STUDIES ON THE ADDITION OF REACTIVE COMPOUNDS TO THE DYE-BATH OF NON-REACTIVE DYES PART III[1,2] FACTORS AFFECTING FORMATION OF REACTIVE DYES FROM DISPERSED-LIKE DYES

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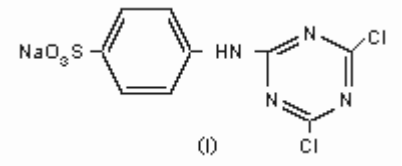
SUMMARY: It is shown that, in spite of the known ease of hydrolysis of 2,4-dichloro-6-(4-sulphoanilino)-s-triazine (I) and the spare solubility of the model disperse-like dyes (II-V), yet soluble reactive dyes can be obtained in different yields by reaction of I and these dyes. Some optimal conditions for dyeing cotton with the in-situ formed reactive dyes are explored.

Key Word: Reactive dyes.

INTRODUCTION

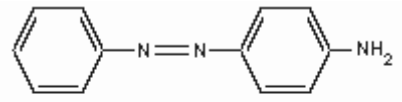
In connection with another study carried out to dye polyester/cotton blends with dispersed-type dyes and reactive compounds (3), it was observed that coloration of the cotton component in the blend could be achieved, with varying degrees of success, via a dye formed in-situ by the reaction of 2,4-dichloro-6-(4-sulphoanilino)-s-triazine (I) with dyes used for coloring the polyester component.



(I)

In the present part, a study is undertaken to asses whether this process would be viable for dyeing cellulosic fibres alone and if so under what optimal conditions.

For understanding the mechanism of the process, we selected simple colored molecules as model compounds. Consequently, dyes (II-VII) containing one or more nucleophilic groups (amino or hydroxy) were used.



p - Aminoazobenzene
Solvent yellow I, C.I. 11000
(II)

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Dyeing experiments have shown that from all dyes used, dyes (VI) and (VII) containing hydroxy groups only, proved to be unsuitable for application by this method and gave only staining on cotton. This may be explained by the insufficient deactivating effect when one residue of (VI) or (VII) replaces one chlorine atom in (I), and consequently the second chloride atom is also replaced by another dye residue giving a non reactive dye (4). Another reason could be the unstability towards hydrolysis of the ester bond formed by the reaction of (I) with the hydroxy groups in the two dyes.

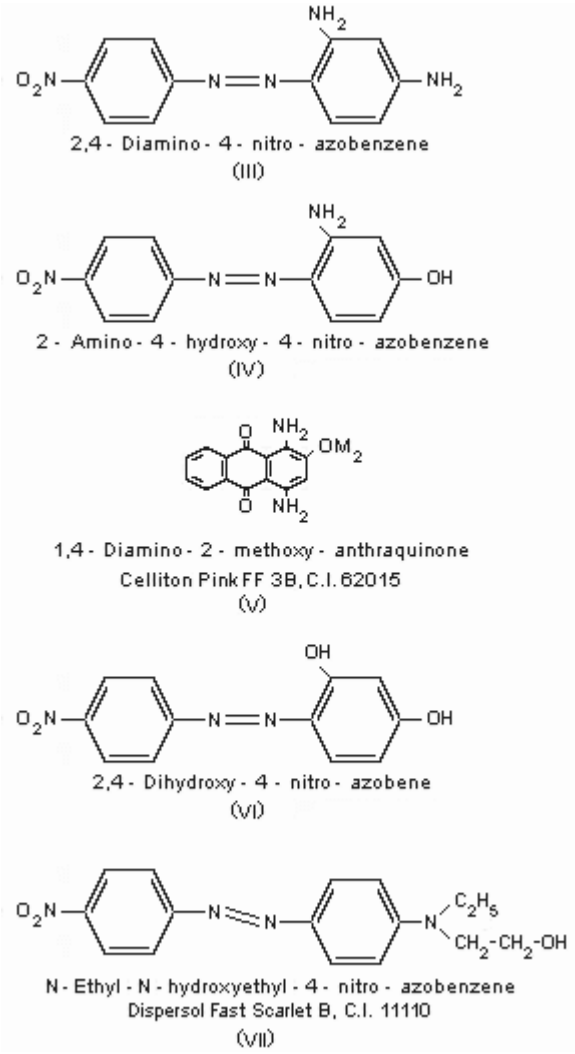
The reaction between compound (I) and dyes (II-V) containing amino groups was carried out under a variety of conditions, and the soluble dyes formed in-situ were not isolated, but added directly without using a standardized procedure for reactive dyes.

The color strength on cotton as measured by color strength values was estimated for the soaped fabrics. Reactive dye fixation was assessed after washing the soaped fabrics with 50% dimethylformamide as described in the experimental section.

EXPERIMENTAL

Materials

Cotton Fabric: Cotton fabric, mill-scoured and bleached (140 g/m^2), was kindly supplied by Misr-El-Mehalla Co., Egypt. The fabric was treated with 5 g/L sodium carbonate solution and 3 g/L non-ionic detergent (Hostapal C.V., Hoechest) at the boil for 4 hours, the fabric was thoroughly washed with water and dried at the ambient temperature.



Reagents: All reagents used were laboratory chemical grade.

Dyestuffs: The following commercial dyestuffs were used.

a. p-Aminoazobenzene (II) (solvent yellow 1, C.I. 11000) supplied as a commercial sample from ISMADYE Egypt.

b. Cellition Pink FF3B (V), C.I. 62015, supplied as a commercial sample from BASF.

c. Dispersol Fast Scarlet B (VII), C.I. 11110, supplied as a commercial sample from ICI.

The following two dyestuffs were prepared according to methods cited in literature.

2,4-Diamino-4-nitro-azobenzene (III) (5) and

2,4-dihydroxy-4-nitro-azobenzene (VI) (6)

2-Amino-4-hydroxy-4-nitro-azobenzene (IV), was prepared from the diazonium salt of p-nitroaniline (0.1 mole) and m-aminophenol, (0.1 mole), crystallized from chlorobenzene, m.p. above 300°C ($C_{12}H_{10}N_4O_3$ requires: C 55.8, H 3.88; found C 55.42, H 3.99).

Reactive compound: 2,4-Dichloro-6-(4-suphoanilino)-s-triazine (I) was prepared according to the method cited in Fierz-David and Matter (7,8).

General method for the preparation of the reactive dyes in-situ

The reaction between 2,4-dichloro-6- (4-suphoanilino)-s-triazine (I) and insoluble dyes (II-V) was carried out before dyeing as follows:

In aqueous medium: The weighed quantity of reactive compound (I) was gradually added to the calculated quantities of dyes (II-V), suspended in 50 ml distilled water. The pH was kept at 6.5 during the reaction using sodium carbonate solution. The reaction was carried out at different temperature (30-100°C) and for different intervals of time (10-50 minutes). The mixture was then filtered off from any unreached dye, and the filtrate obtained was added as such to the dye bath. The quantities of reactive compound (I) and dyes used are given in Tables 1-4.

In an acetone-water or water-dimethylformamide medium: In this case the method of preparation of the reactive dyes was similar to the above except for the addition of acetone or dimethylformamide in increasing amounts as given in Tables 5 and 6. The weights of compound (I) or dyes used were those which gave maximum color strength values in aqueous medium.

Dyeing of Cotton: The dyeing method was carried out according to the method of ICI(9) as follows:

The cotton fabric (6.25 g) was entered in a bath containing anhydrous sodium sulphate (22.5 g/150 mL distilled water), the fabric was shaken for 15 minutes at 30°C and pH 6-7 to allow the salt to be uniformly distributed. The prepared reactive dye solution in water (50 mL) or in water/organic solvent, as indicated above, was added to the bath over 10 minutes, dyeing was continued at 30°C and pH 6-7 for 15 minutes. Then the temperature was raised to 80°C in 30 minutes and the dyeing was continued at 80°C for 30 minutes. An alkaline solution of sodium carbonate (5 g/50 mL distilled water) was added to the bath over 10 minutes, therefore the total bath volume was 250 mL. Dyeing was continued at 80°C and pH 10-11 for 1 hour, then the dyed cotton fabric was finally soaped.

Testing: Color measurement of the dyed fabrics (10)

The dyed fabric obtained was divided into three pieces:

i) A control sample.

ii) The second piece was soaped for 30 minutes at the boil in a bath containing 3 g/L non-ionic detergent (Hostapal C.V., Hoechst).

iii) The third piece was soaped and extracted with 50% aqueous dimethylformamide for 15 minutes at the boil.

The color yield of the dyed samples were evaluated using a Perkin-Elmer Spectrophotometer and by applying the Kubelka-Munk equation as follows:

$$K/S = \frac{(1-R)^2}{2R} - \frac{(1-R_o)^2}{2R_o}$$

where:

R = Decimal fraction of the reflectance of the dyed fabric.

R_o = Decimal fraction of the reflectance of the undyed fabric.

K = Absorption coefficient

S = Scattering coefficient.

RESULTS AND DISCUSSION

Dyeing experiments indicate that although compounds (II-V) are insoluble or sparingly soluble in water, yet they react partially with the reactive compound (I) under a variety of conditions and with varying yields to give dyes which can be applied on cotton in the same manner as reactive dyes. It is thus plausible to assume that coloration proceeds in this case via the following two steps:

$D\text{-}NH_2 + R\text{-}(Cl)_2 \rightarrow D\text{-}NH\text{-}R\text{-}Cl + HCl$ step (1)

Dye (II-V) Reactive compound (I)

$Cell\text{-}O\text{-}Na + Cl\text{-}R\text{-}NH\text{-}D \rightarrow Cell\text{-}O\text{-}R\text{-}NH\text{-}D + NaCl$ step (2)

where

R= Reactive compound residue

D= Dyes (II-V) moieties

At the same time, it is also plausible to suppose that both compound (I) and the reactive dye formed in solution would also undergo hydrolysis as follows:

$R\text{-}(Cl)_2 + 2HOH \rightarrow R\text{-}(OH)_2 + 2HCl$

$D\text{-}NH\text{-}R\text{-}Cl + HOH \rightarrow D\text{-}NH\text{-}R\text{-}OH + HCl$

In order to explore the potentialities of this method for dyeing cotton, several experiments were undertaken to obtain optimal coloration on this fibre.

Effect of reaction temperature

Although, we are aware that the first chlorine atom in the dichlorotriazinyl compound (I) reacts with dyebases at temperatures ranging from (30-40°C), yet for purposes of understanding the factors affecting the coloration of cotton using the present process we chose to follow, the reaction at higher temperature also. Results of experiments on the effect of temperature on the extent of reaction between compound (I) and insoluble compounds (II_a, III_b, IV, V) as measured by color strength values are summarized in Table (1).

Table 1: Effect of reaction temperature of dyes (II-V) and compound (I) on the color strength of dyed cotton fabrics.

Type, weight (g) and no. of mmole of dye (II-V) and compound (I)	Temperature (°C)	Color strength (K/S)	
		After soaping	After DMF
(II); 0.122 (0.62) and (I); 0.213 (0.62)	30	5.07	3.77
	45	11.52	10.65
	60	19.01	14.17
	75	20.8	20.80
	85	24.0	22.80
	100	18.24	18.24
(III); 0.143 (0.55) and (I); 0.190 (0.55)	30	0.356	0.307
	60	0.802	0.515
	75	1.624	1.156
	90	1.883	1.475
	100	5.89	3.33
(IV); 0.143 (0.55) and (I); 0.190 (0.55)	30	0.199	0.216
	50	0.277	0.237
	60	0.430	0.315
	80	0.430	0.354
	100	0.718	0.536
(V); 0.146 (0.54) and (I); 0.187 (0.54)	30	0.932	0.486
	50	1.649	0.718
	60	1.961	0.718
	80	1.423	0.714
	100	1.674	0.926

Reaction time 20 min.; at ph 6.5.

The above data reveal that a) compound (I) has some stability under the experimental conditions used and that an increase in temperature of the reaction between this compound and dyes (II-V) generally causes a corresponding increase in the concentration of the reactive dye, partially formed in-situ, as indicated by increase of color strength values on cotton fabrics.

b) Compound II gives always appreciably higher values of K/S as compared to all other compounds at different temperatures.

c) In case of dye (II) an increase in temperature of the reaction is accompanied by an increase in color strength until it reaches a maximum at 85°C. Further increase of temperature causes a slight decrease.

d) Although the increase of the color strength in the case of dye (III) is considerable (about 10 times) when the temperature is raised from 30 to 100°C, yet the values of K/S obtained are relatively low due to the insolubility of this dye in the reaction medium and to the enhanced hydrolysis of I at higher temperatures.

e) The increase of color strength values of dyes (IV) and (V) between 30 and 100°C are also relatively small. The K/S values remain also low.

f) Maximum color strength values in case of dyes (III), (IV) and (V) are attained at 100°C.

Effect of varying the concentration of reactive compound (I)

In view of the insolubility problems of dyes (II-V) in water, it seemed also of interest to determine the weights of reactants which would produce optimal color strength values on cotton keeping all other conditions constant. In the following series of experiments, the weights of dyes (II-V) were kept constant while the weight of compound (I) was increased gradually (Table 2).

The results in the above table show the following:

Table 2: Effect of increasing the concentration of compound (I) at constant weight of dye on the color strength of dyed cotton fabrics.

Type, weight (g) and no. of mmole of dye (II-V)	Weight (g) and no. of mmole of compd. (I)	Color strength (K/S)	
		After soaping	After DMF
(II); 0.122 (0.62)	0.213 (0.62)	24	22.8
	0.277(0.81)	22.25	22.25
	0.341(0.99)	22.25	22.25
	0.405(1.18)	22.8	22.8
	0.469 (1.36)	22.8	22.8
	0.533 (1.55)	22.25	22.25
(III); 0.143 (0.55)	0.190 (0.55)	5.89	3.33
	0.247 (0.72)	9.89	7.96
	0.304 (0.88)	10.39	8.64
	0.361 (1.05)	13.72	10.13
	0.418 (1.21)	16.26	13.30
	0.475 (1.38)	16.26	13.30
	0.532 (1.54)	17.53	13.30
	0.589 (1.71)	16.26	13.30
(IV); 0.143 (0.55)	0.190 (0.55)	0.718	0.536
	0.285 (0.83)	0.875	0.664
	0.418 (1.21)	0.812	0.676
	0.475 (1.38)	0.987	0.908
	0.570 (1.65)	1.316	1.060
	0.760 (2.2)	1.945	1.637
	0.950 (2.75)	2.41	1.767
	1.140 (3.3)	1.809	1.781
	1.330 (3.85)	1.824	1.809
(V); 0.146 (0.54)	0.187 (0.54)	1.674	0.926
	0.281 (0.81)	1.824	1.171
	0.374 (1.08)	2.08	1.220
	0.468 (1.35)	2.67	1.600
	0.561 (1.62)	3.68	1.993
	0.655 (1.89)	3.41	1.961
	0.748 (2.16)	3.64	2.24
	0.842 (2.43)	3.81	2.37
	0.935 (2.7)	3.44	2.64
	1.122 (3.24)	4.1	2.74
	1.309 (3.78)	4.60	3.86
	1.496 (4.32)	4.93	3.52
	1.683 (4.86)	4.60	3.77

Reaction time 20 min, reaction temp. 85°C for dye (II) and 100°C for dye (III), (IV) and (V); at pH 6.5.

a) In case of dye (II) increase of the concentration of the soluble reactive compound (I) from 0.62 mmole to 1.55 mmole does not appreciably affect the K/S values after DMF.

b) The increase of the concentration of compound (I) causes appreciable increases in the case of dyes (III), (IV) and (V) respectively.

Effect of reaction time

The effect of reaction time on color strength is shown in Table 3.

These data are self explanatory and show that under the conditions used a time ranging from 20-30 minutes gives optimal color strength values depending on the type of insoluble dye used. Increase in time above these limits seems to favor the hydrolysis of compound I or the in situ formed dye.

Table 3: Effect of reaction time of dyes (II-V) and compound (I) on the colour strength of dyed cotton fabrics.

Type, weight (g) and no. of mmole of dye (II-V) and compound (I)	Time (minutes)	Color strength (K/S)	
		After soaping	After DMF
(II); 0.122 (0.62) and (I); 0.213 (0.62)	10	15.68	15.68
	20	24.0	22.8
	30	17.53	17.53
	40	17.53	17.53
	50	17.53	17.53
(III); 0.143 (0.55) and (I); 418 (1.21)	10	13.30	11.52
	20	16.26	13.30
	30	17.17	14.17
	40	16.26	14.17
	50	16.26	14.17
(IV); 0.143 (0.55) and (I); 0.95 (2.75)	10	0.797	0.773
	20	2.41	1.767
	30	1.530	1.228
	40	1.519	1.254
(V); 0.146 (0.54) and (I); 1.309 (3.73)	10	2.88	2.39
	20	4.20	3.52
	30	4.93	3.16
	40	5.70	2.74

Reaction temp. 85°C for dye (II) and 100°C for dye (III), (IV) and (V); at pH 6.5.

Effect of varying the concentration of dyestuffs (II-V)

A series of experiments were carried out by increasing the weights of dyes (II-V) at optimal constant concentration of compound (I) and reaction time which were obtained from Table 2 and 3 respectively (Table 4).

Table 4: Effect of varying the quantities of dyes (II-V) at constant concentration of compound (I) on the color strength of dyed cotton fabrics.

Weight (g) and no. of mmole of compound (I)	Type weight (g) and no. of mmole of commpd. (II-V)	Color strength (K/S)	
		After soaping	After DMF
0.213 (0.62)	II; 0.122 (0.62)	24.00	22.8
	II; 0.183 (0.93)	19.85	19.85
	II; 0.244 (1.24)	19.85	19.85
	II; 0.305 (1.55)	19.01	19.01
0.418 (1.21)	III; 0.143 (0.55)	14.64	14.17
	III; 0.215 (0.83)	12.91	12.18
	III; 0.358 (1.38)	12.53	12.18
	III; 0.572 (2.2)	9.2	8.5
0.95 (2.75)	IV; 0.143 (0.55)	2.41	1.767
	IV; 0.286 (1.1)	2.66	2.50
	IV; 0.429 (1.65)	3.30	3.13
	IV; 0.572 (2.2)	3.86	3.60
	IV; 0.715 (2.75)	5.89	4.60
	IV; 0.858 (3.3)	5.70	4.73
1.309 (3.73)	V; 0.146 (0.54)	4.20	3.52
	V; 0.292 (1.08)	7.23	4.42
	V; 0.438 (1.62)	9.89	5.53
	V; 0.584 (2.16)	9.02	4.42

Reaction time 30 min for dye (III) and 20 min for dye (II), (IV) and (V); reaction temp. 85°C for dye (II) and 100°C for dye (III), (II) and (V); at pH 6.5.

The results in the above table show the following:

Increase of weights of dyes (II) and (III) leads to a decrease in color strength values due probably to the reaction of compound (I) with two molecules of the dye under the experimental conditions used. This would definitely lead to decreased concentration of the reactive dye in the reaction medium.

On the other hand, increase of weights of dyes (IV) and (V) leads to increase in color strength.

Effect of solubility of dye in reaction medium and type of solvent used

Addition of acetone to the reaction medium between compound (I) and dyes (II-V) has been found to cause two distinct effects:

(a) A general increase in the color strength values of dyed fabrics. (b) To lower the reaction temperature to 30°C. These two observations are undoubtedly due to the increased solubility of the insoluble dyes in the reaction medium. This effect is shown in Table 5.

On the other hand, addition of dimethylformamide which is a good solvent for compounds (II-V) to the reaction mixture, gave different results, since the increase of the former solvent causes a decrease in color strength values. This effect can be attributed to a possible reaction of the solvent with compound (I) (11). This effect is shown in Table (5).

Table 5: Effect of addition of acetone to the reaction medium between dyes (II-V) and compound (I) on the color strength of dyed cotton fabrics.

Type, weight (g) and no. of mmole of dye (II-V) and compound (I)	Volume of acetone (mL)	Color strength (K/S)	
		After soaping	After DMF
(II); 0.122 (0.62) and (I); 0.213 (0.62)	5.6	14.89	12.36
	8.8	15.48	15.41
	12.5	17.53	16.87
	16.7	22.25	21.25
	21.4	23.4	22.8
	26.9	24.0	22.8
	33.3	23.4	22.8
(III); 0.143 (0.55) and (I); 0.418 (1.21)	10	6.97	5.70
	20	10.95	10.39
	30	12.53	11.52
	50	16.87	15.68
	70	16.87	15.68
(IV); 0.858 (3.3) and (I); 0.95 (2.75)	10	2.52	1.961
	20	3.73	2.72
	40	5.70	5.14
	60	9.60	7.23
	80	10.39	7.80
(V); 0.438 (1.62) and (I); 1.309 (3.73)	10	5.07	2.83
	20	5.45	2.85
	40	5.98	2.91
	60	6.97	3.30
	80	7.10	3.30

Reaction time 30 min. for dye (III) and 20 min. for dye (II), (IV); reaction temp. 30°C at pH 6.5.

Table 6: Effect of addition of dimethylformamide to the reaction medium between compound (I) and dye (II) on the colour strength of dyed cotton fabrics.

Weight (g) and no. of mmole of dye compound (I)	Volume of DMF (mL)	Color strength (K/S)	
		After soaping	After DMF
(II); 0.122 (0.62) and (I); 0.213 (0.62)	5	4.86	2.48
	10	4.15	2.01
	15	3.44	1.82
	30	2.03	1.16
	60	1.39	0.74

Reaction time 20 min; reaction temp. 30°C; at pH 6.5.

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