

# Effect of Chemical Modification of Cotton Fabrics on Dyeing Properties

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**ABSTRACT:** The presented research deals with modifying the chemical structure of the cellulosic cotton fabrics by introducing amino groups as new active centers. The properties of the resulting aminated cotton, dimethylaminoethyl (DMAE)-cotton, are evaluated and discussed by studying the dyeability, light fastness characteristics, and fading kinetics. The goal of this study was achieved. The modification succeeded in saving energy by decreasing both the dyeing time and temperature, and the dyeability and light fastness characteristics were improved. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1897–1903, 2002

**Key words:** modification; dyeability; light fastness; amorphousity; catalyst; reflection spectra; color strength

## INTRODUCTION

Many factors influence the dyeability and light fastness of dyes, among them are the chemical and physical state of both the dye and substrate, environmental factors, the source and intensity of illumination, and other additives in the dyeing bath.<sup>1–4</sup> Several changes can be made in the physical and chemical properties of the fabric to impart better properties than those found in unmodified fabric.<sup>5–7</sup> It is reported that chemical modification of cellulosic fabrics is generally achieved by blocking the functional groups (OH) already present in the fiber or by introducing new functional groups to increase the affinity of cotton fibers for different dye classes.<sup>8</sup> The behavior of the chemically modified cellulose (e.g., acetylated cellulose, cyano-ethylated cellulose, oxidized cellulose, cellulose graft copolymers, and cellulose thermally treated with aminated starch to improve dyeing properties), using different dye

classes, has been studied.<sup>8–10</sup> In this study, the effect of modifying the chemical structure of the cellulosic fabrics by introducing amino groups as a new active center was effective in increasing the extent of fixation of several dye classes by strengthening the bond formed between the dye and the chemically modified fabrics.<sup>11,12</sup> The stronger the bond formed, the greater is the light fastness (LF) of the dyed substrate and the easier the transfer of the excitation energy from the dye molecules to the fabric.<sup>12,13</sup>

## EXPERIMENTAL

### Materials and Chemicals

Mill desized, scoured, and bleached cotton fabrics (poplin) were kindly supplied by El-Shorbagy Company. The fabrics were purified in the laboratory by scouring with a solution containing 2.5 g of a nonionic detergent dissolved in 1 L of distilled water. The fabric was then thoroughly washed and dried at ambient conditions.<sup>14–16</sup>

2-Chloro-2-dimethylaminoethyl hydrochloride (Cl-CH<sub>2</sub>-CH<sub>2</sub>-NH(CH<sub>3</sub>)<sub>2</sub>Cl) was kindly supplied

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**Table I Color Strength (K/S) Values of the Dyed Samples at Different Dye-Bath Concentrations<sup>a</sup>**

Dye-Bath Conc. (g/L)	K/S Values of the Different Dyed Samples								
	Without Catalyst (Unmodified)			Using Sodium Carbonate Catalyst (2 g/L)			Using Zinc Acetate Catalyst (1 g/L)		
	Samples I	Samples II	Samples III	Samples I	Samples II	Samples III	Samples I	Samples II	Samples III
0.035	0.081	0.311	0.817	0.152	0.29	0.768	0.084	0.356	0.897
0.1	0.143	0.637	1.039	0.265	0.586	0.987	0.152	0.68	1.125
0.5	0.246	0.9841	1.335	0.527	0.926	1.289	0.25	1.03	1.6
1	0.328	1.289	1.413	0.723	1.163	1.384	0.336	1.454	1.795
2	0.338	1.383	1.612	0.869	1.289	1.6	0.386	1.63	1.868
6	0.880	1.6	2.15	1.125	1.486	2.03	1.103	1.87	2.41

<sup>a</sup> Where samples I are unmodified, samples II are modified with N% (0.386), and samples III are modified with N% (0.0.798).

by Fluka AG, Buch SC, and used as an aminating reagent in the modification process. The reactive dye, Cibacron Blue (B-E) (C.I.39), used in this study was kindly supplied by Ciba-Giegy Company. Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and zinc acetate  $\text{Zn}(\text{CH}_3\text{COO})_2$  of laboratory grade were used as catalysts in the dyeing process.

#### Preparation of Dimethylaminoethyl Cellulose (DMAE-Cell)

Aminated cotton fabrics (DMAE-Cell) with two different nitrogen contents were prepared from the purified cotton fabrics according to the reported Hartmann process.<sup>14–17</sup> The nitrogen content in the resulting aminated cotton fabrics was determined by the Kjeldal method.<sup>18</sup>

#### Dyeing, Testing, and Analysis

##### Dyeing Method

The unmodified cotton fabrics (samples I) and those modified with two different nitrogen contents (0.386 and 0.795%; samples II and III, respectively) were independently dyed according to the conventional exhaustion dyeing method. The dyeing was allowed to proceed for 30 min at 70 °C, using a liquor ratio of 1:100. The dyeing bath contained zinc acetate (1 g/L) and sodium carbonates (2 g/L), each in a separate experiment for a series of different dye-bath concentrations (0.035, 0.1, 0.5, 1, 2, and 6 g/L).

##### Testing and Analysis

**Color Strength Determination (K/S).** The color strength (K/S) values of the examined dyed sam-

ples based on the reflection spectra (at a wavelength of ~450 nm) were determined with the Kubelka Munk equation.<sup>19</sup> The spectral reflection curves were measured with a double-beam recording spectrophotometer attached by an integrating sphere (Shimadzu UV300, Japan).

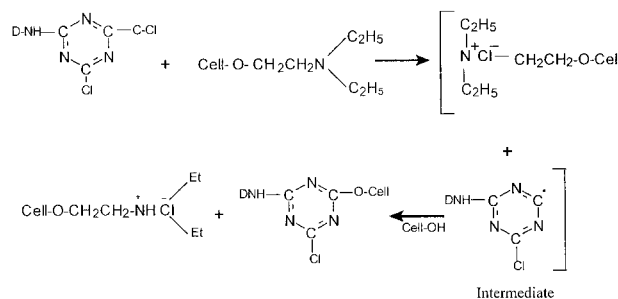
**Light Exposure.** Irradiation of the dyed samples alongside a Standard Blue Scale was performed for different periods (20–160 h) at a temperature of  $25 \pm 2$  °C and relative humidity of  $60 \pm 5$  % with a Tera Light Fastness Tester.<sup>20</sup>

**Reflectance Measurements.** The reflection spectra of all samples tested were measured in the visible range (360–700 nm) before and after the different exposure times (20, 40, 80, 120, and 160 h).

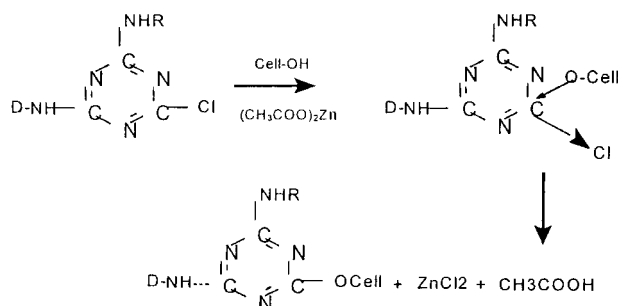
## RESULTS AND DISCUSSION

### Dyeability and Color Strength (K/S) Values

The K/S values, which were taken as a measure of the dyeability for the different examined dyed



**Scheme 1**



Scheme 2

samples, are shown in Table I. It is clear that K/S values generally increase with the increase in dye-bath concentrations. Furthermore, K/S values follow the order samples III > samples II > samples I. The higher K/S values of the modified cotton fabrics (samples II and III) in comparison with those of unmodified fabrics (sample I) must be due to the presence of DMAE groups in the molecular structure of cotton cellulose. These groups cause an increase in cellulose swellability by opening up its structure, thus enhancing the rate of dye adsorption, diffusion, and penetration into the fiber.<sup>6,7,22</sup> Moreover, DMAE groups act as a built-in catalyst in the molecular structure of cotton cellulose

and affect the reaction of the reactive dye with cellulose hydroxyls, as is clear from the reaction shown in Scheme 1.<sup>14-16,22</sup>

It was also observed that the higher the nitrogen content, the higher the dyeability (i.e., K/S of samples III > K/S of samples II) because of the increment in the ratio of the cationic site to the anionic dye.

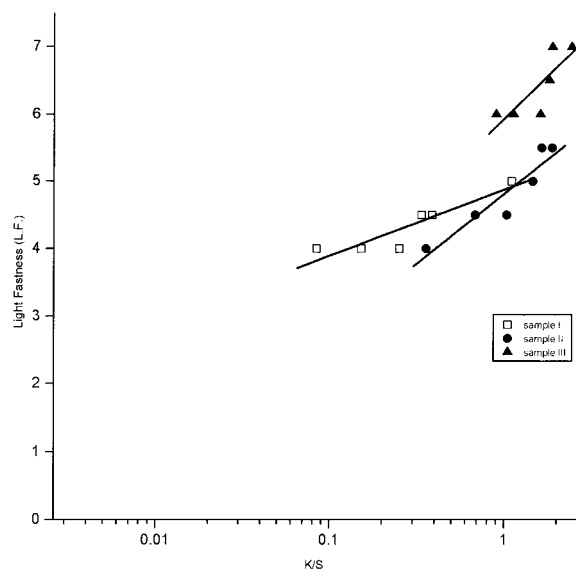
Another result was the K/S values of modified samples dyed in acidic medium using zinc acetate (pH 6) are higher than those of the corresponding samples dyed in alkaline medium using sodium carbonate (pH 12). The presence of zinc acetate in the dyeing media may increase both the substitution reaction between the modified cotton and the dye and the polarization of the dyeing media; thus, the rate of dyeing increases. In contrast the presence of sodium carbonate in the dyeing media of the aminated samples may increase the alkalinity, leading to increase in dye hydrolysis and resulting in a decrease in dye uptake.

Finally, the results in Table I indicate the role of modification in improving the dyeability either without using catalyst or with minimum catalyst concentration. Higher dyeability was obtained for samples III that were formed by reaction with zinc acetate (1 g/L), as shown in Scheme 2.

Table II Light Fastness (L.F.) and Fading Rate Constant (K) of the Samples Dyed in Different Media

Catalyst	Dye-Bath Conc. (g/L)	Samples I*			Samples II*			Samples III*		
		K/S	$K \times 10^{-3}$	LF	K/S	$K \times 10^{-3}$	LF	K/S	$K \times 10^{-3}$	LF
None (unmodified)	0.035	0.081	4.6	2/3	0.311	3.85	3	0.817	1.4	4
	0.1	0.143	4.43	3	0.637	3.08	4	1.039	1.3	4
	0.5	0.246	3.55	3/4	0.9841	2.59	4	1.335	1.21	4/5
	1	0.328	2.8	3/4	1.289	2.16	4/5	1.413	1.15	5
	2	0.338	2.66	4	1.383	1.97	5	1.612	1.12	5
	6	0.880	2.63	4/5	1.6	1.67	5	2.15	1.11	6
Sodium carbonate (2 g/L)	0.035	0.152	2.3	3	0.29	1.86	3/4	0.768	1.4	4/5
	0.1	0.265	1.7	3/4	0.586	1.24	4	0.987	1.01	5
	0.5	0.527	1.3	4	0.926	1.109	4/5	1.289	0.92	5
	1	0.723	1.2	4	1.163	0.96	4/5	1.384	0.73	5/6
	2	0.869	1.15	4/5	1.289	0.89	5	1.6	0.55	5/6
	6	1.125	1.11	4/5	1.486	0.84	5	2.03	0.51	5/6
Zinc acetate (1 g/L)	0.035	0.084	2.9	4	0.356	1.5	4	0.897	1.3	6
	0.1	0.152	2.2	4	0.68	1.35	4/5	1.125	0.91	6
	0.5	0.25	1.25	4	1.03	0.78	4/5	1.6	0.47	6
	1	0.336	1.16	4/5	1.454	0.74	5	1.795	0.411	6/7
	2	0.386	0.85	4/5	1.63	0.63	5/6	1.868	0.38	7
	6	1.103	0.78	5	1.87	0.57	5/6	2.41	0.33	7

\* Where: samples I = unmodified, samples II = modified with N% (0.386) and samples III = modified with N% (0.0798).



**Figure 1** Characteristic fastness grade (CFG) curves of the examined samples dyed in the presence of zinc acetate catalyst: sample I, unmodified; sample II, modified with  $N\% = 0.386$ ; sample III, modified with  $N\% = 0.795$ .

### Light Fastness Properties

The light fastness (LF) values of the dyed samples were assessed according to Standard Method,<sup>2, 3</sup> and the results are shown in Table II. Generally, LF rises with the increase in K/S values. Also, LF is affected largely by the nitrogen content ratio; that is, the LF values follow the order samples III > samples II > samples I. This result indicates that the presence of DMAE groups in the molecular structure of cellulose enhances both swellability<sup>13</sup> of the fiber and penetration of the dye particles inside it. In addition, with DMAE groups, the dye aggregation within fiber pores<sup>22</sup> increases and the surface/weight ratio decreases, thereby increasing the LF values. Characteristic fastness grade (CFG) curves, obtained from the data in Table II, are shown in Figure 1. It is clear that modified samples are at higher positions and possess higher slope values than the unmodified fabrics (samples I). Also, modified samples III with higher nitrogen content have higher slope values and are at higher positions than samples II, reflecting the effect of the amination process in increasing the fiber porosity and leading to an increase in size of aggregated dye particles inside their pores.

### Evaluation of the Fading Rate Constant ( $K$ )

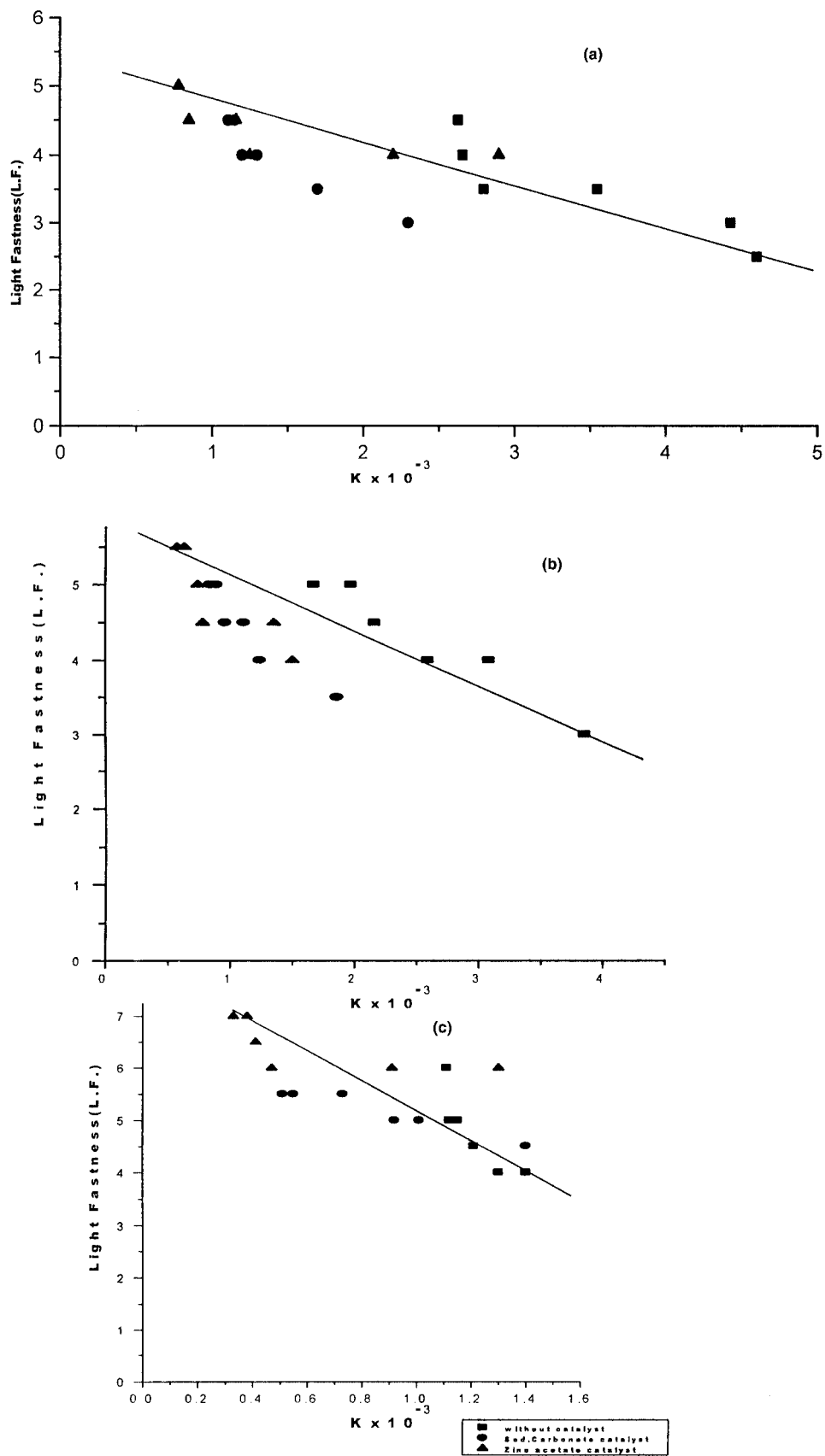
Plots of log values of the ratio  $K/S_t/K/S_0$ , at the different exposure times ( $t$ ), where  $K/S_t$  repre-

sents the color strength values of the exposed dyed samples at time  $t$ , and  $K/S_0$  represents unexposed samples, result in straight lines.<sup>3, 4, 14, 21, 26</sup> The slope values of these lines give the fading rate constant  $K$ , as indicated in Table. It was evident that  $K$  decreases with the increase both the K/S and the LF values. Thus,  $K$  values follow the order samples I > samples II > samples III. Also the values of  $K$  are greatly affected by the dyeing media; that is, at nearly comparable (K/S) values,  $K_{\text{for dyeing without catalyst}} > K_{\text{for dyeing with alkaline catalyst (sodium carbonate)}} > K_{\text{for dyeing with acid catalyst (zinc acetate)}}$ .

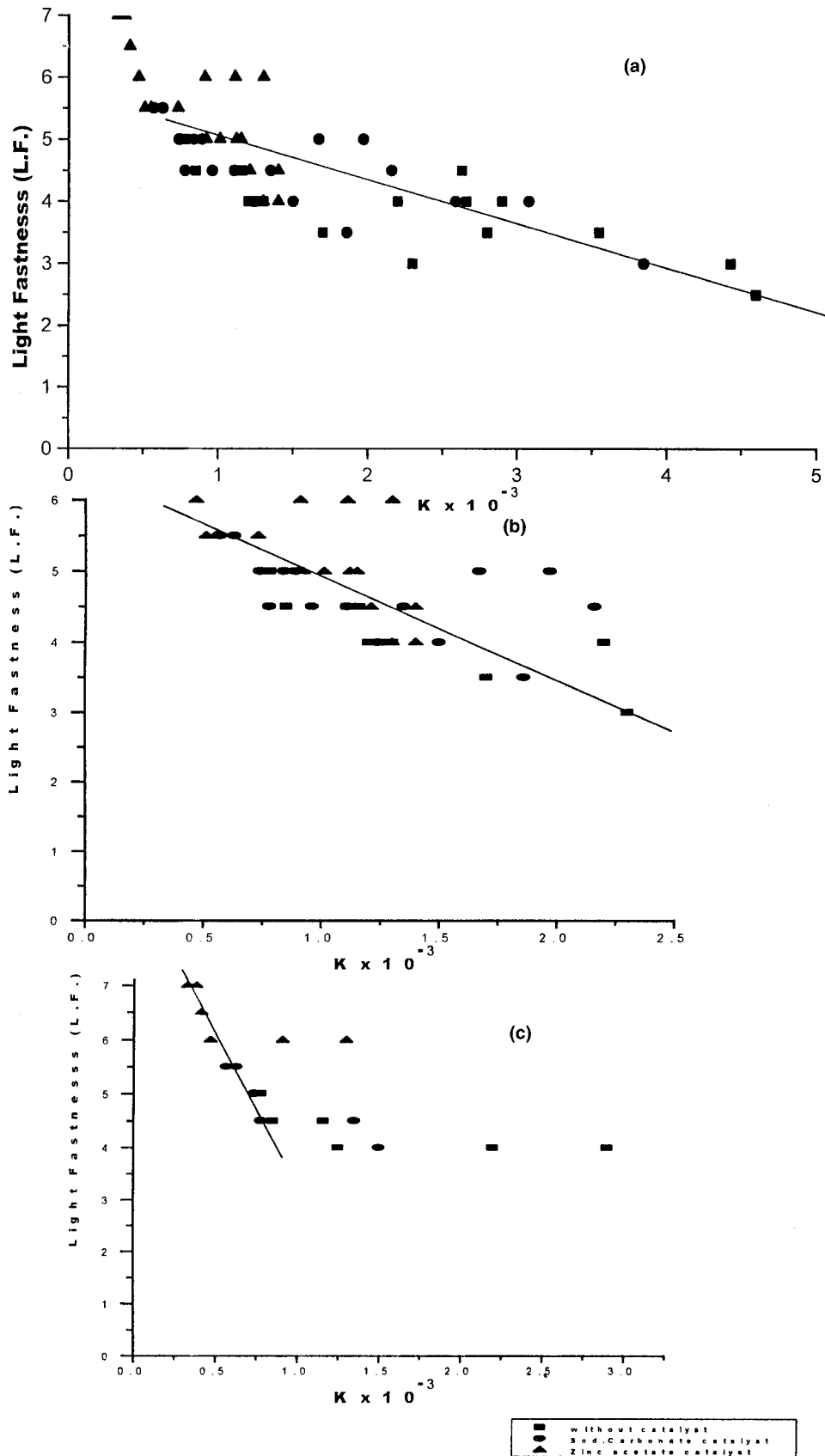
With respect to the blank dyed samples,  $K$  values in the presence of zinc acetate are much lower than their counterparts dyed in the presence of sodium carbonate, but their dyeability exhibits the reverse trend. This result agrees well with the previous LF results and may be due to the effect of zinc acetate as a coordinating compound between the fiber and the dye particles, which leads to more aggregation and accumulation of the dye particles inside the fiber pores. On the other hand, the lower  $K$  values of the dyed modified cotton in the presence of zinc acetate may be due to its effect of promoting the formation of nucleophilic cellulosate residues. These residues are readily formed by such modification, increase the amount and strength of the covalent bonds, and create a greater chance for other links to occur.<sup>28, 29</sup> All of these effects render the dye more bonded, more aggregated in a highly uniform manner, and less accessible to the diffusion restriction effect. As a consequence, fading accrues very slowly. The presence of sodium carbonate in the dyeing media may cause hydrolysis of the dye to the extent that the magnitude of dye uptake decreases, so aggregation and LF values decrease.

The slopes of the straight lines (Figure 2) determine the role of modification on the range of change in size of aggregated dyed particles inside the fiber pores. Lower slope (higher negative values) obtained for dyed modified samples with higher nitrogen content (samples III) means that the dye particles are distributed inside these substrates in a more uniform and highly aggregated state.

The results in Figure 3 demonstrate the role of catalyst on dye particle size distribution. A higher slope (lower negative value) was obtained for samples dyed without using catalyst, which indicates that a wide range of particle size distribution occurred. In contrast, a lower slope value was obtained when zinc acetate was used as a cata-



**Figure 2** Fading rate constant ( $K$ ) versus light fastness (LF) values of the examined dyed samples: (a) samples I (unmodified); (b) samples II ( $N\% = 0.380$ ); (c) samples III ( $N\% = 0.795$ ).



**Figure 3** Fading rate constant ( $K$ ) versus light fastness (LF) values of the examined dyed samples: (a) dyeing without catalyst; (b) dyeing with sodium carbonate (2 g/L); (c) dyeing with zinc acetate (1 g/L).

lyst, which indicates that the dye was more uniform and highly aggregated inside fabric pores.

## CONCLUSION

The effects of a chemical modification process using DMAE (2-chloro-2-dimethylaminoethyl hydrochloride) on cotton fabrics were evaluated by studying the dyeing properties. The resulting DMAE-cotton fabrics with two different nitrogen contents (0.386 and 0.785% N) together with the blank samples were dyed with reactive dye in three different conditions: (a) without using catalyst, (b) using the classical method with sodium carbonate (2 g/L), and (c) using zinc acetate (1 g/L). The results indicate that the presence of DMAE groups in the molecular structure of cellulose act as a built-in catalyst, thereby creating a cationic site on the fabrics to increase the attraction of the anionic dye. Also, DMAE increases the swellability of the fibers (i.e., increases pore size), thereby encouraging both diffusion and aggregation of dye particles inside the fiber pores. As a result, better dyeability and higher light fastness were obtained for modified samples, especially at higher nitrogen content, in the presence of minimum zinc acetate concentration, and at shorter dyeing times.

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