

## Acetylation of Some Azo Dyes and Its Effects on the Thermodynamic Parameter, Colour and Fading Values on Nylon 6, 6 and Wool Fabric.

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### ABSTRACT

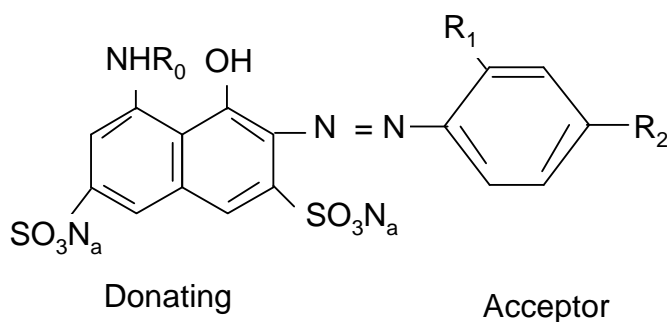
Azo dyes containing free amino group were derived from H-acid and the free amino group was acetylated to obtain another group of dyes. The two groups of dyes were applied to wool and nylon 6.6 fabrics and their colour fastness properties assessed. It was found that acetylated dyes gave hypsochromic effects on colour, and dyeing fastness such as washing and perspiration improved on acetylated dyes when compared with unacetylated dyes on both fabrics. For the light fastness, however, there was no noticeable improvement on nylon 6.6 fabric but general improvement was made on acetylated dyes when applied to wool fabric. For the thermodynamic parameters such as the equilibrium constant (partition coefficient K) and the standard affinities  $\Delta\mu^0$  the acetylated dyes have lower values when compared with the unacetylated dyes on fabrics. [Report and Opinion, 2009;1(6):12-17]. (ISSN 1545-4570).

**Keywords:** Azo dyes, Hypsochromic, Unacetylated dyes, Nylon 6, 6, Standard affinities.

### 1. Introduction

Light and weather fastness is an important factor in the determination of the useful life span of textiles. Light may produce two different changes in dyed fibrous materials; on the one hand the colour can fade, on the other hand photochemical degradation of the fibrous material can take place. It is well known that certain yellow and orange vat dyes sensitizes the photodegradation of cellulose fibres such as cotton while acid metal-complex dyes serve to protect nylon fibres <sup>1</sup>, (Kricserskz kij 1975) Baumann<sup>2</sup> (1970) concluded for experimental results obtained from amino acids that certain reactive dyes linked to the side chain slow down the photodegradation of wool, while they promote reaction when attached to the principal peptide chain.

It has also been reported that acetylation of free amino groups of some dyes lead to an improvement in the light fastness to such an extent as much as 3-4 units on wool fabrics<sup>3</sup> (Okubu 1953) and it has been proved that both  $-\text{NH}_2$  and  $-\text{OH}$  groups are the source of fugitiveness in the dyes containing them<sup>3</sup> (Okubu 1953). It was therefore considered of interest to study the effects of acetylating only the free amino group contained in acid dyes derived from H-acid to study the change in the thermodynamic value and effects on fading behaviours of the resulting dyes on wool and nylon 6.6, the  $-\text{OH}$  group is left intact. The general formula of the azo dyes used in this study is given in Fig. 1.



**Fig. 1: General formula of the azo dye used in the study**

Dye No.	Substituents		
	R <sub>0</sub>	R <sub>1</sub>	R <sub>2</sub>
1	-H	-H	-COOH
2	-COCH <sub>3</sub>	-H	-COOH
3	-H	-CN	-NO <sub>2</sub>
4	-COCH <sub>3</sub>	-CN	-NO <sub>2</sub>
5	-H	-Cl	-NO <sub>2</sub>
6	-COCH <sub>3</sub>	-Cl	-NO <sub>2</sub>
7	-H	-NO <sub>2</sub>	-Cl
8	-COCH <sub>3</sub>	-NO <sub>2</sub>	-Cl

## 2. Materials and Methods

### 2.1 Experimental Acetylation of H-acid

1g (0.0033 moles) of H-acid was dissolved at 50°C in 7.00cm<sup>3</sup> of water containing (0.0019 moles) 0.2g of soda ash in a three necked round bottom flask fitted with a mechanical stirrer, reflux condenser and thermometer. With vigorous stirring (0.006 moles) 0.58g of acetic anhydride was added into the flask over a period of 15 min. stirring was continued for at least one hour to ensure complete acetylation of the H-acid. After complete acetylation, (0.02 moles) 1.66g of soda ash was added to the reaction mixture to hydrolyse off any acetyl group that may have substituted the hydrogen atom in the hydroxyl group of the H-acid.

### 2.2 Dyes

The alkaline solution of acetyl H-acid obtained above was used directly in the coupling reaction with the proper N, N-dialkylaniline according to usual procedures<sup>4</sup> (Fieze-mild 1949). The impure dyes were recrystallised from alcohol and water mixture and their purity was controlled by TLC.

### 2.3 Physico-chemical properties

Visible spectra of the dyes were obtained with a specord u.v.-vis spectrophotometer using water solutions at concentrations of 10<sup>-4</sup>-10<sup>-5</sup> mol/l. The results obtained are summarized in Table 1.

### 2.4 Dyeing procedure

Wool and nylon fabric samples were dyed in a Waterman dyeing machine. The liquor ratio was 50:1 at pH 3. The dyeing was carried out with the samples entered at 45°C to 100°C over 15 minutes and maintained at this temperature for 45 minutes. When the dyeing was complete the temperature was lowered and the samples were rinsed and washed under standard conditions<sup>7</sup>.

### 2.5 Measurement of % Exhaustion

The exhaustion of the dye was determined by measurements of optical density using a colorimeter at the λ<sub>max</sub> of each dye. The optical density of the dyebath was measured before the commencement of dyeing by taking a sample from a control dyebath. At the completion of dyeing, the dyed sample was removed and excess dye liquor squeezed back into the dyebath. The dye liquor was cooled, made up to the initial volume with distilled water, a sample was taken and its optical density measured. Percentage exhaustion was calculated using the relationship below. Duplicate measurement was made and the average exhaustion value taken.

$$\%Exhaustion = \frac{(InitialO.D - FinalO.D)}{InitialO.D} \times 100$$

Dye No.	$\lambda_{\max}$ (water) (nm)	$\epsilon_{\max} \times 10^{-4}$ $1/\text{mol}^{-1}\text{cm}^{-1}$	$\Delta\lambda^*$ (nm)
1	539	2.39	
2	510	1.85	29
3	569	1.55	
4	499	1.26	70
5	577	1.72	
6	515	1.85	42
7	541	1.37	
8	495	1.17	46

\* $\Delta\lambda = (\lambda_{\max} \text{ unacetylated dye} - \lambda_{\max} \text{ acetylated dye})$

## 2.6. Wash fastness test

The washing fastness test was carried out using a Linitest was wheel machine following ISO procedure<sup>5</sup> (SOC 1978). In this case, soap solution was prepared containing 5g/l soap and 2g/l Na carbonate in distilled was cut. Each of the dyed fabrics was two adjacent white fabrics of same dimensions and stitched together. For the wool fabric, one of the adjacent fabrics was made of wool, while second was cotton. Also, in case of nylon 6.6, one of the adjacent fabrics was cotton, which the other was nylon 6.6. The composite was then placed in the container of the Linitest machine and necessary amount of sopa solution previous heated to  $60 \pm 2^{\circ}\text{C}$  added to a liquor ratio of 50:1. Washing was carried out at this temperature for 30 min. The composition were then removed, rinsed opened, dried and finally assessed with the aid of gey scales. The results obtained as summarized in Table 2.

## 2.7. Acid and Alkaline Perspiration Tests

Composite specimens of the dyed samples were prepared as for the wash fastness test. These were then treated in freshly prepared alkaline and acid perspiration test solutions. The artificial perspiration solution used in this study were perpared in the following ways:

- Alkaline perspiration solution 5g/l sodium chloride 0.5g/l Histidine monohydrochloride monohydrate. The solution was brought to pH 8.0 with 0.1N solution of sodium hydroxide.
- Acid perspiration solutions 5g/l sodium chloride 2.2g/l disodium hydrogen orthophate 0.5g histidine monohydrochloride phhydrate. The solution was brought to pH 5.5 with 0.1N sodium hydroxide. The composite sample was improved in he artificial perspiration solutions separately with liquor ratio of 20:1 for 30 min.

**Table 2: Fastness properties of the Dyes on Nylon 6.6 fabric**

Dye	Wash change in shade	Fastness degree staining in	Perspiration Alkali		Fastness Acid		Light fastness	% Exhaustion
			(a)	(b)	(a)	(b)		
1	3	5	4	4	4-5	4-5	2	71.2
2	4	5	3-4	3	4-5	4	2-3	51.5
3	2	5	2-3	5	4-5	3	3-4	87.9 39.4
4	4-5	5	4	4-5	3	4	2	
5	2-3	5	2	4-5	2	4-5	4	71.2 60.6
6	3	5	3-4	5	5	5	2	
7	2-3	5	2-3	3	2-3	4-5	2	76.7
8	4-5	5	2-3	5	2-3	5	1	66.7

Change in shade (a)

Staining of adjacent white material (b)

**Table 3: Percentage Exhaustion and fastness properties of the dyes on wool**

Dye No	% Exhaustion	Light fastness	Wash (a)	Fastness (b)
1	92.8	6	4	5
2	97.2	7	4-5	5
3	98.4	3	3	4-5
4	96.0	4	3-4	5
5	99.2	4	4	4-5
6	98.9	5-6	4-5	4-5
7	99.4	6	3-4	5
8	98.6	7	3-4	5

a = Change in shade

b = Staining of adjacent white material

**Table 4: Thermodynamic Parameters (K and  $\Delta\mu^0$ ) on Nylon 6, 6**

Dye	% E	Partition coefficient K ( $l g^{-1}$ )	Standard affinity $\Delta\mu^0$ (kJ mol <sup>-1</sup> )
1	71.2	123.6	14.94
2	51.5	53.1	12.32
3	87.9	363.2	18.28
4	39.4	32.5	10.79
5	71.2	123.6	14.94
6	60.6	76.8	13.47
7	76.7	164.5	15.83
8	66.7	100.2	14.29

The composite was removed and arranged between glass plates one on top of another and a weight of 4.5kg placed on top. The entire assembly was then placed in an oven at  $37 \pm 2^\circ\text{C}$  for 4 hours. The assembly was then removed after four hours from the oven, and the composites were then dismantled and air dried at temperature not exceeding  $60^\circ\text{C}$ . The degree of perspiration fastness was judged using a grey scale for assessing colour change and staining of adjacent materials.

## 2.8. Light Fastness Test

An artificial light source (exxon arc) was used to determine the light fastness following procedure described elsewhere<sup>6</sup>.

## 3.0. Results and Discussion

### 3.1. Light Absorption Properties

The visible absorption property of the dyes was measured in water and the molar absorption coefficient calculated for the same solvent, the results obtained are summarized in Table 1. The dye can be classified as donor-acceptor chromogen in which the phenyl ring is serving as electron acceptor half and the naphthalene ring is acting as the electron donating half of the chromogen. For example dye (1) which contains the carboxylic group as electron withdrawing substituent in the acceptor half absorbs at 539nm in water with molar extinction coefficient of  $2.39 \times 10^4 \text{ l/mol}\cdot\text{cm}^{-1}$ . When the electron donating amino group in dye (1) is substituted with acetyl group as in dye (2), the resulting dye (2) absorbs at 510nm which is at a shorter wavelength of 29nm relative to dye (1). In this case the acetyl group has reduced the electron donating property of the amino group in dye (1) and thus caused an hypsochromic effect of 29nm.

In dye (3) the carboxylic group in the parent dye (1) has been substituted with nitro group and additional electron withdrawing cyano group was introduced in the acceptor group ortho to the azo group, and in this case the dye (3), absorbs at relatively longer wavelength at 569 nm when compared with dye (1). This is expected as a result of two powerful electron withdrawing groups substituted in the acceptor half of the chromogen. This has actually resulted in bathochromic shift of 30nm relative to dye (1). The acetylation of the amino group in dye (3) to give (4) also results in hypsochromic shift of 70nm relative to dye (3). This is consistent with the result obtained when dye (1) is acetylated to give

(2). The acetyl group is in effect an electron withdrawing group substituted in the electron donor half of the chromogen.

The results obtained with dyes (5) and (6) also follow the same trend, as can be seen from Table 1. dye (5) absorbs at 557 nm whereas, dye (6) in which the amino group has been acetylated absorbs at 515 nm, showing hypsochromic shift of 42 nm in dye (7) and (8), the relative positions of chlorine and nitro groups are interchanged from the positions in which they were in dye (5) and (6). When the corresponding pairs of the two dyes are compared, it can be seen that nitro group in the para position to the azo group gave dyes which are more bathochromic than the corresponding dyes with chloro group in the same position. For example dye (5) absorbs at 557nm whereas substitution of nitro group with chloro group to give dye (7) absorbs at 541nm, a hypsochromic shift of 16nm. The same effect is observed when dye (6) and (8) are compared.

### 3.2. Thermodynamic Parameters

For the thermodynamic parameter the trend followed the same pattern observed in the various  $\lambda_{max}$ . For instance dye 1 which has the carboxylic group as electron withdrawing substituent in the acceptor half absorbs at 539nm and has standard affinity of  $14.94\text{kJmol}^{-1}$  whereas dye 2 having acetyl group in position of amino group absorbs at 519nm, and standard affinity of  $12.32\text{kJmol}^{-1}$ . It implies that dye 2 absorbs at a shorter wavelength of 29nm relative to dye 1, and  $2.62\text{kJmol}^{-1}$  of standard affinity (energy) less than that of dye 1. This is the trend between dyes that were acetylated and those that were unacetylated (Table 4). All the 'odd' numbered dyes were unacetylated, while all the 'even' numbered dyes were acetylated.

For dyes 3 and 4, the results obtained in their % exhaustion can be explained on the platform of the fact that both  $\text{CN}^-$  and  $-\text{NO}_2$  are electron withdrawing group and this enhanced the release of a lone pair of electrons on amino group ( $\text{R}^\circ$ ) i.e. protonation easily occurred there and this positively affect dye uptake by polyamide fabrics such as nylon and wool, hence very high equilibrium exhaustion (87.9 %). On the other hand, dye 4 that is acetylated is not easily protonated, despite the presence of  $-\text{CN}$  and  $-\text{NO}_2$  groups that are electron withdrawing groups, hence very low equilibrium exhaustion (39.4 %). The same thing applies to dyes 5 and 6 even though to a lesser magnitude compared with the pair dyes 3 and 4.

The results summarized in table 1, generally show that acetylation of amino group in the azo dyes under study lead to hypsochromic effects when the corresponding pairs of dyes are compared. This is due to the fact that the strength of the electron donating half of the chromogen has been reduced when the acetyl group is placed at that position. When the relative strength of the electron withdrawing groups incorporated in the acceptor half of the chromogen is compared, the nitro group para to the azo group influenced a powerful electron withdrawing strength, though with the aid of cyano group ortho to the azo group which gives the most bathochromic dye in the series.

### 3.3. Dyeing fastness

The results of the I.S.O. No. 3 wash fastness test summarized in Table 2 and 3 shows that all the dyes gave dyeing of excellent wet fastness on nylon 6.6 materials, however, the wet fastness ratings obtained with the dyeing of the dyes on wool are not as good as on nylon 6.6. This is due to the fact that wool fabric absorbed more dyes as indicated by the percentage exhaustion in Table 3 than nylon 6.6 as in Table 2 and in this way more dyes will be desorbed out of wool during the washing treatment. The results of the perspiration test also show that both the alkaline and acid perspiration fastness is good on nylon 6.6 materials and it can not be seen whether the acetylation has any effect on this fastness property.

The results of light fastness test summarized in Table 3 for wool fabrics clearly show the effects of acetylation on light fastness property. When all the dyes are compared on wool, it is seen that acetylated dyes have good resistance to light than the unacetylated dyes. All the dye that contain free amino group gave reduced light fastness property. Free amino group in dyes increases the surface activity of the molecule and consequently reduces its photo-stability. The nature of the dye molecule allows the dye molecule to react with surrounding materials such as free oxygen in the air when some form of light is absorbed. In this respect, the dye molecule decomposes and loses its colour. The activity of the free amino groups in dyes 1, 3, 7 and 9 have been reduced by acetylation and these account for the improved light fastness for other dyes with acetyl group in the dyes under study.

When the light fastness properties of the dyes under study are compared on both nylon 6, 6 and wool fabrics, the dyes have better light fastness on wool than on nylon 6, 6. It is possible however, that particular amino acid residues in wool retard photo-oxidation of the dye by reacting preferentially with oxidants generated on exposure of the dye fiber. Another reason for increased light fastness of the dye on wool can be seen from the percentage exhaustion of dye on both fabrics. The dyes are generally

more exhausted on wool than on nylon 6, 6, and therefore the amount of dyes contain by wool fabric in each case of the dyes are more and for this reason, light destruction will take a very long period before it can be noticed on wool being that they are present larger amount than on nylon 6, 6.

From the results of light fastness properties there is no improvement on nylon 6.6 when the dyes are acetylated and this show that different mechanism of fading on nylon 6, 6. It is well known however, that resistance of a dye or pigment to chemical in photochemical attack is directly related to the chemical structure and physical characteristics of the fiber itself.

#### 4.0. Conclusion

The results of the study clearly show that acetylation of the amino group leads to hypsochromic effect in terms of colour and constitution study. By extension the partition coefficient and standard affinities (energies) of the dyeing which are the driving forces behind dyeing process. Also acetylated dyes enhanced light fastness properties on wool but not on nylon 6,6. It is strongly suspected that there is an empirical relationship between the thermodynamic parameter of dyeing such as partition coefficient  $K$ , standard affinity  $\Delta\mu^0$ , heat of dyeing  $\Delta H^0$  and indeed, the entropy of dyeing  $\Delta S^0$  and then where a particular dye has its  $\lambda_{max}$ . This is still under investigation.

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