The Effect of Electrolytes on Direct Dyes for Cotton

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Synopsis

Electrolytes generally promote dyebath exhaustion when direct dyes are used for cellulosic fibers, but the extent with which they do so usually varies from one electrolyte to another. Two direct dyes with varying numbers of sulfonic acid groups were investigated. Cotton cellulose was dyed with these dyes using different electrolytes and a phosphate buffer system. The relationship between strength loss with increase in number of sulfonic acid groups was an obvious observation. Wash fastness results had indicated that the most important consideration is the molecular weight and the overall molecular architecture of the dye.

INTRODUCTION

Direct dyes are anionic[1] and water soluble (sodium salts of sulfonic acids) having substantivity for cellulosic fibers, and are normally applied from a neutral or slightly alkaline bath containing an electrolyte (dyebath assistant e.g., sodium chloride or sodium sulfate).

Some direct dyes, in the complete absence of electrolytes do not practically exhaust onto cotton fibers. The addition of electrolytes to the dye-liquor tends to promote dye exhaustion, although the effect varies considerably with different dyestuffs as observed in this investigation.

It is also believed that cellulosic fibers acquire a negative charge when immersed in aqueous media because of their lower dielectric constant[2] compared with that of water and that this has the effect of repelling the similarly charged ion of the substantive dye. But it is claimed[3] that electrolytes tend to reduce or extinguish the charge on the fiber, thus facilitating a transfer of dye from water to the fiber. Earlier workers[4-6] had explained the effect of electrolytes on the basis of a decrease in the negative surface potential of the fiber.

In the investigation reported in this paper, the major role being played by different electrolytes was studied. The factors responsible for strength loss and wash fastness after dyeing were also investigated.
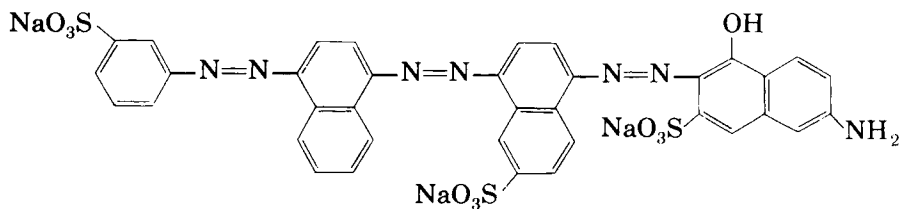
EXPERIMENTAL

Materials

Desized, scoured, and bleached cotton fabrics were supplied by Funtua Textiles Ltd., Funtua, Kaduna State, Nigeria. The dyestuffs, Durazol Red 2B (C.I. 28160) and Durazol Blue 3 R (C.I. 34138), were supplied by Chemical and

Allied Products Ltd., Lagos, Nigeria. The chemical structures of these dyes are shown in Figures 1(a) and 1(b), respectively.
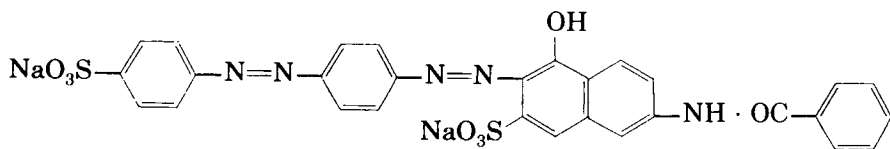
(a) Mol. wt. = 675

(b) Mol. wt. = 877

Fig. 1. Chemical structures of: (a) Durazol Red 2B (C.I. Direct Red 81, C.I. No. 28160); (b) Durazol Blue 3R (C.I. Direct Blue 258, C.I. No. 34138).

SELECTION OF ELECTROLYTES

The following anhydrous electrolytes were selected in order to assess their effectiveness in promoting dye uptake: Sodium chloride (NaCl); sodium sulfate (Na_2SO_4); aluminium chloride ($AlCl_3$); aluminium sulfate $Al_2(SO_4)_3$; calcium chloride ($CaCl_2$); magnesium chloride ($MgCl_2$); ammonium chloride (NH_4Cl); ammonium sulfate ($NH_4)_2SO_4$; zinc acetate ($CH_3COO)_2Z_n$; and zinc chloride (Z_nCl_2).

Dyeing Process

Purification of Dyes. Durazol Red 2B (Colour Index Direct Red 81) and Durazol Blue 3R (Colour Index Direct Blue 258) were purified by the method of Robinson and Mills[7]: fairly concentrated solutions of the dyes were prepared in distilled water, and pure crystals of sodium acetate were added to salt out the dyes, followed by filtration. The filtered dyes were again dissolved in distilled water and salted out with sodium acetate crystals. The sequence was repeated five times. The final filtered dyes containing sodium acetate were extracted with absolute alcohol in a Soxhlet extractor to remove sodium acetate. The dyes were filtered and then crystallized from 50/50 ethanol/water mixture.

The purified dyes were dried *in vacuo* over phosphorus pentoxide for one week. The purity was checked colorimetrically by purifying until the optical density in a standard solution remained unchanged.

Effect of Buffer Solutions in Dyeing. In carrying out a dyeing process it is often necessary to adjust the pH of the dyebath to a definite predetermined pH and to prevent any change in pH that would otherwise occur during the

dyeing process. In the dyeing of cotton under neutral conditions with the two direct dyes mentioned above, a phosphate buffer system[8,9] was used as follows: 0.5M sodium dihydrogen orthophosphate ($NaH_2PO_4 \cdot 2H_2O$) and 0.17M disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$) giving an optimum pH value of 7.

Dyeing of Samples. The cotton samples (1 g each; 36 pieces) were dyed by the method of Ibe and Valko[10] using the Dyemaster machine to a 2% (owf) shade. The dyeings were carried out at the boil for 60 min with the addition of 20% (owf) of each electrolyte using the phosphate buffer system mentioned above so as to achieve a neutral dyebath pH of 7 with a liquor ratio of 75:1.

Measurement of Dye Uptake (%). During dyeing, a small sample of the fabric (1 g) was taken at 10 min intervals and the dye adsorbed was extracted with 20% aqueous pyridine solution. A complete extraction was carried out at 60°C in a round-bottomed flask fitted with a condenser, using a liquor ratio of 75:1 for two hours. Concentrations of the dye extracts were calculated from the previously constructed calibration graphs for the dyes in 20% aqueous pyridine solution using UV Spectrophotometer SP 1750 at their λ_{max} and interpolating the values of percentage dye adsorption.

WASH-FASTNESS TESTS

Wash-fastness tests were carried out on all the dyed samples using the Linitest in accordance with the ISO Tests Nos. 1–5[11,12] and the grey scales were used to assess the degree of staining and change of shade.

STRENGTH TESTS

It was necessary to find if any strength loss exists as a result of dyeing cotton with the selected dyes. The Instron Table Model 1026 was used for carying out tensile tests for both dyed and undyed samples.

All the tests were carried out using a maximum load of 20 Kg, gauge length of 5 cm and cross-head speeds of 50 mm/min respectively. All measurements were carried out at 70% relative humidity and 20°C.

RESULTS AND DISCUSSIONS

Dyeing Results

Under the conditions employed, it can be observed that dye uptake showed a steadily increasing amount of dye on the fiber for the first 40–50 min. After this time very little further adsorption then took place (Tables I & II).

Dyeing results obtained under neutral conditions with Durazol Red 2B showed that in the presence of the following equal amounts of uni-univalent electrolytes, (i.e., NH_4Cl; $NaCl$; $(NH_4)_2SO_4$ and Na_2SO_4), deeper shades were obtained with the chlorides than with the sulfates. The increasing order is:

$$NH_4Cl > NaCl > (NH_4)_2SO_4 > Na_2SO_4.$$

With the sulfates, the reason for moderate depth of shade may be attributed to the reduced dye-fiber attraction (high repulsion) due to the presence

TABLE I
Dye Uptake with Durazol Red 2B (MW 675) 2 × SO₃Na

Time (min)	20% (owf) CaCl$_2$	20% (owf) ZnCl$_2$	20% (owf) MgCl$_2$	20% (owf) ZnAc	20% (owf) NH$_4$Cl	20% (owf) NaCl	20% (owf) (NH$_4$)$_2$SO$_4$	20% (owf) Na$_2$SO$_4$	20% (owf) AlCl$_3$	20% (owf) Al$_2$(SO$_4$)$_3$
10	42.3	36.4	34.3	32.1	30.2	28.6	25.2	25.0	16.5	13.4
20	60.2	55.3	52.4	49.3	46.4	43.2	38.3	35.6	20.4	17.3
30	71.4	66.6	65.3	60.4	54.2	49.6	45.7	41.4	22.1	20.1
40	80.8	72.5	70.4	69.2	61.5	54.5	49.8	45.2	26.1	23.2
50	86.2	80.1	78.2	73.6	67.8	62.2	58.4	54.6	28.3	25.5
60	88.6	82.8	80.1	78.5	72.4	71.3	64.5	61.9	30.2	27.8

TABLE II
Dye Uptake (%) with Durazol Blue 3R (MW 877) 3 × SO₃Na

Time (min)	20% (owf) ZnCl$_2$	20% (owf) MgCl$_2$	20% (owf) CaCl$_2$	20% (owf) ZnAc	20% (owf) NH$_4$Cl	20% (owf) NaCl	20% (owf) (NH$_4$)$_2$SO$_4$	20% (owf) Na$_2$SO$_4$	20% (owf) AlCl$_3$	20% (owf) Al$_2$(SO$_4$)$_3$
10	40.1	34.1	34.1	33.4	29.1	27.6	25.3	23.7	15.1	11.6
20	58.5	53.4	50.3	47.6	43.6	40.8	36.2	33.6	18.3	14.8
30	69.1	64.2	62.2	58.1	52.8	49.1	41.4	39.6	20.6	18.6
40	78.3	70.1	68.4	67.4	59.4	53.4	47.2	43.2	25.1	22.1
50	85.1	78.6	76.2	71.6	66.2	60.6	57.1	53.1	27.2	23.1
60	86.3	80.1	78.4	76.6	70.1	69.4	62.1	59.8	29.1	24.3

of sulfate ions ($-SO_4^{2-}$). Because they are similar in nature to the two sulfonic acid groups ($-SO_3^-$) in the dye molecule, they therefore, exert a much higher repulsion than do the chloride ions.

With the following uni-divalent electrolytes, the increasing order is: $CaCl_2$ > $ZnCl_2$ > $MgCl_2$ > ZnAc. The nature of the divalent cations (Ca, Zn, or Mg) may be the major contributing factor responsible for this.

In the case of the aluminium salts, the order is $AlCl_3$ > $Al_2(SO_4)_3$. The aluminium ion here is a trivalent cation in both electrolytes but the amount of dye uptake is not as high as the univalent or divalent cations. The nature of the anion of the electrolytes may explain this observation better. It was observed that high unlevel dyeings were obtained with the aluminium salts and this could be attributed to the large-sized trivalent cation (aluminium ion). Another obvious reason for low dye sorption and unlevelness could be due to the formation of the insoluble aluminium salt of the dye.

In the case of the Durazol Blue 3R dye having three sulfonic acid groups, the same reason previously outlined above also holds for NH_4Cl > NaCl > $(NH_4)_2SO_4$ > Na_2SO_4. But for the other divalent electrolytes, the increasing order is slightly changed as follows: $ZnCl_2$ > $MgCl_2$ > $CaCl_2$ > ZnAc. This could be explained from the nature of the cations present in these electrolytes. For the aluminium salts, the order is the same as before:

$$AlCl_3 > Al_2(SO_4)_3$$

FASTNESS RESULTS

The wash-fastness results obtained in this work (Table III) have indicated that the important factor determining the wash fastness of direct-cotton dyes is the overall molecular architecture of the individual dye and also the size of their molecules, and not just the anionic sulfonate groups in their molecules. Hence the blue dyeings having three sulfonic acid groups, larger molecular size, and higher molecular weight displayed a better wash-fastness property as compared to the other red dye.

TABLE III
Wash-Fastness Test Results

| | | | Fastness grading for staining | | | |
| | Fastness grading for colour change | | Durazol Red 2B | | Durazol Blue 3R | |
Iso test	Durazol Red 2B	Durazol Blue 3R	Cotton	Wool	Cotton	Wool
1	2	4	1–2	5	4	5
2	1–2	3	1–2	3–4	3–4	4–5
3	1–2	2–3	1–2	2–3	3	4–5
4	1–2	2	1	1–2	2–3	2–3
5	1–2	2–3	1	1	2	1–2

TABLE IV
Strength Test Results Using Durazol Blue 3R

Sample	Specimen extension (cm)	Extension at break (%)	Breaking load (k)
Undyed cotton	1.00	20.12	6.20
Dyed cotton	0.76	15.32	5.13

TABLE V
Strength Test Results Using Durazol Red 2B

Sample	Specimen extension (cm)	Extension at break (%)	Breaking load (kg)
Undyed cotton	1.00	20.12	6.20
Dyed cotton	0.83	16.52	5.60

STRENGTH TEST RESULTS

Apparently, dyeing of cotton is an exothermic process for dye adsorption on to the fiber surface to take place. The higher temperature affects the rate of dyeing. At equilibrium more dye is adsorbed at lower temperatures. In normal practice, the dyebath is heated to nearly boiling and then allowed to cool down to a lower temperature to increase the total dye adsorption on the fiber.

As the fiber is being dyed at higher temperatures, the dye molecules penetrate and rupture the fiber molecular structure thus weakening the bonds. This in agreement with our strength test results obtained (Tables IV & V) for the dyeings in this work.

The direct relationship between strength loss with varying number of sulfonic acid groups or increase in molecular weight is quite obvious. As the molecular weight of dye increased, fiber strength is equally reduced as a result of dyeing and this is consistent with reports of investigations[10] on the mechanical properties of cotton which showed that the breaking strength decreases during dyeing. This may be attributed to both the decrease in degradation of cellulose and to breaking of internal structural elements.

CONCLUSIONS

Electrolytes generally promote dyebath exhaustion, although the extent to which they do so varies very widely. In one respect it varies with the nature and type of the cation and in another it is with the anion. From the earlier discussions, it is concluded that as far as promoting dyebath exhaustion is concerned the uni-divalent electrolytes (e.g., $CaCl_2$, $MgCl_2$, etc.) outstand others. These are closely followed by the uni-univalent electrolytes (e.g., NH_4Cl, NaCl, etc.) and then come the trivalent electrolytes (i.e., the aluminium salts). It was observed that Dye B with high molecular size has lower dye uptake values when compared with Dye A.

From the inference on strength loss, it is concluded that a direct relationship exists between strength loss and varying number of sulfonic acid groups.

As the molecular weight of dye increased, fiber strength is equally reduced as a result of dyeing.

From the wash-fastness data, it is concluded that direct dyes do not possess good fastness to washing and that the most important consideration is the molecular weight and the overall molecular architecture of the dye. Thus, high molecular weight dyes usually possess better wash-fastness properties.

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