washing has high values which may be attributed to an increase in the molecular size of the dye.

Table-1: Effect of light , wash and dry heat on various acid dyes baded on anthranilic acid

Dye Ref. No.	Light fastness	Wash fastness			Fastness to dry heat		
		Change in Colour	Staining Wool	Staining Cotton	Change in Colour	Staining Wool	Staining Cotton
1	4/5	¾	¾	¾	4.0	4.0	4.5
2	4/5	¾	¾	¾	4.0	4.0	4.5
3	4/5	¾	¾	¾	4.0	4.0	4.5
4	4/5	¾	¾	¾	4.0	4.0	4.5
5	4/5	¾	¾	¾	4.0	4.0	4.5

Table-2: Effect of light , wash and dry heat on various acid dyes. On sulphoanthranilic acid

Dye Ref. No.	Light fastness	Wash fastness			Fastness to dry heat		
		Change in Colour	Staining Wool	Staining Cotton	Change in Colour	Staining Wool	Staining Cotton
1a	4/5	4/5	4/5	5	4/5	4/5	5
2b	4/5	4/5	4/5	5	4/5	4/5	5
3c	4/5	4/5	4/5	5	4/5	4/5	5
4d	4/5	4/5	4/5	5	4/5	4/5	5
5e	4/5	4/5	4/5	5	4/5	4/5	5

Fastness to light of these dyes are good and are found to depend on the influence of the substituents which changes the electron density around the azo group. The high fastness to light may be attributed to an electron accepting –COOH-group, which reduces the susceptibility of these dyes to oxidative degradation resulting in improvement of fastness to light. These results are in conformity with an earlier observation, wherein a correlation between light fastness and dye absorption spectra has been attempted. Here π- π^* electronic transition has been proposed as an important parameter in determining the stability of the system and the light fastness related to the ease of excitation of the π system around the azo group [12].

Fastness to dry heat is also good for all the dyes studied. However, the fastness of dyes of 1a-5e series is found higher (4.0 –5) than those of type 1-5. This may be due to their high molecular weights. Similar data has been mentioned by Blus who has synthesised a range of acid dyes and evaluated with respect to application, fastness and spectroscopic properties [13].

Colour Assessment

The substitution in diazo and coupling component of both 1-5 and 1a-5e type of dyes affords the range of different colours (yellow-red–green). Table-1 and Table-2 show the effect of different substituents on the λ_{max} of the dyes. The basic structure of dye type 1 has λ_{max} value of 440nm. In 2-5 series λ_{max} for different substituents in pyrazolone and acetoacetanilide structure are: 445 nm for type 2; 425 nm for type 3; 420 nm for type 4 and 430 nm for type 5. On the other hand, in 1a-5e series of dyes the basic structure of dye of type 1a has λ_{max} value of 450 nm.The λ_{max} for 2b-5e series of dyes are: 480 nm for type 2b; 460 nm for type 3c; 435 nm for 4d and 440 nm for 5e. The present investigation regarding effects of substitution on the colour, dyeing and fastness properties of acid dyes supports an earlier work [14].

The data presented in Table-3 indicate that for the dye series 1-5 the CIE coordinates a* and b* have positive values for dyestuff # 1,2 and 5. Thus, the colour of these dyes are along the yellow and red axis in CIE Colour Space, whereas for the negative values of a* and positive value b*, as in the case of dyestuff # 3 and 4, the colours are along the yellow and green axis.

As shown in Table-4 the coordinates a* and b* have positive values for dyestuff # 1a, 3c and 4d which proves that the position of the colours is along the yellow and red axis in the CIE Colour Space, whereas the negative values of a* and positive values of b* for dyestuff # 2b and 5e indicate that the colours in the Space are along yellow to green axis.

The results of chromaticity coordinates and Munsell renotations have good relationship with CIE LAB coordinates and λ_{max} determined .

Experimental

Materials

Anthranilic acid and sulfoanthranilic acids have been used as diazo components in the dye series 1-5 and 1a-5e respectively. The coupling components used in both series are i. 3-methyl-1-phenyl-5-

pyrazolone ii. 3-carboxy-1-phenyl-5-pyrazolone iii. acetoacetanilide, iv. acetoacet-4-chloroacetanilide and v. 2,5-dichloro-3-methyl -1-(*p*-sulfophenyl)-5-pyrazolone.

Equipments

The dyeing was performed in dyeing machine (Roche). The visible spectra were recorded on spectrophotometer (Hitachi) and the assessment of colour was made by Colorimeter (Z- Σ 80 II).

Procedure

All the dyes were prepared by diazotization of anthranilic acid and coupling with pyrazolone and acetoacetanilide derivatives in weakly basic systems and are listed as 1-5. The dyes were separated from the reaction medium as sodium salts, which were then crystallised from water. Dyes from sulfoanthranilic acid were prepared in a similar manner and are listed as 1a-5e.The structure of the dyes synthesised are presented in Scheme-1.

Purification

Purification was carried out by dissolving dye in a minimum quantity of water and the solution was filtered and the dye was precipitated by adding isopropanol to the filtrate. The precipitate was washed first with acetone and then with petroleum ether (b.p. 40-60 C) and dried. The purity of each dye was confirmed by spotting a 1% solution of the dye onto a thin layer of silica gel on a glass plate and developing with an eluent consisting of chloroform /methanol (95/5, v/v). The resulting chromatogram was dried, sprayed with iodine vapours and examined under UV light. The resulting chromatogram obtained with each dye showed only one spot in each case, indicating that the dyes were isolated in reasonably pure states.

Direct Dyeing of Wool with Acid Dyes

Woollen fabric was dyed with acid dyes using a high temperature dyeing machine by the following proceedure :

200 mgs of acid dye was taken in a mortar and a few drops of water were added to it .It was then ground with a pestle to form a very fine paste followed by dilution with 200mL warm water (dye stock solution 0.1 %). The fabric (3.5 gm) was wetted with water and transterred to dyeing pot containing dye (2%, 70mL of 0.1% dye stock solution) in 50:1 liquor: fabric ratio. The pH of dyeing solution was maintained at 4.0 to 4.5 with formic acid. Now the dyeing pots were fitted in the dyeing machine and the temperature of the machine was slowly raised to 70-80°C at the rate of 2°C/ minute and maintained for 60 minutes. Lifted the pattern from the bath, added 50 mL of cold water and 1% of potassium dichromate, replaced the pattern at 70°C, raised the temperature to the boil and boiled for 30 minutes . The bath temperature was decreased to 50°C at the same rate. The specimens were then removed from the dyeing pots, rinsed with cold water and finally dried in an oven at 60°C.

Exhaustion

Dye uptake by fabric was measured by sampling the dyebath before and after dyeing. The absorbance of diluted dye solution was measured at the given λ_{max} of the dye.Percentage of dyebath exhaustion S was calculated using Equation -1.

$$S = \frac{1 - A_2}{A_1} \times 100$$

Where A and A are absorbances of dye solution before and after dyeing respectively. The percentage exhaustion are presented in Tables -1 and 2.

After Treatment

Reduction clearing was carried out by treatment for 20 minutes at 75°C in an aqueous solution containing sodium hydroxide (5mL /L) and 85 % sodium hydrosulphite (2g /L) while using a liquor ratio of 20:1. The treated sample was then rinsed thoroughly in water and allowed to dry in the open air .

Wash Fastness Test

The washing fastness test was carried out following ISO CO 5 procedure[15]. In this test soap solution was prepared containing 5g/L of soap and

2g/L sodium carbonate in distilled water . Each of the specimen (4 cm x 5 cm) was cut and placed between two adjacent white fabrics of the same dimensions and then stitched together . For woollen fabric , one of the adjacent fabrics was made of wool , while the second piece was cotton. The composite was then placed in the container and necessary amount of soap solution previously heated to 60°C was added to give a liquor ratio of 50:1. Washing was carried out on water bath at this temperature for 30 minutes. The composites were then removed, rinsed, opened, dried and finally assessed with the aid of grey scales. The change in colour of the specimen and the staining of the adjacent fabrics was assessed with the grey scale. The results obtained are summarized in Tables -1 and 2

Fastness to Dry-Heat

The method though originally intended for determining the resistance of the colour on polyester was used for the present study by following ISO-105 standard procedure [15]. The specimen(10 cm x 4 cm) was placed between the two adjacent fabrics of woollen fibre and sewed along one of the shorter sides . Placed the composite specimen in the oven and left it there for 30 s at 210°C. Removed the composite specimen and left it for 4h in air at room temperature (27°C) at relative humidity of 65 %.

Assessed the change in colour of the specimen with the grey scale and the staining of the adjacent fabrics against pieces of the adjacent fabrics similarly treated in the absence of a specimen (Tables -1 and 2).

Fastness to Day Light

This test was also carried out by following ISO BO1 standard procedure [15]. An area of the material (strip of cloth) not less than 1 cm x 6 cm were arranged parallel in a card. An opaque cover was laid across the middle third of the specimen. The card was mounted on the exposure rack sloping at an angle from the horizontal and covered with window glass to protect the specimens from rain and other elements of the weather. Exposed the rack to daylight for 110h. The effect of light was followed by removing the cover and inspecting the specimen frequently. Regardless of the character of the change, the assessment was based upon the magnitude of the visual contrast between the specimen covered and original one. The fastness rating of the specimen i.e. number of grey which corresponds to the contrast between the original and the faded sample are given in Tables-1 and 2.

Assessment of Colour

The assessment of colour was made on the dyed samples by colorimeter and are reported in Tables -3 and 4. The study was made by calculating the values of Y, X and Z (tristmulus values), L*, a* and b* (Cartesian coordinates), x and y (Chromaticity coordinates) and Munsell coordinates in terms of hue, lightness and chroma. The L* value represents the amount of whiteness or blackness present in the colour. The a* value corresponds to the color's position on the red -green axis and the b* value is its position in the yellow-blue axis. Hue refers to the name of the colour, such as red, blue,

Table-3 Effect of substitution on the colorimetric properties of acid dyes

Dye	λ_{max}	Exhaustion	Tristimulus value				CIE LAB		Chromaticity coordinate		Munsell renotation		
Ref #	(nm)	%	Y	X	Z	L*	a*	b*	x	y	Hue	Value	chroma
1	440	99	41.51	44.44	07.54	39.01	08.31	68.16	0.4658	0.4593	1.38Y	6.35	7.19
2	445	98	40.57	43.33	04.72	38.82	09.96	74.19	0.4817	0.3395	1.29Y	6.14	8.01
3	425	96.2	53.19	52.02	29.22	39.50	-1.91	35.29	0.3829	0.3940	3.65Y	7.21	7.15
4	420	97.9	61.43	59.00	27.13	39.81	-1.29	3.43	0.3246	0.3910	0.55GY	7.84	7.65
5	430	98.5	40.84	40.38	04.27	39.33	01.33	58.40	0.4560	0.4297	4.02Y	7.19	7.89

Table-4 Effect of substitution on the colorimetric properties of acid dyes

Dye	λ_{max}	Exhaustion	Tristimulus value				CIE LAB		Chromaticity coordinate		Munsell renotation		
Ref #	(nm)	%	Y	X	Z	L*	a*	b*	X	y	Hue	value	chroma
1a	450	98.8	42.38	46.95	05.10	38.67	-4.45	87.94	0.4611	0.4864	5.47Y	6.19	8.1
2b	480	97.9	43.61	46.66	04.77	37.98	19.22	82.14	0.5022	0.4431	8.72YR	6.03	8.0
3c	460	96.8	43.35	43.13	13.82	38.81	-3.83	55.43	0.4207	0.4423	5.28Y	7.01	7.51
4d	435	98.3	49.14	47.21	15.89	38.97	-1.72	54.83	0.4206	0.4378	4.66Y	7.40	7.81
5e	440	97.1	42.87	44.38	05.39	38.09	5.30	77.22	0.4790	0.4627	2.23Y	6.98	8.0